The Twenty-Ninth Colloquium on
High-Resolution Molecular Spectroscopy

August 25 – August 29, 2025

Universität zu Köln

Köln – GERMANY

The Twenty-Ninth Colloquium on High Resolution Molecular Spectroscopy

HRMS 2025 – Köln

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CRC1601

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COLOGNE CENTER FOR
TERAHERTZ SPECTROSCOPY

DYNAVERSE

CCTS, the Cologne Center for THz Spectroscopy, is a DFG core facility project of the laboratory astrophysics group at University of Cologne. DYNAVERSE is a DFG funded Cluster of Excellence between the Universities of Cologne and Bonn, the Forschungszentrum Jülich, the Max Planck Institute for Radio Astronomy, the German Aerospace Center and the Heidelberg Institute for Theoretical Studies.

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Twenty-Ninth Colloquium on High-Resolution Molecular Spectroscopy
Universität zu Köln, August 25 - 29, 2025
Program of the Colloquium

Hours	Aug 24 2025 Sunday	Aug 25 2025 Monday	Aug 26 2025 Tuesday	Aug 27 2025 Wednesday	Aug 28 2025 Thursday	Aug 29 2025 Friday
8:30		Welcome				
9:00		A: Plenary **Marsha I. Lester** **Laura Kreidberg**	E: Plenary **Sonia Melandri** **Jérôme Loreau**	I: Plenary **Pierre Asselin** **Wolfgang E. Ernst**	K: Plenary **Olivier Pirali** **Jeremy Harrison**	O: Posters
10:30		Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
11:00		B: Posters	F: Contributed Talks	J: Contributed Talks	L: Posters	P: Plenary **Sandra Eibenberger-Arias** **Jürgen Gauss**
12:30		Lunch	Lunch	Lunch	Lunch	Lunch
14:00		C: Minisymposium Interstellar Astrophysics **Arshia Jacob** **Laurent Marguès** **Maria-Luisa Senent** **Silvia Spezzano**	G: Minisymposium Non-Covalent Interactions **José Andrés Fernández** **Qian Gou** **Melanie Schnell**	**14:30** Cologne Sightseeing Tour	M: Minisymposium Clocks and Metrology Molecular Physics Lecture **Jun Ye** **Tanya Zelevinsky** **Piet Schmidt**	
16:00	Welcome & Registration	Coffee break	Coffee break		Coffee break	
16:30		D: Contributed Talks	H: Posters		N: Contributed Talks	
18:00				**18:30** Conference Dinner Haus Unkelbach		
19:30	Welcome Talk: **Stefanie Walch-Gassner**					
20:00			Public Evening Talk: **Markus Röllig**			

Hörsaal I	**Hörsaal I**	**Hörsaal I**	**Hörsaal I, II, or III**	**Foyer**	**Foyer**

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Program of Sessions

A: Plenary

Monday, August 25, 9:00, Hörsaal I

Chair: Frédéric Merkt

A1 – *INFRARED SPECTROSCOPY AND UNIMOLECULAR DYNAMICS OF REACTIVE INTERMEDIATES* (9:00 – 9:45)
Marsha I. Lester

A2 – *EXOPLANET ATMOSPHERIC CHEMISTRY IN THE JWST ERA* (9:45 – 10:30)
L. Kreidberg

B: Posters

Monday, August 25, 11:00, Foyer

B1 – *INFRARED SPECTROSCOPY OF* H_5^+
S.J.P. Marlton, J. Sarka, P. C. Schmid, T. Salomon, O. Asvany, and S. Schlemmer

B2 – *HIGH RESOLUTION VIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF PROTONATED METHANOL* ($CH_3OH_2{}^+$)
W.G.D.P. Silva, O. Asvany, S. Thorwirth, T. Salomon, I. Kleiner, I. Gulaczyk, M. Kreglewski and S. Schlemmer

B3 – *CONFORMATIONAL ANALYSIS OF 2-(METHYLTHIO)ETHYLAMINE AND 2-(ETHYLTHIO)ETHYLAMINE USING ROTATIONAL SPECTROSCOPY*
A. Chaudhary, P. Chheang, and J. van Wijngaarden

B4 – *COUPLED METHYL INTERNAL ROTATIONS WITH INTERMEDIATE AND LOW TORSIONAL BARRIERS IN 2,5-DIMETHYLANISOLE AND 2,5-DIMETHYLFLUOROBENZENE INVESTIGATED BY MICROWAVE SPECTROSCOPY*
H. Sun, I. Kleiner, S. Khemissi, L. Ferres and H. V. L. Nguyen

B5 – *ANALYSIS OF 5-METHYL-2-NITROPHENOL BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS*
E. Antonelli, V. Tsoi, M. E. Sanz, I. Kleiner and H.V.L. Nguyen

B6 – *ETHYNYL ISOCYANATE, YET ANOTHER QUASILINEAR TROUBLEMAKER*
K. Vávra, L. Kolesniková, P. Kania, Š. Urban and J.-C. Guillemin

B7 – *ROTATIONAL SPECTROSCOPY OF THE AMINOMETHYL RADICAL* CH_2NH_2
L. Zou, R. Chahbazian, L. Margulès, M.-A. Martin-Drumel, and O. Pirali

B8 – *FT-UV EMISSION SPECTROSCOPY OF THE* $B^2\Sigma^+ - X^2\Sigma^+$ *SYSTEM OF* $^{12}C^{16}O^+$ *AND* $^{12}C^{17}O^+$
W. Szajna, K. Jachymek, R.W. Field and R. Hakalla

B9 – *LABORATORY ROTATIONAL SPECTRA AND INTERSTELLAR IDENTIFICATION OF DEUTERATED COMPLEX ORGANIC MOLECULES*
H. A. Bunn, S. Spezzano, L. H. Coudert, J.-C. Guillemin, Y. Lin, P. Perez Rickert, C. P. Endres, Jes Jørgensen, V. Lattanzi, and P. Caselli

B10 – *SINGLE PHOTOIONIZATION OF VINYLCYANOACETYLENE AND METHACRYLONITRILE IN ASTROPHYSICAL OBJECTS*
H.R. Hrodmarsson, M. Schwell, J.-C. Guillemin, B. Madebène, E.-L. Zins

B11 – *FREQUENCY COMB-STABILIZED HIGH-RESOLUTION IR-UV DOUBLE RESONANCE SPECTROSCOPY ON A COLD MOLECULAR BEAM*
J. Jakob, F. Peterß, V. Grigorian, S. Schwetje, M. A. Kaufmann, A. Breier, T. F. Giesen, G. W. Fuchs

B12 – *LABORATORY MEASUREMENTS OF SULFUR BEARING CYCLIC HYDROCARBONS BY MICROWAVE SPECTROSCOPY*
M. Araki, C. P. Endres, P. Caselli, and V. Lattanzi

B13 – *HIGH-RESOLUTION IR SPECTROSCOPY OF THE* HCN^+ *AND* HNC^+ *CATIONS*
P.C. Schmid, S.J.P. Marlton, W.G.D.P. Silva, T. Salomon, D. Gupta, S. Thorwirth, O. Asvany, and S. Schlemmer

B14 – *COMBINING A CRYOGENIC ION TRAP WITH A 2 THZ MULTIPLIER CHAIN SOURCE: REVISITING THE* $J = 1 \leftarrow 0$ *FUNDAMENTAL ROTATIONAL TRANSITION OF* HHe^+
O. Asvany, U. Graf, W. G. D. P. Silva, L. Schneider, S. Kabanovic, V. Ossenkopf, J. Stutzki, I. Savić, R. Güsten, O. Ricken, B. Klein and S. Schlemmer

B15 – *MILLIMETER-WAVE SPECTRUM AND NUCLEAR HYPERFINE STRUCTURE OF THE (para)-*NH_3*–(ortho)-*H_2 *VAN DER WAALS COMPLEX*
I. Tarabukin, V. Panfilov, D. Poydashev, and L. Surin

B16 – *THE PROGRESS ON HIGH RESOLUTION SPECTRA MEASUREMENTS OF VAN DER WAALS COMPLEXES WATER*–CO_2 *IN THE SECOND WATER OVERTONE RANGE*
A.S. Bogomolov, S. Collignon, R. Glorieux, N. Moazzen-Ahmadi, M. Herman, and C. Lauzin

B17 – *GAS PHASE VIBRATIONAL SPECTROSCOPY OF* $PF_6{}^-(H_2O)_{0-7}$*: DECODING THE ONSET OF HYDROGEN-BOND NETWORK FORMATION*
H. Buttkus, M. Barp, K. Asmis

B18 – *EXPLORING HALOGEN EFFECTS IN THE ESTERIFICATION REACTION OF FORMIC ACID AND ETHANOL*
W. Sun and M. Schnell

B19 – *A NEARLY COMPLETE TREATMENT OF THE EFFECT OF NON-ADIABATICITY (NO DIABATISATION) ON ROVIBRATIONAL ENERGIES OF* H_3^+
R. Jaquet

B20 – *REINVESTIGATION OF PROPYLENE OXIDE BY FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY*
Y. Kawashima and K. M. T. Yamada

B21 – *NEAR-INFRARED SPECTROSCOPY OF METHANOL AT THE* 10^{-13} *LEVEL FOR RADIO ASTRONOMY*
A. Altman, F.M.J. Cozijn, A. S. Bogomolov, A. Libert, W. Ubachs and C. Lauzin

B22 – *HIGH-RESOLUTION VUV AND VIS FT SPECTROSCOPY AND EXTENDED DEPERTURBATION ANALYSIS OF THE* $^{13}C^{18}O$ $A^1\Pi(v=2)$ *LEVEL*
S. Ryzner, A. Stasik, M.I. Malicka, W. Szajna, R.W. Field, W. Ubachs, K.F. Lai, A. Pashov, P. Jasik, J.E. Sienkiewicz, N. de Oliveira and R. Hakalla

B23 – *ANALYSIS OF THE HIGH RESOLUTION INFRARED SPECTRUM OF MONODEUTERO-OXIRANE*
K. Keppler, S. Albert, Z. Chen, C. Manca Tanner, G. Seyfang, G. Wichmann, A. Brandenberger, M. Perrino, J. Stohner, M. Quack

B24 – *(SUB-)MM AND INFRARED ANALYSIS OF VINYL CHLORIDE*
M. Lazaridou, F. Happ, O. N. Ulenikov, O. V. Gromova, E. S. Bekhtereva, Yu. V. Khudyakova, M.-A. Martin-Drumel, O. Pirali, L. von Rötel, L. Bonah, S. Thorwirth, S. Schlemmer

B25 – *HIGH-RESOLUTION INFRARED SPECTROSCOPIC INVESTIGATION OF THE* ν_{12} *BREATHING MODE OF PROPYLENE OXIDE AND ITS FERMI-TYPE RESONANCE WITH THE* $2\nu_{24}+\nu_{19}$ *TORSIONAL COMBINATION BANDS*
B. Asadpour, T. F. Giesen, E. Döring, J.Jakob, F. Peterß, K. Luková, K.Vávra, G. W. Fuchs

B26 – *PHOTODETACHMENT SPECTROSCOPY OF THE LOWEST S- AND P-WAVE THRESHOLDS OF* C_2^-
Sruthi Purushu Melath, Michael Hauck, Christine Lochmann, Robert Wild, Katrin Dulitz, Roland Wester

B27 – *MACHINE LEARNING FOR ISOTOPOLOGUE EXTRAPOLATION*
M. Barnfield, J. Tennyson, and S.N. Yurchenko

B28 – *LASER SPECTROSCOPY OF NEW UV* $A^2\Pi$ - $X^2\Sigma^+$ *BANDS OF CALCIUM MONOHYDRIDE*
J. Xiong, Y. Moriwaki, and K. Kobayashi

B29 – *EXOMOL EXTENSIONS: EXOATOM AND EXOPHOTO – SPECTROSCOPIC DATABASES FOR ATOMS AND MOLECULAR PHOTODISSOCIATION*
Qing-He Ni, Christian Hill, Sergei N. Yurchenko, and Jonathan Tennyson

B30 – *LINE BY LINE ANALYSIS OF THE* ν_{10} *AND* ν_9 *BANDS OF ALLENE BETWEEN 600 AND 1200* cm^{-1}
S. Perot, A. Rizopoulos, and J. Vander Auwera

B31 – *HIGH-RESOLUTION INFRARED SPECTROSCOPY OF* N_2O *AND* SO_2 *BROADENED BY HELIUM TO ASSIST IN ANALYSIS OF EXOPLANETARY ATMOSPHERES.*
Himanshi Singh, Hayley A. Bunn, Laura Schöller, Silvia Spezzano, Paola Caselli, Christian Röske, Manfred Birk, and Georg Wagner

B32 – *SOLIS: AN ACCURATE IR/VIS LINE LIST FOR SULFUR MONOXIDE* ($^{32}S^{16}O$) *& UV PHOTOABSORPTION AND PHOTODISSOCIATION CROSS SECTION PREDICTIONS*
R. P. Brady, S. N. Yurchenko, and J. Tennyson

B33 – *AB INITIO SPECTROSCOPIC INVESTIGATION OF HYDROGEN FLUORIDE*
Nariman Abu Elkher, Maha Shibli, Mahmoud Korek, Sergey N. Yurchenko, Jonathan Tennyson, and Nayla El-Kork

B34 – *LINE PARAMETERS MEASUREMENTS OF THE $2\nu_3$ BAND OF CH_3F: LINE INTENSITIES AND LINE AIR-BROADENING COEFFICIENTS*
J. Tison, H. Ziadi, M. Rey, L. Manceron, B. Grouiez, A. V. Nikitin, H. Aroui and M. Rotger

B35 – *EXOMOL LINE LISTS FOR 12 ISOTOPOLOGUES OF CO_2*
S. N. Yurchenko, M. Barnfield, C. A. Bowesman, R. P. Brady, K. Kefala, Q. Ni, O. Smola, A. N. Perri, C. Tao, A. Sokolov, J. Tennyson

C: Minisymposium on Interstellar Astrophysics

Monday, August 25, 14:00, Hörsaal I

Chair: Sandra Brünken

C1 – *INTERSTELLAR CHEMISTRY: WHAT MOLECULES TELL US ABOUT THE UNIVERSE* (14:00 – 14:30)
A. M. Jacob

C2 – *FROM LILLE TO THE STARS: THE QUEST FOR MOLECULES IN THE INTERSTELLAR MEDIUM* (14:30 – 15:00)
L. Margulès

C3 – *HIGHLY CORRELATED AB INITIO CALCULATIONS APPLIED TO THE CHARACTERIZATION OF ASTROPHYSICAL SPECIES* (15:00 – 15:30)
M.L. Senent

C4 – *HIGH-RESOLUTION SPECTROSCOPY OF MOLECULES OF ASTROPHYSICAL IMPORTANCE* (15:30 – 16:00)
S. Spezzano

D-I: Contributed Talks

Monday, August 25, 16:30, Hörsaal I

Chair: Marie-Aline Martin-Drumel

D-I.1 – *SHEDDING LIGHT ON SiC^+: FIRST LABORATORY SPECTRA OBTAINED BY ELECTRONIC PHOTODISSOCIATION* (16:30 – 16:45)
Kai Pollow, Alexander Breier, and Otto Dopfer

D-I.2 – *HIGH-RESOLUTION RO-VIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF THE OPEN-SHELL, LINEAR CCH^+ ION* (16:45 – 17:00)
K. Steenbakkers, W.G.D.P. Silva, O. Asvany, G.C. Groenenboom, P. Jusko, B. Redlich, S. Brünken, and S. Schlemmer

D-I.3 – *HIGH-RESOLUTION ELECTRONIC AND THRESHOLD PHOTOELECTRON SPECTROSCOPY OF ${C_{70}}^+$* (17:00 – 17:15)
H. R. Hrodmarsson, L. Ganner, G. A. Garcia, L. Nahon, and E. Gruber

D-I.4 – *NON-LTE MOLECULAR OPACITIES AND RADIATIVE TRANSFER FOR EXOPLANETS* (17:15 – 17:30)
C. A. Bowesman, S. N. Yurchenko

D-I.5 – *ROTATIONAL SPECTRA OF ASTROPHYSICALLY RELEVANT CYANO ALIPHATIC COMPOUNDS: MOLECULAR STRUCTURE AND PUCKERING TUNNELLING IN CYCLOPENT-1-ENECARBONITRILE* (17:30 – 17:45)
D. Heras, Y. Li, N. Osseiran, C. Bermúdez, G. Feng, C.Pérez and A. Lesarri

D-I.6 – *MILLIMETER-WAVE SPECTROSCOPY OF TRANS-METHYL FORMATE.* (17:45 – 18:00)
C. P. Endres, M. Araki, V. Lattanzi, M. Sanz-Novo, V. M. Rivilla, I. Jimenez-Serra, and P. Caselli

D-II: Contributed Talks

Monday, August 25, 16:30, Hörsaal II

Chair: Jeremy Harrison

D-II.1 – *TIME-RESOLVED ROTATIONAL SPECTROSCOPY OF TRANSIENT SPECIES PRODUCED BY UV PHOTOLYSIS* (16:30 – 16:45)
N. Chen, B. M. Hays, E. Alekseev, R. A. Motiyenko, L. Margulès and S. Bailleux

D-II.2 – *LINE SHAPE PARAMETER STUDY OF HELIUM-BROADENED METHANE LINES IN THE* ν_4 *BAND BY A HIGH-RESOLUTION DUAL-COMB SPECTROMETER* (16:45 – 17:00)
J. Clément, B. Vispoel, O. Browet, N. Dricot, and M. Lepère

D-II.3 – *TEMPERATURE DEPENDENCE OF THE SELF AND FOREIGN WATER VAPOR CONTINUA IN THE 1.6* μm *WINDOW* (17:00 – 17:15)
M. Toureille, A. Campargue, J.-L. Martin, S. Kassi, and D. Mondelain.

D-II.4 – *HIGH-RESOLUTION SPECTROSCOPIC INSIGHT INTO METHYL FORMATE DEHYDROGENATION: DETECTION AND CHARACTERIZATION OF* CH_2OCHO *AND* CH_3OCO *RADICALS* (17:15 – 17:30)
R. Chahbazian, M. L. Senent, M. Carvajal-Zaera, and O. Pirali

D-II.5 – *COLLISIONAL LINE BROADENING FOR (EXO)PLANETARY ATMOSPHERES* (17:30 – 17:45)
J. Buldyreva

D-II.6 – *CARS THERMOMETRY OF BURNED* C_2H_4*: CALCULATION OF COLLISIONAL BROADENING COEFFICIENTS* (17:45 – 18:00)
S. Clavier and J. Buldyreva

D-III: Contributed Talks

Monday, August 25, 16:30, Hörsaal III

Chair: Jennifer van Wijngaarden

D-III.1 – *METHYL INTERNAL ROTATION AND NUCLEAR QUADRUPOLE COUPLING EFFECTS IN THE MICROWAVE SPECTRUM OF 1-BROMOPROPENE* (16:30 – 16:45)
T. A. Nguyen, I. Kleiner, and H. V. L. Nguyen

D-III.2 – *METHYL INTERNAL ROTATION AND NUCLEAR QUADRUPOLE COUPLING EFFECTS IN THE MICROWAVE SPECTRUM OF 2-FLUORO-3-PICOLINE* (16:45 – 17:00)
I. Hadj Said, I. Kleiner, H. V. L. Nguyen and S. Khemissi

D-III.3 – *A CHLORINE, A NITROGEN, AND A METHYL ROTOR: 2-CHLORO-5-PICOLINE ANALYZED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS* (17:00 – 17:15)
M. Buttkus-Barth, S. Herbers and H. V. L. Nguyen

D-III.4 – *BROADBAND ROTATIONAL SPECTRUM OF 2,2,3,3,4,4,4-HEPTAFLUORO-1-BUTANOL AND ITS 1:1 COMPLEXES WITH WATER AND HELIUM* (17:15 – 17:30)
F. Baroncelli, A. Maris, L. Evangelisti, S. Melandri, A. Vazquez, A. Insausti, and E. J. Cocinero

D-III.5 – *2,6-LUTIDINE: OVERCOMING THE CHALLENGE OF TWO EQUIVALENT LOW-BARRIER METHYL INTERNAL ROTATIONS AND ^{14}N QUADRUPOLE COUPLING* (17:30 – 17:45)
E. Antonelli, M. Buttkus-Barth, V. V. Ilyushin, and H. V. L. Nguyen

D-III.6 – *SPECTROSCOPIC QUALITY AND VARIATIONAL VIBRATIONAL STATES OF METHANOL AND ENHANCEMENT OF PARITY-VIOLATING SHIFT IN SUBSTITUTED METHANOLS* (17:45 – 18:00)
A. Sunaga and E. Mátyus

E: Plenary

Tuesday, August 26, 9:00, Hörsaal I

Chair: Wolfgang Jäger

E1 – *EXPLORING CONFORMATIONS AND NON-COVALENT INTERACTIONS IN COMPLEX MOLECULAR SYSTEMS WITH ROTATIONAL SPECTROSCOPY* (9:00 – 9:45)
S. Melandri

E2 – *COLLISIONAL EXCITATION OF MOLECULES IN ASTROPHYSICAL ENVIRONMENTS: RECENT ADVANCES AND CHALLENGES* (9:45 – 10:30)
J. Loreau

F-I: Contributed Talks

Tuesday, August 26, 11:00, Hörsaal I

Chair: Lucile Rutkowski

F-I.1 – *LASER SPECTROSCOPIC INVESTIGATION OF DESORPTION ENERGY OF CO_2 FROM THE DISPERSION-DOMINATED CO_2 COMPLEXES: ROLE OF N-SUBSTITUTION AND -OH FUNCTIONAL GROUP COLLISIONAL LINE BROADENING FOR (EXO)PLANETARY ATMOSPHERES* (11:00 – 11:15)
Muhammed Shabeeb

F-I.2 – *HIGH-RESOLUTION VIBRATION-ROTATIONAL SPECTRA AND ABSOLUTE LINE STRENGTHS OF HO_2 RADICAL IN THE ν_1, ν_2 AND ν_3 FUNDAMENTAL BANDS* (11:15 – 11:30)
P.-L. Luo, I-Y. Chen, and C.-W. Chang

F-I.3 – *INFRARED SPECTRA OF ACETALDEHYDE AND ITS AGGREGATES IN HELIUM NANODROPLETS* (11:30 – 11:45)
R. Hamidi Mejlej, S. Parshotam, W. Jaeger and Y. Xu

F-I.4 – *TWO-DIMENSIONAL FLUORESCENCE AND MASS-SELECTIVE SPECTROSCOPY OF SMALL SILICON CARBIDES: SiC_2, l-SiCCSi, AND c-SiC_6H_4* (11:45 – 12:00)
D. Kaur, J. Flores, and N. J. Reilly

F-I.5 – *THE R-INDEX METRIC FOR EVALUATING OAM CONTENT AND MODE PURITY IN OPTICAL FIELDS* (12:00 – 12:15)
Monika Bahl, Georgios M. Koutentakis, Mikhail Maslov, Tom Jungnickel, Timo Gaßen and Oliver H. Heckl

F-I.6 – *HIGH-RESOLUTION TWO-PHOTON DOPPLER-FREE UV SPECTROSCOPY OF XENON WITH DIRECT MEASUREMENT OF THE AC-STARK SHIFT* (12:15 – 12:30)
M. H. Rayment, R. Stech, and F. Merkt

F-II: Contributed Talks

Tuesday, August 26, 11:00, Hörsaal II

Chair: Stefan Willitsch

F-II.1 – *PRECISION TIME-DOMAIN SPECTROSCOPY OF THE 12.2 GHz MASER TRANSITION IN METHANOL* (11:00 – 11:15)
S. Collignon, B. M. Hays, D. Lederer, M. Daman and C. Lauzin

F-II.2 – *PRECISION MEASUREMENTS IN THE MOLECULAR HYDROGEN IONS FROM RYDBERG-STATE SPECTROSCOPY* (11:15 – 11:30)
I. Doran, L. Jeckel, M. Beyer, Ch. Jungen, and F. Merkt

F-II.3 – *ULTRA-PRECISE LINE-INTENSITY RATIOS REDEFINING PRIMARY OPTICAL THERMOMETRY WITH PARTS-PER-MILLION ACCURACY* (11:30 – 11:45)
J.-K Li , J. Wang , R.-H. Yin , Q. Huang , Y. Tan , C.-L. Hu , Y.-R. Sun , Oleg L. Polyansky, Nikolai F. Zobov, Evgenii I. Lebedev, Rainer Stosch, Jonathan Tennyson, Gang Li, and S.-M. Hu

F-II.4 – *ACCESSING ALL VIBRATIONALLY EXCITED STATES OF THE* $X^+\ {}^2\Sigma_u^+$ *ELECTRONIC GROUND STATE OF* He_2^+ (11:45 – 12:00)
M. Holdener, V. Wirth, N. A. Shahin, and F. Merkt

F-II.5 – *PROBING FUNDAMENTAL CONSTANTS AND TESTING QED THEORY OF MOLECULES THROUGH HIGH-PRECISION SPECTROSCOPY OF MOLECULAR HYDROGEN IONS* (12:00 – 12:15)
S. Alighanbari, M.R. Schenkel, M. Bakhshi, V.I. Korobov, J.-Ph. Karr, and S. Schiller

F-II.6 – *QUANTUM-LOGIC SPECTROSCOPY OF FORBIDDEN ROVIBRATIONAL TRANSITIONS IN SINGLE MOLECULAR IONS* (12:15 – 12:30)
A. Shlykov, M.L. Diouf, R. Karl, M. Roguski and S. Willitsch

F-III: Contributed Talks

Tuesday, August 26, 11:00, Hörsaal III

Chair: Iouli Gordon

F-III.1 – *MACHINE LEARNING PRESSURE BROADENING PARAMETERS FOR EXOPLANETARY STUDIES* (11:00 – 11:15)
E. R. Guest, J. Tennyson, and S. N. Yurchenko

F-III.2 – *AIR-PERTURBED OXYGEN B-BAND LINE-SHAPE PARAMETERS FOR THE HITRAN2024 DATABASE* (11:15 – 11:30)
K. Bielska, S. Wójtewicz, J. Domysławska, R. Ciuryło, and D. Lisak

F-III.3 – *SPECTROSCOPY OF TRITIATED WATER SPECIES: NEW RESULTS ON THE* $\nu_2 + \nu_3$ *AND* $\nu_1 + 2\nu_2$ *BANDS OF HTO AND THE* ν_3 *BAND OF DTO* (11:30 – 11:45)
V. Hermann , B. Rothmundt , F. Hase , M. Schlösser and J. Orphal

F-III.4 – *LINE POSITIONS AND INTENSITIES OF THE SILANE MOLECULE* (SiH_4) *FOR ITS FUNDAMENTAL BANDS AND SOME COMBINATION AND OVERTONES* (11:45 – 12:00)
R. Kamel, V. Boudon, C. Richard, F. Kwabia Tchana, and L. Bruel

F-III.5 – *NEW BEYOND-VOIGT LINE-SHAPE PROFILE RECOMMENDED FOR THE HITRAN DATABASE* (12:00 – 12:15)
P. Wcisło, N. Stolarczyk, M. Słowiński, H. Jóźwiak, D. Lisak, R. Ciuryło, A. Cygan, F. Schreier, C.D. Boone, A. Castrillo, L. Gianfrani, Y. Tan, S-M. Hu, E. Adkins, J.T. Hodges, H. Tran, N.H. Ngo, J.-M. Hartmann, S. Beguier, A. Campargue, R.J. Hargreaves, L.S. Rothman, and I.E. Gordon

F-III.6 – *AB INITIO SPECTROSCOPY OF METHANOL* CH_3OH (12:15 – 12:30)
O. Smola, S. N. Yurchenko, and J. Tennyson

G: Minisymposium on Non-Covalent Interactions

Tuesday, August 26, 14:00, Hörsaal I

Chair: Yunjie Xu

G1 – *MOLECULAR AGGREGATION: LESSONS I LEARNED FROM MOLECULAR SPECTROSCOPY IN JETS* (14:00 – 14:30)
José A. Fernández

G2 – *THE ROLE OF π-π INTERACTION IN DRIVING DIELS-ALDER CYCLOADDITION: INSIGHTS FROM ROTATIONAL SPECTROSCOPY* (14:30 – 15:00)
Q. Gou

G3 – *INTERMOLECULAR INTERACTIONS REVEALED WITH ROTATIONAL SPECTROSCOPY: STRUCTURE, DYNAMICS & CHIRALITY* (15:00 – 15:30)
Melanie Schnell

H: Posters

Tuesday, August 26, 16:30, Foyer

H1 – *HIGH-RESOLUTION ROTATIONAL SPECTRUM ANALYSIS OF HETEROCYCLIC COMPOUNDS FOR FUTURE ATMOSPHERIC APPLICATIONS*
G. Oubouali, H. El Hadki, A. El Hadki, I. Hadj Said, A. Cuisset, M. Carvajal-Zaera, H. V. L. Nguyen and I. Kleiner

H2 – *ROTATIONAL SPECTROSCOPY AND STRUCTURE OF BORNYL ACETATE*
L. Wang, W. Sun, J. Li, and M. Schnell

H3 – *PRESSURE-BROADENING LINE-SHAPE PARAMETERS OF CO ROVIBRONIC TRANSITIONS*
R. Hakalla, W. Ubachs, A. Stasik, N. de Oliveira, and J. Buldyreva

H4 – *LINE-SHAPE PARAMETERS OF METHANE BROADENED BY DRY AND HUMIDIFIED AIR FROM THE R(0) TO R(10) MANIFOLDS OF THE $2\nu_3$ BAND*
N. Dricot, D. Mondelain and A. Campargue

H5 – *ACCURATE INTENSITIES AND LINE PARAMETERS FOR THE $2\nu_3$-BAND OF METHANE BASED ON COORDINATED FOURIER-TRANSFORM AND CAVITY RING-DOWN SPECTROSCOPY MEASUREMENTS FROM THREE INDEPENDENT LABORATORIES*
R.-H. Yin, J.-K. Li, Z. D. Reed,J. Wang, A.-W. Liu, J. T. Hodges, M. Birk, Y. Tan, S.-M. Hu

H6 – *HIGH-RESOLUTION FT SPECTROSCOPY OF THE* $^{12}C^{16}O$ $a^3\Pi - X^1\Sigma^+$ *SYSTEM*
A. Stasik, W. Ubachs, R.W. Field, N. de Oliveira, W. Szajna, S. Ryzner, M. I. Malicka, S. Mahmoud, N. El-Kork, N. Abu Elkher, M. Al Mehairbi, R. Al Abdallah, T. Furtenbacher, O. P. Yurchenko, S. N. Yurchenko, J. Tennyson and R. Hakalla

H7 – *FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF THE FCS AND ClCS RADICALS*
Cheng-Han Tsai and Yasuki Endo

H8 – *MAGNETO OPTICAL TRAPPING OF ALUMINUM MONOFLUORIDE*
J. E. Padilla-Castillo, J. Cai, P. Agarwal, P. Kukreja, R. Thomas, B. G. Sartakov, S. Truppe, G. Meijer and S. C. Wright

H9 – *SHAPED LIGHT IN SPECTROSCOPY: HOW USING LIGHT CARRYING OAM CAN ENHANCE MOLECULAR SPECTROSCOPY*
Timo Gaßen, Mikhail Maslov, Georgios M. Koutentakis, Tom Jungnickel, Mirela Encheva, Monika Bahl and Oliver H. Heckl

H10 – *HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY OF THE* X^+ $^2\Sigma^+$ *GROUND STATE OF* $CaAr^+$
Joel R. Schmitz, David Walk, and Frédéric Merkt

H11 – *HIGH-RESOLUTION LASER AND MILLIMETER-WAVE SPECTROSCOPY AND MQDT ANALYSIS OF HIGH RYDBERG STATES IN Kr, Xe, AND Yb*
E. N. Toutoudaki, H. Herburger, U. Hollenstein, and F. Merkt

H12 – *LETOKHOV-CHEBOTAYEV TRAPPING SPECTROSCOPY OF* H_2
W. Ubachs, F.M.J. Cozijn, M. L. Diouf, C. Lauzin, H. Jóźwiak and P. Wcisło

H13 – *ON THE TUNNELLING DYNAMICS OF PROTONATED ACETYLENE: THE C-H-C STRETCHING BAND OF ITS BRIDGED CONFIGURATION*
E. Plaar, J. Sarka, T. Salomon, M. Fatima, O. Asvany, W. G. D. P. Silva, P. C. Schmid and S. Schlemmer

H14 – *LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER*
T. Salomon, C. Markus, O. Asvany, and S. Schlemmer

H15 – *THE GROUND STATE SUPERMULTIPLET OF NiD*
A. Pashov, A. J. Ross, and P. Crozet

H16 – *HIGH-POWER, LOW-NOISE MID-INFRARED OPTICAL FREQUENCY COMB FOR CAVITY-ENHANCED LAMB-DIP SPECTROSCOPY*
Vito F. Pecile, Filipp Lausch, Maximilian Prinz, Norbert Modsching, Valentin J. Wittwer, Thomas Südmeyer, Oliver H. Heckl

H17 – *HIGH-RESOLUTION ROVIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF THE* $C_2H_2N^+$ *ISOMERIC SYSTEM*
L. von Rötel, D. Gupta, W.G.D.P. Silva, O. Asvany, E. Plaar, J. Böing, S. Schlemmer and S. Thorwirth

H18 – *LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE JET-COOLED SiNSi RADICAL: ROTATIONAL ANALYSIS OF THE ELECTRONICALLY FORBIDDEN* $\tilde{D}\ ^2\Sigma_g^+$ – $\tilde{X}\ ^2\Pi_g$ *TRANSITION*
C. Motoyoshi, Y. Sumiyoshi, Y. Endo, M. Fukushima, and T. Ishiwata

H19 – *LINE PARAMETERS MEASUREMENTS AND SPECTROSCOPIC MODELING OF* CH_3F *IN THE 20–100* cm^{-1} *AND 1900–2400* cm^{-1} *SPECTRAL REGIONS*
H. Ziadi, M. Rey, J. Tison, B. Grouiez, A. Voute, L. Manceron, A. V. Nikitin, V. Boudon, H. Aroui, M. Rotger

H20 – *COMPETITION BETWEEN PRODUCT CHANNELS IN ION-MOLECULE REACTIONS NEAR 0 K:* $H_2{}^+$, HD^+ *AND* $D_2{}^+$ $+$ CH_3F
D. Schlander, R. Hahn, J. O. Richardson, T. P. Softley and F. Merkt

H21 – *MICROWAVE-CONTROLLED COLD CHEMISTRY*
F. B. V. Martins, H. Schmutz, J. A. Agner, V. Zhelyazkova, and F. Merkt

H22 – *THE STRUCTURE OF GAUCHE-1,3-BUTADIENE: FURTHER INSIGHTS FROM THE CENTIMETER-WAVE, MILLIMETER-WAVE, AND FAR-INFRARED HIGH RESOLUTION SPECTRA*
M.-A. Martin-Drumel, J. H. Baraban, P. B. Changala, M. J. Nava, J. P. Porterfield, B E. Billinghurst, G. B. Ellison, O. Pirali, J. F. Stanton, and M. C. McCarthy

H23 – *MILLIMETER-WAVE MEASUREMENTS IN HIGH-FINESSE CAVITY OF NITRO-DERIVATIVES TRACES: A NEW INSIGHT IN THE EXPLOSIVE VAPOR SENSING*
A. Roucou, M. Chrayteh, F. Simon, F. Hindle, G. Mouret, M. Goubet, J. Mory, C. Nicollet, A. Cuisset

H24 – *ADVANCEMENTS IN HOME-BUILT CHIRPED-PULSE SPECTROMETERS AT KÖLN*
P. Misra, M. Fatima, B. Heyne and S. Schlemmer

H25 – *DISENTANGLING THE SPECTRA OF COMPLEX ORGANIC RADICALS USING FARADAY-ROTATION-BASED MILLIMETER-WAVE INSTRUMENTATION*
R.Chahbazian and O. Pirali

H26 – *MILLIMETERWAVE CHIRPED-PULSE FOURIER TRANSFORM SPECTROSCOPY OF* $BiBr_3$ *BY LASER ABLATION IN A MULTIPASS CELL*
J. Bosmann, F. Peterß, Thomas F. Giesen and Guido W. Fuchs

H27 – *A HIGH-PURITY PARA-*H_2 *SOURCE FOR THE STUDY OF COLD ION-MOLECULE CHEMISTRY*
Jakob M. Braun, Raphaël Hahn, Josef A. Agner, Hansjürg Schmutz, Daniel Zindel, and Frédéric Merkt

H28 – *IMPROVING SPECTRAL ASSIGNMENT WITH NORMALIZING-FLOW COORDINATES*
Emil Vogt, Yahya Saleh, Álvaro Fernández Corral, Jochen Küpper, Andrey Yachmenev

H29 – *CRAZY ACCURACIES FROM THE FIRST PRINCIPLE. LINE INTENSITIES AND LINE CENTERS*
O.L.Polyansky, I.I. Mizus, J. Tennyson and N.F. Zobov

H30 – *CALCULATIONS OF COLLISION-INDUCED LINE-SHAPE PARAMETERS FOR* N_2*-PERTURBED LINES IN HF*
J. Behrendt, H. Jóźwiak, and P. Wcisło

H31 – *HYPERFINE ROVIBRATIONAL STATES OF* H_3^+ *IN A WEAK EXTERNAL MAGNETIC FIELD*
G. Avila, A. Sunaga, S. Komorovsky, and E. Mátyus

H32 – *HIGH RESOLUTION X-RAY SPECTRA OF* CH_2Cl_2 *- A QUANTUM CHEMICAL SIMULATION*
T. Uhlíková and E. Muchová

H33 – *AN EXACT OMEGA REPRESENTATION AS AN ADIABATIC TRANSFORMATION OF SPIN-ORBIT INTERACTIONS AND THEIR ASSOCIATED NON-ADIABATIC COUPLINGS: COMMON MISCONCEPTIONS*
R. P. Brady, S. N. Yurchenko, and J. Tennyson

H34 – *AB INITIO LINE INTENSITIES OF ROVIBRATIONAL TRANSITIONS IN* $O_2(X^3\Sigma_g^-)$
M. Gancewski, H. Jóźwiak, H. Cybulski, and P. Wcisło

H35 – *VIBRATIONAL SPECTRA OF 3,4-DIMETHYLMETHCATHINONE (3,4-DMMC)*
B. Kolářová, T. Uhlíková

H36 – *ELECTRON SPIN-TORSION COUPLING IN THE OBLATE-TOP ACETONYL RADICAL*
O. Pirali, R. Chahbazian, and L. H. Coudert

I: Plenary

Wednesday, August 27, 9:00, Hörsaal I

Chair: Thérèse Huet

I1 – *HIGH RESOLUTION INFRARED SPECTROSCOPIES OF JET-COOLED LARGE MOLECULES RELEVANT FOR ASTRONOMICAL AND ATMOSPHERIC ISSUES* (9:00 – 9:45)
P. Asselin, S. Chawananon, O. Pirali, M. Goubet and A. Cuisset

I2 – *MOLECULAR SPECTROSCOPY IN HELIUM NANODROPLETS: NEW INSIGHTS AND OPPORTUNITIES* (9:45 – 10:30)
Wofgang E. Ernst

J-I: Contributed Talks

Wednesday, August 27, 11:00, Hörsaal I

Chair: Silvia Spezzano

J-I.1 – *INVESTIGATING ENOLS CHEMISTRY IN THE INTERSTELLAR MEDIUM: ROTATIONAL SPECTROSCOPY AND INTERSTELLAR SEARCH OF (E)-1-PROPENOL* (11:00 – 11:15)
M. Nonne, M. Melosso, F. Tonolo, L. Bizzocchi, S. Alessandrini, J.-C. Guillemin, V. M. Rivilla and C. Puzzarini

J-I.2 – *TEMPERATURE-DEPENDENT PHOTODISSOCIATION RATES OF THE CH RADICAL* (11:15 – 11:30)
A. Sokolov, R. P. Brady, S. N. Yurchenko, and J. Tennyson

J-I.3 – *ROTATIONAL SPECTROSCOPY OF NAPHTHYLAMINES* (11:30 – 11:45)
Gayatri Batra, Colin Sueyoshi, Wenhao Sun, Mark D. Marshall, Helen O. Leung, Marie-Aline Martin-Drumel, Melanie Schnell

J-I.4 – *A MULTI-LEVEL EXCITATION DIAGRAM ANALYSIS OF VIBRATIONALLY EXCITED TiO IN THE ENVELOPE OF THE VARIABLE STAR χ CYG AT HIGH SPECTRAL RESOLUTION* (11:45 – 12:00)
E. Döring, J. H. Lacy, R. S. Giles, T. K. Greathouse, T.F. Giesen and G. W. Fuchs

J-I.5 – *SIMULATING SOLAR WIND–PAH COLLISIONS: A NEW PERSPECTIVE ON SMALL HYDROCARBON CATION FORMATION IN ASTROPHYSICAL ENVIRONMENTS* (12:00 – 12:15)
E. Dudás, P. Moretto-Capelle, M. Rapacioli and J-P. Champeaux

J-I.6 – *VIBRONIC AND OVERTONE BANDS OF HNC^+ AND HCN^+* (12:15 – 12:30)
M. Jiménez-Redondo, J. Palotás, H. A. Bunn, C. Schleif, P. Dohnal, O. Roncero, P. Caselli, and P. Jusko

J-II: Contributed Talks

Wednesday, August 27, 11:00, Hörsaal II

Chair: Wim Ubachs

J-II.1 – *CRYOGENIC OPTICAL CAVITY FOR HIGH-ACCURACY DOPPLER-LIMITED SPECTROSCOPY OF HYDROGEN* (11:00 – 11:15)
K. Stankiewicz, M. Makowski, M. Słowiński, K. L. Sołtys, B. Bednarski, H. Jóźwiak, N. Stolarczyk, M. Narożnik, D. Kierski, S. Wójtewicz, A. Cygan, G. Kowzan, P. Masłowski, M. Piwiński, D. Lisak, P. Wcisło

J-II.2 – *HIGH PRECISION MID-INFRARED VIBRATIONAL SPECTROSCOPY WITH COLD MOLECULES* (11:15 – 11:30)
R. Hahn, A. Bonifacio, M. Saffre, W. Dong, Y. Liu, S. Viel, M. N. Ngo, O. Lopez, E. Cantin, A. Amy-Klein, M. Manceau, B. Darquié

J-II.3 – *INELASTIC RECOIL SPECTROSCOPY: ROTATIONALLY RESOLVED SPECTROSCOPY OF A SINGLE POLYATOMIC MOLECULE* (11:30 – 11:45)
A.Calvin, S. Kresch, M. Brzeczek, L. Satterthwaite, D. Patterson

J-II.4 – *DETECTION AND QUANTIFICATION OF HNC AND HCN ISOMERS IN MOLECULAR PLASMAS REVEALED BY FREQUENCY COMB AND QCL SPECTROSCOPY* (11:45 – 12:00)
I. Sadiek, Simona Di Bernardo, Uwe Macherius, and Jean-Pierre H. van Helden

J-II.5 – *HIGH RESOLUTION SPECTROSCOPY OF* $PF^{35}Cl_2$ *AND* $PF^{35}Cl^{37}Cl$ *AND ISOTOPIC CHIRALITY* (12:00 – 12:15)
V. Horká-Zelenková, K. Keppler, A. Sieben, G. Seyfang, G. Wichmann, S. Albert, J. Stohner, and M. Quack

J-II.6 – *A DEEP ULTRAVIOLET MAGNETO-OPTICAL TRAP OF ALUMINIUM MONOFLUORIDE* (12:15 – 12:30)
J. E. Padilla-Castillo, J. Cai, P. Agarwal, P. Kukreja, R. Thomas, B. G. Sartakov, S. Truppe, G. Meijer and S. C. Wright

J-III: Contributed Talks

Wednesday, August 27, 11:00, Hörsaal III

Chair: Isabelle Kleiner

J-III.1 – *COMPLEX TUNNELLING DYNAMICS AND CONFORMATIONS IN 3,3,3-TRIFLUOROPROPANOL*$\cdots$ *WATER*$_N$ *(N=1-4) CLUSTERS* (11:00 – 11:15)
Alex Mort, Colton D. Carlson, and Yunjie Xu

J-III.2 – *LIGAND EXCHANGE IN A SUPERSONIC EXPANSION* (11:15 – 11:30)
B. Hartwig, J. N. Hasselhorn, R. Tovtik, N. A. Simeth and D. A. Obenchain

J-III.3 – *STUDY OF GEARED MOTION IN WATER-AFFECTED METHYL INTERNAL ROTATION BY MICROWAVE SPECTROSCOPY* (11:30 – 11:45)
Xiaolong Yi, Yongtao Wang, and Haoran Li

J-III.4 – *ELUCIDATING STRUCTURES AND NONCOVALENT INTERACTIONS IN MICRO-SOLVATED ALLYL PHENYL ETHER VIA ROTATIONAL SPECTROSCOPY* (11:45 – 12:00)
X.Wang, J.Li, J.-U. Grabow, and M. Schnell

J-III.5 – *STEPWISE MICROSOLVATION STUDY OF PREBIOTIC AMINOACETONITRILE BY ROTATIONAL SPECTROSCOPY:* (12:00 – 12:15)
N. Jiang and M. Schnell

J-III.6 – *WATER COMPLEXES ON A CYCLIC THIOETHER FROM BROADBAND ROTATIONAL SPECTROSCOPY* (12:15 – 12:30)
Farha Sajeev Hussain, Noureddin Osserian, Amanda L.Steber, and Cristóbal Pérez

K: Plenary

Thursday, August 28, 9:00, Hörsaal I

Chair: Jonathan Tennyson

K1 – *PROBING NEW RADICAL SPECIES USING HIGH RESOLUTION THZ SPECTROSCOPY* (9:00 – 9:45)
O. Pirali, R. Chahbazian, L. Juppet, M.-A. Martin-Drumel

K2 – *USING MOLECULAR SPECTROSCOPY TO INVESTIGATE THE EARTH'S ATMOSPHERE FROM ORBIT* (9:45 – 10:30)
Jeremy J. Harrison

L: Posters

Thursday, August 28, 11:00, Foyer

L1 – *THE ROTATIONAL-TORSIONAL SPECTRUM OF SINGLY DEUTERATED HYDROGEN PEROXIDE HOOD*
D. Herberth, K.M.T. Yamada, and T.F. Giesen

L2 – *HIGH RESOLUTION SPECTROSCOPY OF VIBRATIONAL TUNNELING DOUBLETS AND OVERTONES OF THE INVERSION IN ANILINE*
G. Wichmann, S. Albert, P. Lerch, K. Keppler, and M. Quack

L3 – *A THEORETICAL LINE LIST FOR THE HOPO MOLECULE*
Sergei N. Yurchenko, Ryan Mok, Oleksyi Smola

L4 – *A CRYOGENIC ION TRAP BEAMLINE AT HFML-FELIX FOR ASTROCHEMICAL STUDIES*
M. Gerlach, H. Kaur, P.A. Paunikar, K. Steenbakkers, D.B. Rap, S. Schlemmer, B. Redlich, and S. Brünken

L5 – *DECIPHERING THE COMPLEXITY IN THE ROTATIONAL SPECTRUM OF DEUTERATED ETHYLENE GLYCOL*
Jordan A. Claus, Mattia Melosso, Agathe Maillard, Luca Bizzocchi, Vincenzo Barone and Cristina Puzzarini

L6 – *MILLIMETER-WAVE SPECTRUM OF HYDANTOIN IN ITS VIBRATIONALLY EXCITED STATES*
Haruto Ishii, Kazuha Hirano, Hiroyuki Ozeki, and Kaori Kobayashi

L7 – *ELUSIVE TAUTOMER OF ACETONE CHARACTERIZED BY ROTATIONAL SPECTROSCOPY*
L. Kolesniková, M. Kříž, K. Vávra, T. Uhlíková, P. Kania, Š. Urban, and J.-C. Guillemin

L8 – *ROTATIONAL SPECTROSCOPY AS A TOOL TO STUDY VIBRATION-ROTATION INTERACTION: INVESTIGATIONS OF* ^{13}*CH*$_3$*CN AND CH*$^{13}_3$*CN UP TO* $v_8 = 2$ *AND A SEARCH FOR* $v_8 = 2$ *TRANSITIONS TOWARD SAGITTARIUS B2(N)*
H. S. P. Müller, A. Belloche, F. Lewen, and S. Schlemmer

L9 – ^{13}*C- AND* ^{15}*N-MONOSUBSTITUTED ISOTOPOLOGUES OF HC*$_3$*N: CHARACTERIZATION OF THE RESONANCE SYSTEMS*
G. Panizzi, M. Nonne, L. Bizzocchi, M. Melosso, S. Alessandrini, and C. Puzzarini

L10 – *HIGH-RESOLUTION INFRARED INVESTIGATIONS OF CIRCUMSTELLAR ENVIRONMENTS OF LATE-TYPE STARS USING SMALL MOLECULES AS PROBES*
G. W. Fuchs, Eileen Döring,

L11 – *INVESTIGATION OF WATER-CONTAINING CLUSTERS WITH A 6-18 GHz CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER*
S. Collignon, A. S. Bogomolov, B. M. Hays, N. Moazzen-Ahmadi, M. Herman, D. Lederer and C. Lauzin

L12 – *CONFORMERS OF THE* α*-PINENE - WATER COMPLEX: ROTATIONAL SPECTROSCOPY AND ELECTRONIC STRUCTURE CALCULATIONS*
Arsh S. Hazrah, Colton D. Carlson, Mohamad H. Al-Jabiri, Yunjie Xu, and Wolfgang Jäger

L13 – *INVESTIGATION ON NON-COVALENT INTERACTIONS IN 3-FLUOROBENZYLAMINE-WATER COMPLEXES BY MEANS OF MICROWAVE SPECTROSCOPY*
A. Maggio, P. Pinillos, W. Song, F. Sun, T. Coccia, Y. Liang, A. Maris, L. Evangelisti, W. Li, M. Zhou, and S. Melandri

L14 – *ROTATIONAL SPECTROSCOPY AND TAUTOMERIC EQUILIBRIA IN COMPLEXES FORMED WITH ISOTHIAZOLINONE*
J. Li , D. Loru, W. Sun, L. Wang , and M. Schnell

L15 – *STRUCTURE AND MICRO-SOLVATION OF A PROTOTYPE PYRANOSE MOLECULE: A ROTATIONAL SPECTROSCOPIC STUDY*
J. Ma, E.R. Alonso, A. Insausti, W. Jäger, Y. Xu and E.J.Cocinero

L16 – *MID-INFRARED DETECTION OF MOLECULAR SPECIES IN REACTIVE PLASMAS USING A QUANTUM CASCADE LASER-BASED ABSORPTION SPECTROMETER*
Simona Di Bernardo, Ibrahim Sadiek, Uwe Macherius, and Jean-Pierre H. van Helden

L17 – *PRECISE FREQUENCIES OF H*$_2{}^{16}$*O LINES PROTECTED FOR RADIO ASTRONOMY*
A. Altman, R. Tóbiás, A. S. Bogomolov, M.L. Diouf, F.M.J. Cozijn, A.G. Császár, C. Lauzin and W. Ubachs

L18 – *ROVIBRATIONAL ASSIGNMENTS OF HIGHLY CONGESTED SPECTRA BASED ON VARIATIONAL CALCULATIONS: APPLICATION TO ETHYLENE (C*$_2$*H*$_4$*) AND CH*$_3$*D*
O. Ben Fathallah, A. Campargue, S. Beguier, D. Mondelain, L. Manceron, M. Rey, J. Vander Auwera

L19 – *HIGH-RESOLUTION SPECTROSCOPY OF COMPLEX ORGANIC MOLECULES UNDER UV FIELDS*
A. Potapov, S. Schlemmer, H. S. P. Müller, and F. Lewen

L20 – *DENSITY DEPENDENCE OF THE MEASURED LINE INTENSITY FOR* O_2 *TRANSITIONS*
H. Tran, J.T. Hodges, H. Fleurbaey, E. Adkins, E. C. Gross, J. Klemm, A. Campargue, D. Mondelain

L21 – *ROTATIONAL SPECTROSCOPY OF EPIIODOHYDRIN AND THE* ^{127}I *NUCLEAR QUADRUPOLE COUPLING TENSOR*
W. Sun and M. Schnell

L22 – *COMB-ASSISTED CAVITY RING-DOWN SPECTROSCOPY AT 2* μ
M.A. Khan, E. Fasci, V. D'Agostino, S. Gravina, A. Castrillo, and L. Gianfrani

L23 – *NEW LOOK AT PERTURBATIONS IN THE* $N_2(C^3\Pi_U, V)$ *ELECTRONIC STATE. INDIRECT PREDISSOCIATION THROUGH* $C''^5\Pi_U$ *AND* $1^7\Sigma_U^+$ *STATES*
Laiz R. Ventura, Ramon S. da Silva, Jayr Amorim and Carlos E. Fellows

L24 – *SYSTEMATIC AB INITIO CALCULATION OF ROVIBRATION LINELISTS AND EFFECTIVE HAMILTONIANS USING CANONICAL VAN VLECK OPERATOR PERTURBATION THEORY*
S.V. Krasnoshchekov, E.O. Dobrolyubov, I.M. Efremov

L25 – *SATURATED ABSORPTION SPECTROSCOPY OF M1 TRANSITIONS OF* $^{16}O_2$ *IN THE 761-768nm*
Y.-Q. Cheng, Z.-T. Zhang, Y.-R. Xu, Y. Tan, A.-W. Liu and S.-M. Hu

L26 – *ELECTRONIC SPECTRUM OF JET-COOLED* CO_3^-
Masaru Fukushima

L27 – *A COMPLETE AB INITIO SPECTROSCOPIC DATASET OF THE HYDROGEN MOLECULE FOR ASTROPHYSICAL STUDIES*
N. Stolarczyk, J. Behrendt, H. Jóźwiak, M. Słowiński, R. J. Hargreaves, I. E. Gordon, and P. Wcisło

L28 – *HITRAN2024: MORE MOLECULES/ISOTOPOLOGUES, BROADER SPECTRAL AND DYNAMIC RANGES, MORE PARAMETERS, BETTER QUALITY*
I.E. Gordon, R. J. Hargreaves, F. M. Gomez, T. Bertin, M. O'Donnel and L. S. Rothman

L29 – *NEW METROLOGICAL AMMONIA ABSORPTION LINE DATA NEAR 6500* cm^{-1}
V. Gorshelev, J. Nwaboh, G. D. Banik, A. Pogany, F. Witt

L30 – *LINE POSITIONS OF* CH_3F *IN THE* $20 - 100\ cm^{-1}$ *AND* $1900 - 2400\ cm^{-1}$ *SPECTRAL REGIONS*
H. Ziadi, M. Rey, J. Tison, B. Grouiez, A. Voute, L. Manceron, A. V. Nikitin, V. Boudon, H. Aroui and M. Rotger

L31 – *MARVEL ANALYSIS OF THE MEASURED HIGH-RESOLUTION ROVIBRATIONAL AND ROVIBRONIC SPECTRA OF* $^{12}C^{16}O$ *MOLECULE*
Salman Mahmoud, Nayla El-Kork, Nariman Abu Elkher, Chenyi Tao, Mubarak Almehairbi, Malathe Samir Khalil, Rania Al Abdallah, Tibor Furtenbacher, Attila G. Császár, Aleksandra Stasik, Rafal Hakalla, Wim Ubachs, Robert W. Field, Nelson de Oliveira, Wojciech Szajna, Stanislaw Ryzner, Marzena I. Malicka, Olga P. Yurchenko, Sergey N. Yurchenko, and Jonathan Tennyson

L32 – *HIGH RESOLUTION STUDY OF THE ν_{14} BAND OF PYRROLE (C_4H_5N) NEAR 14 μm*
C. Silva Tafur, A. Rizopoulos , and J. Vander Auwera

L33 – *EXOMOL LINE LIST FOR THE $A\,^1\Pi$–$X\,^1\Sigma^+$ BAND SYSTEM OF ^{12}C^{16}O AT HIGH TEMPERATURE*
Chenyi Tao, Jonathan Tennyson, Sergei N. Yurchenko and Nayla El-Kork

L34 – *CASDA24: LATEST UPDATES TO THE DIJON CALCULATED SPECTROSCOPIC DATABASES*
V. Boudon and C. Richard

L35 – *THE ROTATIONAL CONFORMATIONAL BEHAVIORS OF PHENOL – THIOPHENOL HETERODIMER*
W. Li, C. Pérez, and A. Lesarri

L36 – *THE THRESHOLD PHOTOELECTRON SPECTRUM OF THE THIOFORMYL RADICAL: EXPERIMENT AND MODELING*
M. Drissi, G. A. Garcia, L. H. Coudert, B. Gans, S. Boyé-Peronne, H. L. Le, M. Jiang, and J.-C. Loison

M: Minisymposium on Clocks and Metrology

Thursday, August 28, 14:00, Hörsaal I

Chair: Paolo De Natale

M1 – *COHERENCE, CLOCKS, AND FUNDAMENTAL PHYSICS* (14:15 – 15:00)
Jun Ye

MOLECULAR PHYSICS LECTURE

M2 – *MOLECULAR LATTICE CLOCKS* (15:00 – 15:30)
T. Zelevinsky

M3 – *HIGHLY CHARGED ION CLOCKS TO TEST FUNDAMENTAL PHYSICS* (15:30 – 16:00)
Piet O. Schmidt

N-I: Contributed Talks

Thursday, August 28, 16:30, Hörsaal I

Chair: Neil Reilly

N-I.1 – *QUANTITATIVE ABSORPTION SPECTROSCOPY OF ACETYLENE IN THE BLUE REGION* (16:30 – 16:45)
H. Fleurbaey, G. Méjean, S. Kassi, and A. Campargue

N-I.2 – *PRECISION SPECTROSCOPY AND FREQUENCY STABILIZATION USING A COMPACT DUAL-MODE CAVITY-ENHANCED ABSORPTION SPECTROMETER AT 1550 nm* (16:45 – 17:00)
W.-T. Wang, T.-P. Hua, Z.-T. Zhang, Z.-J. Yuan, Y.-R. Sun, A.-W. Liu, and S.-M. Hu

N-I.3 – *SPECTROSCOPIC GAS TEMPERATURE AND CONCENTRATION DETERMINATION USING CARBON MONOXIDE LINE INTENSITIES* (17:00 – 17:15)
S. Wójtewicz, D. Lisak, V. D'Agostino, A. Cygan, M. Gibas, P. Wcisło, R. Ciuryło, K. Bielska

N-I.4 – *LEAK-OUT SPECTROSCOPY OF RENNER-TELLER DISTORTED* $HNCS^+$ (17:15 – 17:30)
M. Gerlach, J. van der Hulst, H. Kaur, G. C. Groenenboom and S. Brünken

N-I.5 – *JET-COOLED ETHYLENE SPECTROSCOPY IN THE 5880-6200* cm^{-1} *REGION TO STUDY COLD AND HOT BAND TRANSITIONS* (17:30 – 17:45)
S. Perot, J. Lecomte, N. Suas-David, L. Rutkowski, M. Rey, S. Kassi, and R. Georges

N-I.6 – *A VERSATILE INSTRUMENT TO STUDY THE REACTIVITY AND SPECTROSCOPY OF ISOMER-SELECTED MOLECULAR IONS* (17:45 – 18:00)
C. Rossi, A. P. Rasmussen, B. Gans, J. Jašík, J. Žabka, and U. Jacovella

N-II: Contributed Talks

Thursday, August 28, 16:30, Hörsaal II

Chair: Sergey Yurchenko

N-II.1 – CS^{2+}*: A COMPLEX MODEL FOR SPECTROSCOPIC APPLICATIONS* (16:30 – 16:45)
L. Hrubcik, T. Uhlíková,

N-II.2 – *TEMPERATURE-DEPENDENT PHOTODISSOCIATION CROSS SECTIONS AND RATES FOR* H_2O *AND* H_2S (16:45 – 17:00)
Armando N. Perri, Alexander O. Mitrushchenkov, Sergei N. Yurchenko, and Jonathan Tennyson

N-II.3 – *THE INVERSION-INTERNAL ROTATION-ROTATION PROGRAMME FOR THE METHYLAMINE MOLECULE* (17:00 – 17:15)
M. Kręglewski and I. Gulaczyk

N-II.4 – *AI-GENERATED SOFTWARE SUITE APPLIED TO RO-VIBRATIONAL ANALYSIS OF HIGH-RESOLUTION FTIR SPECTRA OF THE* ^{13}C*-ENRICHED MIXTURE OF* $CHClF_2$ (17:15 – 17:30)
E.O. Dobrolyubov, I.M. Efremov, S.V. Krasnoshchekov, V.B. Laptev, S.A. Klimin, and O.V. Naumenko

N-II.5 – *METHYL INTERNAL ROTATION AND* ^{14}N *NUCLEAR QUADRUPOLE COUPLING EFFECTS IN THE MICROWAVE SPECTRUM OF 2-FLUORO-4-PICOLINE ANALYZED USING THE* `WESTERFIT` *PACKAGE* (17:30 – 17:45)
J.H. Westerfield, Mike Buttkus-Barth, and Ha Vinh Lam Nguyen

N-II.6 – *COLLISIONAL EFFECTS IN ATMOSPHERIC SPECTRA THROUGH RIGOROUS QUANTUM SCATTERING CALCULATIONS* (17:45 – 18:00)
M. Gancewski, H. Jóźwiak, A. Olejnik, J. Behrendt, M. Żółtowski, and P. Wcisło

N-III: Contributed Talks

Thursday, August 28, 16:30, Hörsaal III

Chair: Guido Fuchs

N-III.1 – *HOT MOLECULES, COLD VALVE: ENHANCING MOLECULE VAPORIZATION FOR ASTRO-CHEMISTRY SEARCHES* (16:30 – 16:45)
R.J.C. Roque, F. Ferreira, R.B.L. Vieira, N.M. Campos and S.R. Domingos

N-III.2 – *TIME RESOLVED MID-INFRARED FREQUENCY COMB SPECTROSCOPY IN* CO_2 *PLASMA ENVIRONMENTS* (16:45 – 17:00)
M. Briend, D. Sadi, O. Guaitella and L. Rutkowski

N-III.3 – *IR SPECTRA OF ASTROCHEMISTRY-RELATED RADICALS PRODUCED VIA HYDROGEN-ATOM REACTIONS USING PARA-HYDROGEN MATRIX ISOLATION* (17:00 – 17:15)
Yuan-Pern Lee

N-III.4 – *ROVIBRATIONAL COMPUTATIONS FOR THE* He_2 $a\ {}^3\Sigma_u^+$, $b\ {}^3\Pi_g$ *AND* $c\ {}^3\Sigma_g^+$ *STATES INCLUDING NON-ADIABATIC, RELATIVISTIC, AND QED CORRECTIONS AND COUPLINGS* (17:15 – 17:30)
Balázs Rácsai, Péter Jeszenszki, Ádám Margócsy, and Edit Mátyus

N-III.5 – *INTEGRATED THEORETICAL AND EXPERIMENTAL INVESTIGATION: ACCURATE STRUCTURE OF NORCAMPHOR AND CONFORMATIONAL LANDSCAPE OF TIOPRONIN* (17:30 – 17:45)
L. Uribe, M. Mendolicchio, S. Mato, S. Municio, J.L. Alonso, E. R. Alonso, I. León, and V. Barone

N-III.6 – *SPECTACLE – SPECTROSCOPY TAILORED ACTIVE LEARNING ALGORITHM FOR MACHINE LEARNING POTENTIALS* (17:45 – 18:00)
B. Schröder

O: Posters

Friday, August 29, 9:00, Foyer

O1 – *ROTATIONAL SPECTROSCOPY OF METHYLALLENE AND SEARCH FOR IT IN SPACE*
H. S. P. Müller, J.-C. Guillemin, F. Lewen, and S. Schlemmer

O2 – *ROTATIONAL SPECTROSCOPY OF* CH_3C_3N: *l-TYPE DOUBLING IN BENDING VIBRATIONS AND GROUND-STATE ANALYSIS OF ITS ISOTOPOLOGUES*
J. Koucký, M. Melosso, L. Bizzocchi, M. Nonne, S. Alessandrini and C. Puzzarini

O3 – *BRANCHED ACYLIUM IONS: INFRARED ACTION-SPECTROSCOPIC STUDY OF* $C_2H_3CO^+$ *AND* $C_2H_5CO^+$
S. Thorwirth, M. Bast, P. C. Schmid, K. Steenbakkers, S. Brünken, O. Asvany, and S. Schlemmer

O4 – *ASAP & ASAP*^{2} *ANALYSIS OF THE IR-SPECTRUM OF CYCLOPENTADIENE*
L. Bonah, S. Thorwirth, S. Schlemmer, O. Pirali, M.-A. Martin-Drumel, J.-C. Guillemin, F. Tonolo, M. Melosso, L. Bizzocchi, C. P. Endres

O5 – *$HOCS^+$ AND $HSCO^+$ SPECTROSCOPY*
J. L. Doménech, W.G.D.P. Silva, V. Lattanzi, S. Thorwirth, S. Schlemmer and O. Asvany

O6 – *DESIGN AND PERFORMANCES OF THE LILLE ICE TERAHERTZ EXPERIMENT (LITE)*
M. Aliekseieva, R. A. Motiyenko, G. Dekyndt and E. Dartois

O7 – *INVESTIGATIONS ON ASTROPHYSICALLY RELEVANT NITRILES PRODUCED VIA DC PLATE DISCHARGE: TOWARDS HIGH-RESOLUTION REMPI SPECTROSCOPY OF AMINOACETONITRILE (NH_2CH_2CN)*
V. Grigorian, J. Jakob, S. Schwetje, M.A. Kaufmann, A. Breier, T.F. Giesen and G.W Fuchs

O8 – *ROVIBRATIONAL OVERTONE AND COMBINATION BANDS OF THE $HCNH^+$ ION*
M. Kassayová, M. Jiménez-Redondo, J. Sarka, P. Dohnal, J. Glosík, P. Caselli, and P. Jusko

O9 – *NO^{2+} DICATION SPECTRAL MODEL FOR ANY KIND OF SPECTROSCOPIC USAGE*
J. Šturma and T. Uhlíková

O10 – *COMPARISON OF ETHYLENE SPECTRA AT 10 μm RECORDED BY FOURIER TRANSFORM AND FREQUENCY COMB SPECTROMETERS*
R. Vallon, H. Ziadi, C. Jacquemin, J. Tison, F. Lecasse, B. Parvitte, V. Zeninari and M. Rotger

O11 – *MEASUREMENTS OF SELF-PERTURBED METHANE LINES IN THE ν_4 BAND BY DUAL-COMB SPECTROSCOPY*
N. Dricot, B. Vispoel, and M. Lepère

O12 – *MEASUREMENTS OF THE INFRARED CROSS-SECTIONS OF POTENTIAL EXOPLANETARY BIOSIGNATURES: CHLOROIODOMETHANE AND 2-IODOPROPANE*
Muhammad Osama Ishtiak, Orfeo Colebatch, Karine Le Bris, Paul J. Godin, and Kimberly Strong

O13 – *QUANTITATIVE FTIR SPECTROSCOPY OF CORROSIVE AND UNSTABLE ATMOSPHERIC GASES : APPLICATION TO HNO_3, HONO AND HOBr*
A. Voute, W. Tchana-Betnga, A. Perrin, F. Kwabia-Tchana and L. Manceron

O14 – *SIMPLIFIED MODELING OF ETHYLENE: IMPACT OF SYMMETRIC-TOP APPROXIMATION ON COLLISIONAL LINE BROADENING*
S. Clavier and J. Buldyreva

O15 – *THEORETICAL SPECTROSCOPIC STUDY OF ISOPRENE AND AMYLENE*
S. Brahem, D. Missaoui, K. Sidi Said, S. Dalbouha, O. Yazidia, F. Najar, N. Jaïdane, M.L.Senent

O16 – *PREDICTION OF N_2-BROADENED LINE-SHAPE PARAMETERS OF CO_2 LINES USING REQUANTIZED CLASSICAL MOLECULAR DYNAMICS SIMULATIONS (rCMDS)*
L. Denis, H. Tran, M. Lepère, B. Vispoel and N.H. Ngo

O17 – *LINEAR OPTICAL FEEDBACK CAVITY RING-DOWN SPECTROSCOPY AT 3-μm WAVELENGTH: MEASURING RESIDUAL GASES IN AN ULTRA-HIGH VACUUM ENVIRONMENT*
V. D'Agostino, S. Gravina, E. Tofani, E. Fasci, A. Grado, A. Castrillo and L. Gianfrani

O18 – *FIGURES OF MERIT QUANTIFYING PRECISION AND BIAS IN MULTISPECTRUM LEAST-SQUARES ANALYSES OF MEASURED SPECTRA*
E. C. Gross, A. J. Fleisher, and J. T. Hodges

O19 – *NON-EMPIRICAL DERIVATION OF AN EFFECTIVE DIPOLE MOMENT OPERATOR FOR ASYMMETRIC TOPS*
E.O. Dobrolyubov, S.V. Krasnoshchekov

O20 – *VIBRATIONAL SPECTRA, RESONANCES AND POLYADS OF C_2H_4 AND C_2D_4 PREDICTED BY THE FOURTH ORDER VIBRATIONAL OPERATOR PERTURBATION THEORY CVPT(4) AND THE A-VCI*
V. Le Bris, S.V. Krasnoshchekov, E.O. Dobrolyubov, I.M. Efremov, I.V. Polyakov, O. Coulaud, and D. Bégué

O21 – *RELATIVISTIC QED CORRECTIONS TO THE CORRELATED NO-PAIR DIRAC–COULOMB(–BREIT) ENERGY*
Á. Nonn, and E. Mátyus,

O22 – *AN ANALYSIS AND AN INTERPRETATION OF THE PHOTO-ELECTRON SPECTRA OF THE NITRATE ANION, NO_3^-*
M. Fukushima

O23 – *BROADBAND MID-INFRARED SPECTROSCOPY IN A $CH_4 + O_2$ PLASMA GLOW DISCHARGE*
M. Briend, M. Budde, O. Guaitella and L. Rutkowski

O24 – *TOWARDS THE MEASUREMENT OF ORBITAL ANGULAR MOMENTUM-ENABLED TRANSITIONS IN MOLECULES*
T. Jungnickel, M. Bahl, G.M. Koutentakis, M. Maslov,T. Gaßen, M. Encheva and O.H. Heckl

O25 – *DEVELOPMENT OF SINGLE-PHOTON DOPPLER-FREE VUV/XUV SPECTROSCOPY EXPERIMENT*
M. H. Rayment, J. A. Agner, H. Schmutz, and F. Merkt

O26 – *MOLECULAR SPECTROSCOPY EXPLOITING RESONANT FREQUENCIES OF AN OPTICAL CAVITY*
A. Cygan, S. Wójtewicz, H. Jóźwiak, G. Kowzan, N. Stolarczyk, K. Bielska, P. Wcisło, R. Ciuryło, D. Lisak

O27 – *DIABATIC AND ADIABATIC APPROXIMATION*
A. Dimova, V. Stoyanov, A. Pashov

O28 – *EXPERIMENTAL AND THEORETICAL STUDY OF THE GROUND AND LOWEST EXCITED STATES OF THE NaSr MOLECULE*
P. Kowalczyk, J. Szczepkowski, M. Gronowski, M. Olko, R. Vexiau, M. Tomza, O. Dulieu, and W. Jastrzebski

O29 – *LOW-TEMPERATURE ABSORPTION SPECTROSCOPY FOR SIMULTANEOUS RETRIEVAL OF VAPOR PRESSURE AND TRANSITION INTENSITIES.*
D. Chernenko, F. Pastierovič, and P. Čermák

O30 – *FOURIER TRANSFORM CAVITY RING-DOWN SPECTROSCOPY: PRECISE RETRIEVAL OF CO-AR LINE PROFILES*
R. Dubroeucq, D. Charczun, P. Masłowski and L. Rutkowski

O31 – *TOWARDS THE DETECTION OF ENANTIOMERIC EXCESS OF CHIRAL MOLECULES USING PHOTOELECTRON CIRCULAR DICHROISM IN A MOLECULAR BEAM*
S. Schwetje, V. Grigorian, J. Jakob, M. A. Kaufmann, A. Breier, T. F. Giesen and G. W. Fuchs

O32 – *ACCURATE MEASUREMENT OF TRACE MOISTURE IN GAS USING LASER-WAVELENGTH-TUNED CRDS*
H. Abe

O33 – *HIGH-RESOLUTION UV SPECTROSCOPY OF CHIRAL CANDIDATES FOR ESST APPLICATIONS*
Shilpa Yadav, JuHyeon Lee, Elahe Abdiha, Nadia González Rodríguez, Boris G. Sartakov, Gerard Meijer, Sandra Eibenberger-Arias

O34 – *NUCLEAR SPIN ISOMER SELECTION VIA LEAK-OUT SPECTROSCOPY*
O. Asvany, D. Gupta, W.G.D.P. Silva, S.J.P. Marlton, T. Salomon, P.C. Schmid and S. Schlemmer

O35 – *LARGE AMPLITUDE MOTION AND GEOMETRY INVESTIGATION FOR SIMILAR COMPLEXES OF 3-PHENYLPROPIONALDEHYDE-H_2O AND 3-PHENYLPROPIONALDEHYDE-H_2S*
M. Li, W. Li, A. Lesarri, J.-U. Grabow

O36 – *PRECISION SPECTROSCOPY OF THE FINE-STRUCTURE IN THE* $a\,^3\Sigma_u^+(v=0)$ *AND* $c\,^3\Sigma_g^+(v=4)$ *STATES OF THE HELIUM DIMER*
V. Wirth, M. Holdener, and F. Merkt

P: Plenary

Friday, August 29, 11:00, Hörsaal I

Chair: Thomas Giesen

P1 – *COHERENT CONTROL OF CHIRAL MOLECULES* (11:00 – 11:45)
S. Eibenberger-Arias

P2 – *RECENT ADVANCES IN THE QUANTUM-CHEMICAL CALCULATIONS OF SPECTROSCOPIC PARAMETERS FOR ROVIBRATIONAL SPECTROSCOPY* (11:45 – 12:30)
Jürgen Gauss

A: Plenary

Monday, August 25, 9:00
Hörsaal I

Chair: Frédéric Merkt

INFRARED SPECTROSCOPY AND UNIMOLECULAR DYNAMICS OF REACTIVE INTERMEDIATES

Marsha I. Lester

University of Pennsylvania

Hydroperoxyalkyl (QOOH) intermediates are important carbon-centered radicals formed during alkane oxidation in atmospheric and low-temperature combustion chemistry. However, direct observation of QOOH intermediates has been challenging due to their transient nature and low steady-state concentration. The QOOH intermediates can decay by unimolecular dissociation to hydroxyl (OH) radicals and cyclic ether products or undergo bimolecular reaction with O_2 leading to low-volatility organic compounds or autoignition. An alternative synthetic method has been developed to generate stabilized QOOH radicals under jet-cooled and collision-free conditions.[1],[2],[3],[4] The QOOH intermediates are characterized by their infrared (IR) fingerprint across the 3500-7100 cm^{-1} spectral region. IR activation also initiates energy- and time-resolved unimolecular dissociation dynamics of QOOH to OH products, which are detected by UV laser-induced fluorescence. The experimental kinetic studies are supported by theoretical characterization of the transition state region to compute energy-dependent and thermal decay rates. The combined experimental and theoretical approaches provide new insights on the unimolecular reaction dynamics, including heavy atom tunneling, of transient QOOH intermediates under controlled laboratory conditions as well as their impact in realistic atmospheric and combustion chemistry.

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[1] Hansen, A. S. et al. **2021** *Science*, 379, 679-682.

[2] Qian, Y. et al. **2024** *Proc. Natl. Acad. Sci.*, 121, e2401148121.

[3] Roy, T.K. et al. **2024** *J. Chem. Phys.*, 161, 034302.

[4] Qian, Y. et al. **2024** *J. Phys. Chem. A*, 128, 9240-9250.

EXOPLANET ATMOSPHERIC CHEMISTRY IN THE JWST ERA

L. Kreidberg[a]

[a] Max Planck Institute for Astronomy

The launch of the James Webb Space Telescope (JWST) heralded a new era in the study of the atmospheric chemistry of extrasolar planets. Thanks to its large mirror, broad spectroscopic wavelength coverage (0.6 - 12 μm), and superb performance, JWST has revealed an unprecedented and high signal-to-noise collection of molecules (illustrated at right).[1] A wider range of planets are accessible than ever before, from hot Jupiters down to sub-Neptunes and possibly even Earth-size planets. Meanwhile, a plethora of ground-based high-resolution spectrographs have opened up the study of exoplanet atmospheres at the level of individual lines, enabling detailed characterization of atmospheric dynamics and the detection of less spectrally active species.

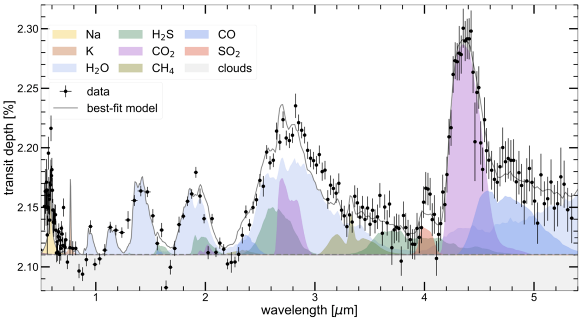

Figure 1: The JWST/NIRSpec transmission spectrum of the hot Jupiter WASP-39b from Rustamkulov et al. 2023. The data (black points) are well explained by contributions from Na (19σ), H_2O (33σ), CO_2 (28σ), CO (7σ), SO_2 (2.7σ) and clouds (21σ). The shading corresponds to the contribution from each individual species.

Together with this progress, some challenges have emerged, including unique identification of chemical species and imperfect line lists, particularly over the diverse range of temperatures observed in exoplanet atmospheres. These issues were highlighted in the recent debate about the presence of dimethyl sulfide in the habitable zone exoplanet K2-18b. In this talk, I will give an overview of recent progress in the chemical characterization of exoplanets, highlighting the critical importance of high-resolution molecular spectroscopy that underpins this field.

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[1] Rustamkulov, Z., et. al. **2023** *Nature*, 614, 7949

B: Posters

Monday, August 25, 11:00
Foyer

INFRARED SPECTROSCOPY OF H_5^+

S.J.P. Marlton[a], J. Sarka[a], P. C. Schmid[a], T. Salomon[a], O. Asvany[a], and S. Schlemmer[a]

[a] I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937, Cologne, Germany.

The H_5^+ molecular ion is of fundamental interest because its complexity pushes the boundaries of molecular spectroscopy. H_5^+ features multiple large amplitude tunneling motions that cause several foundational spectroscopic concepts begin to break down, including molecular structure, normal modes of vibration, typical group theoretical treatments, and the separation of vibrational and rotational degrees of freedom. This complexity is encoded in the rovibrational levels; however, until now there have been no rovibrationally resolved spectra of H_5^+ reported. Using leak-out spectroscopy (LOS)[1] we measure the first rovibrationally resolved infrared spectrum of H_5^+. In this experiment, H_5^+ ions are stored in a cryogenic (20 K) 22-pole ion trap and irradiated with an infrared quantum cascade laser. These photoexcited ions collide with neutral He gas atoms to transfer the vibrational internal energy of the ion into kinetic energy, giving the ion sufficient kinetic energy to leak out of the trap and be detected. The LOS spectrum is constructed by measuring the leak-out ion yield as a function of laser frequency. We employ LOS to measure the H_5^+ vibrational band centered at $940\,\mathrm{cm}^{-1}$ (a combination band exciting the central proton hop and outer hydrogen separation). To attempt to understand the experimental results, we also undertook calculations that numerically solve the nuclear Schrödinger equation on a reduced dimensional (4D) potential energy surface. These calculations include rovibrational coupling, and provided the first comparison between calculated and experimental rovibrational levels of H_5^+. This comparison indicate that the torsional tunneling is reasonably well described by the calculations, and provide evidence that all five protons can feasibly exchange through tunneling. These results are an important step towards understanding the coupling between rotation and large amplitude tunneling motions in H_5^+.

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[1] Schmid et al., **2022**, *J. Phys. Chem. A.*, 126(43), pp.8111-8117.

HIGH RESOLUTION VIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF PROTONATED METHANOL ($CH_3OH_2{}^+$)

W.G.D.P. Silva[a], O. Asvany[a], S. Thorwirth[a], T. Salomon[a], I. Kleiner[b], I. Gulaczyk[c], M. Kreglewski[c] and S. Schlemmer[a]

[a] I. Physikalisches Institut, Universität zu Köln, Köln, Germany
[b] Université Paris Cité and Université Paris-Est Créteil, CNRS, LISA, 75013, Paris, France
[c] Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

Employing the recently developed leak-out action spectroscopy method [1] in a cryogenic ion trap apparatus, we succeeded to measure the first rotationally-resolved infrared spectra of protonated methanol ($CH_3OH_2{}^+$). Rovibrational transitions for three different vibrational bands have been measured; the fundamental symmetric and anti-symmetric C-H stretching vibrations around 3000 cm^{-1} and 3100 cm^{-1}, respectively, as well as the symmetric O-H stretching vibration at 3510 cm^{-1}. Due to coupled large-amplitude motions (CH_3 internal rotation and OH_2 inversion), the observed rovibrational spectra are extremely complex containing numerous tunneling components, which have different symmetries belonging to the permutation-inversion group G_{12}. As a result, more than 6,000 rovibrational transitions were observed within a total coverage range of approximately 90 cm^{-1}. Among this plethora of lines, a few line series matching the expected pattern for specific transitions of two tunneling components (tentatively assigned here to be of B- and A-symmetry) have been observed. Based on these preliminary assignments, frequencies of selected pure rotational transitions of both species were predicted and finally detected in the 40-350 GHz range employing a double-resonance vibrational-rotational spectroscopic scheme. [2] First searches for $CH_3OH_2{}^+$ in space will now be possible.

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[1] Schmid, P.C., Asvany, O., Salomon, T., Thorwirth, S. and Schlemmer, S. **2022** *J. Phys. Chem. A.*, 126, 8111.

[2] Asvany, O., Thorwirth, S., Schmid, P.C., Salomon, T., and Schlemmer, S. **2023** *Phys. Chem. Chem. Phys*, 25, 19740.

CONFORMATIONAL ANALYSIS OF 2-(METHYLTHIO)ETHYLAMINE AND 2-(ETHYLTHIO)ETHYLAMINE USING ROTATIONAL SPECTROSCOPY

A. Chaudhary[a], P. Chheang[a], and J. van Wijngaarden[a]

[a] Department of Chemistry, York University, Canada

This study explores the conformational equilibria of 2-methylthioethylamine (2-mtea) and 2-ethylthioethylamine (2-etea) to elucidate the influence of nitrogen and sulfur in the energy ordering and structures of thioethers. Motivated by the astrochemical relevance of thioether and amine molecules, quantum chemical methods (B3LYP-D3(BJ)/aug-cc-pVTZ) predicted 14 unique conformers for 2-mtea and 43 unique for 2-etea. Rotational spectroscopy using both chirped-pulse Fourier transform microwave (cp-FTMW) and cavity-based FTMW spectrometers have, to date, enabled the identification of three and four low-energy structures, respectively, with more assignments in progress. The observed spectral patterns are complicated by the presence of quadrupolar ^{14}N (both species) and internal methyl rotor (2-mtea) tunnelling providing very unique spectroscopic fingerprints for each conformer. This work lays the foundation for broader investigations of intramolecular interactions involving nitrogen and sulfur and the implications on conformational equilibria.

COUPLED METHYL INTERNAL ROTATIONS WITH INTERMEDIATE AND LOW TORSIONAL BARRIERS IN 2,5-DIMETHYLANISOLE AND 2,5-DIMETHYLFLUOROBENZENE INVESTIGATED BY MICROWAVE SPECTROSCOPY

H. Sun[a], I. Kleiner[a], S. Khemissi[b], L. Ferres[c] and H. V. L. Nguyen[b,d]

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The microwave spectra of 2,5-dimethylanisole (25DMA) and 2,5-dimethylfluorobezene (25DMFB) were measured using a pulsed molecular jet Fourier transform microwave spectrometer in the frequency range from 2 to 26.5 GHz and analyzed with support from quantum chemical calculations. Both molecules share an intermediate and a low torsional barrier hindering the internal rotation of their CH_3 groups, causing splitting of all rotational transitions into five components with large splittings between them. This makes their rotational spectra challenging to analyze. For the 25DMFB, the experimental values of the V_3 potentials were determined to be 226.274(31) cm^{-1} and 16.386(67) cm^{-1}, for the -CH_3 groups at positions 2 and 5 of the benzene ring, respectively. For 25DMA the respective values are 65.723647(84) cm^{-1} and 451.664(21) cm^{-1}. For 25DMA a total of 460 torsional transitions were fitted with root-means-square (rms) deviations close to the measurement accuracy of 4 kHz using two computer programs *XIAM*[1] and *BELGI-C_s-2Tops*,[2] but for the 457 torsional components of 25DMFB, *XIAM* achieves an rms of 384.3 kHz, much higher than the value of 4.7 kHz achieved by *BELGI-C_s-2Tops*. Comparisons with the torsional barriers obtained with other substituted toluene derivatives will be given.[3]

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ANALYSIS OF 5-METHYL-2-NITROPHENOL BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS[1]

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The structure and internal dynamics of oxygenated aromatic compounds are of interest due to their atmospheric relevance and role as potential aerosol precursors. We report in the present work a high-resolution rotational study of 5-methyl-2-nitrophenol using Fourier transform microwave spectroscopy in combination with quantum chemical calculations. A broad survey spectrum was first recorded in the 2-8 GHz range using chirp-excitation. Higher-resolution measurements were then performed using the resonator mode of the recently developed Passage And Resonance In Synergy (PARIS) spectrometer, extending also the frequency coverage to 2-20 GHz. Quantum chemical calculations at the B3LYP-D3BJ/6-311++G(d,p) and MP2/6-311++G(d,p) levels were used to optimize the molecular structure and guide spectral assignment. Splittings due to methyl internal rotation and hyperfine structure arising from the ^{14}N nuclear quadrupole coupling were observed, analyzed, and fitted using the *XIAM* and *BELGI-*C_s*-hyperfine* programs to measurement accuracy. A threefold barrier to internal rotation of 79 cm^{-1} was derived, in good agreement with theoretical predictions. These results contribute to the understanding of structure-dynamics relationships in functionalized aromatic molecules relevant to atmospheric chemistry.

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[1] This work was supported by the King's College London - Université Paris Cité joint reasearh call 2024/2025.

ETHYNYL ISOCYANATE, YET ANOTHER QUASILINEAR TROUBLEMAKER

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Several molecules containing the functional group −N=C=O have been found in the interstellar medium (ISM), namely isocyanic acid[1], methyl isocyanate[2], and ethyl isocyanate[3]. Another relevant candidate for ISM searches from the isocyanate group is ethynyl isocyanate (H−C≡C−N=C=O) for which only low-frequency data (26–40 GHz) are available[4]. The limited availability of spectroscopic data might be caused by both the challenging laboratory synthesis of the compound and the challenging nature of its rotational spectrum. These spectroscopic difficulties arise from the quasi-linear geometry of the molecule, which leads to a dense network of perturbations similar to those observed in other isocyanate-containing species, such as isocyanic acid and vinyl isocyanate[5].

In this study, ethynyl isocyanate was measured using the Prague millimeter-wave spectrometer[6] in the 140–180 GHz frequency range. In addition to transitions from the ground vibrational state, the recorded spectrum revealed a series of transitions corresponding to increasing vibrational quantum numbers of the lowest-lying bending mode. This mode is associated with an increase in linearity of the molecule and a dramatic change in the rotational constant A. Furthermore, transitions from several other excited vibrational states were identified. The analysis was carried out using the General Fitting Code.

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ROTATIONAL SPECTROSCOPY OF THE AMINOMETHYL RADICAL CH_2NH_2

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Methylamine (CH_3NH_2) is the simplest primary amine in the interstellar medium (ISM) and planetary atmosphere. It is proposed to be the precursor of the simplest amino acid: glycine. This study focuses on the aminomethyl radical, CH_2NH_2, which has been proposed to be one of the key radical intermediates in the astrophysical and atmospheric chemistry of methylamine and glycine. The radical can be formed via successive hydrogenation of HCN,[1] or H-abstraction reaction of methylamine,[2,4] and solid-H_2 matrix experiment has proved its existence in interstellar analogue conditions by infrared spectroscopy.[3] High level theoretical calculations[4] have studied this reaction in detail, providing critical structural information on the structure, relative energy, and spectroscopic parameter predictions. Nevertheless, the rotationally resolved spectrum of CH_2NH_2 has never been characterized, which prohibits its potential detection in the ISM.

We report the first rotational spectroscopic measurement of CH_2NH_2 in the submillimeter-wave range, using H-abstraction reaction of methylamine and F atoms and Faraday rotation spectroscopy.[5] Our result reveals an unambiguous collective inversion tunnelling motion of the $-CH_2$ and $-NH_2$ groups in the radical. The two splitted substates present a Coriolis-type interaction. We present our theoretical and experimental results, and spectral analysis that opens the possiblity of searching for CH_2NH_2 in the ISM.[6]

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FT-UV EMISSION SPECTROSCOPY OF THE $B^2\Sigma^+ - X^2\Sigma^+$ SYSTEM OF $^{12}C^{16}O^+$ AND $^{12}C^{17}O^+$

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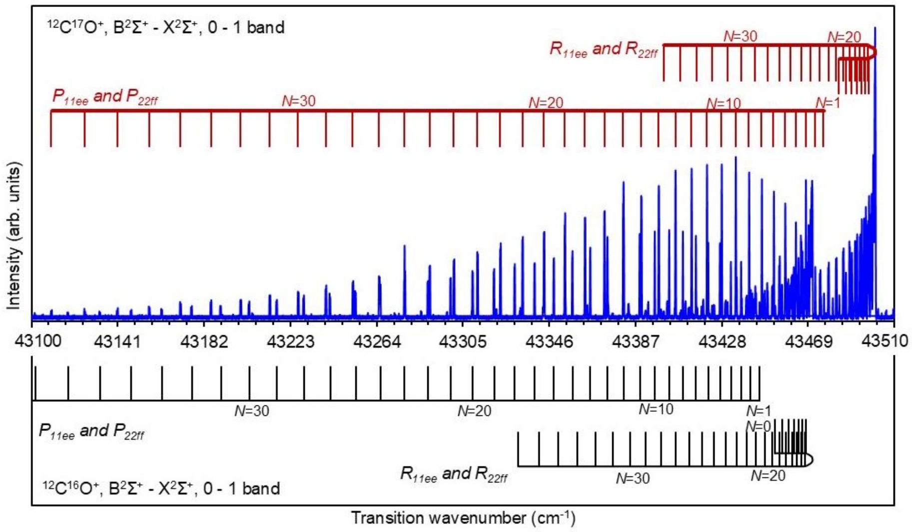

Figure 1: A compressed view of the experimental FT-UV emission spectrum of the $0-1$ band of the $B^2\Sigma^+ - X^2\Sigma^+$ system of $^{12}C^{17}O^+$ recorded with SNR of about $50:1$ and FWHM of the lines of about 0.18 cm^{-1}.

The CO$^+$ molecule is a cation of the second most abundant molecule in space, carbon monoxide. The main isotopologue i.e. $^{12}C^{16}O^+$ was successfully detected towards the interstellar medium (ISM) by the lowest rotational transitions and also in the comets by the $A^2\Pi_i - X^2\Sigma^+$ system bands[1]. There is no evidence about the presence of the $^{12}C^{17}O^+$ cation in space. However, CO molecules bearing the isotope seventeen of oxygen have already been detected in ISM, despite a very low natural abundance of the ^{17}O (about 0.04%). The CO$^+$ isotopolgues have been studied recently in the Materials Spectroscopy Laboratory at the University of Rzeszów trough the $B^2\Sigma^+ - X^2\Sigma^+$ system using FT-UV emission spectroscopy technique: $^{12}C^{16}O^+$[1] and $^{12}C^{17}O^+$ [this work]. In total, about 1000 ro-vibronic transitions, belonging to the $0-0$, $0-1$, $0-2$ and $0-3$ bands, have been measured with an absolute accuracy of 0.0050–0.0100 cm^{-1}. The experimental data were analyzed using the `PGOPHER` program[2], which resulted in a set of high accuracy molecular constants and ro-vibronic level positions for the $X^2\Sigma^+$, $\nu = 0-3$ and $B^2\Sigma^+$, $\nu = 0$ levels for both isotopologues.

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LABORATORY ROTATIONAL SPECTRA AND INTERSTELLAR IDENTIFICATION OF DEUTERATED COMPLEX ORGANIC MOLECULES

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Deuterium fractionation is an important tool for tracing the chemical and physical evolution in the interstellar medium.[1] We have begun a systematic study into deuterated complex organic molecules to help understand their formation pathways and inheritance through the stages of star and planetary formation. In order to do this, however, we require laboratory spectra. First results of this work involved collection and analysis of laboratory rotational spectra resulting in the interstellar identification of doubly deuterated acetaldehyde (CHD_2CHO).[2] More recently the laboratory data and analysis of singly deuterated methyl mercaptan, CH_2DSH, has also led to its interstellar identification.[3] We are currently investigating the spectra of doubly deuterated methyl mercaptan (CHD_2SH), methyl formate (CH_2DOCOD), and methanol (CH_2DOD), as well as of triply deuterated methyl formate (CHD_2OCOD) and methanol (CHD_2OD). Each of these species are non-rigid molecules displaying internal rotation of their asymmetrical CH_2D or CHD_2 methyl group resulting in a complex spectral analysis. I will present an update on the analysis of the rotational spectra of these species and interstellar search towards the solar-like protostar IRAS 16293-2422.

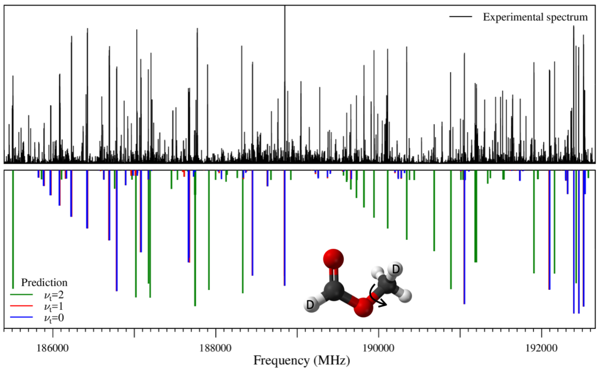

Figure 1: A portion of the experimental (top) and predicted rotational spectrum (bottom) of doubly deuterated methyl formate (CH_2DOCDO), showing the $J'' = 16$ strong a-type R-Branch transitions between 185 to 193 GHz for all three substates resulting from the internal rotation of the asymmetric methyl group.

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SINGLE PHOTOIONIZATION OF VINYLCYANOACETYLENE AND METHACRYLONITRILE IN ASTROPHYSICAL OBJECTS

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In recent years, the detection rate of molecules in the interstellar medium (ISM) has been accelerating. Today, about 330 molecules have been detected in the interstellar medium or circumstellar shells.[1],[2] This is in large part thanks to significant advances in detection techniques and astronomical data processing. Nitriles (or cyanides) are among the most abundant chemical species in the ISM. They are key species in prebiotic chemistry and play an important role in the so-called RNA world. This simple and reactive functional group offers a unique potential to build up more complex molecules such as ribonucleic acids or nucleobases. In terms of formation and evolution of these molecules, many physico-chemical processes play an important role, such as desorption from interstellar grains, radiative recombination, photolysis, to name only a few. In order to estimate the importance of the latter, one must know, for example, absorption cross sections in the UV and VUV spectral domain. The ubiquitous abundance of nitriles might be due, in part, to their photostabilty.

Our group has been investigating the VUV spectroscopy and photophysics of molecules of astrochemical interest for many years. Our data are generally made available through the Leiden international database.[3] For a recent example see our work on 2-aminopropionitrile.[4] In this study we investigate the single photon ionization of two organic nitriles that have been recently detected, namely vinylcyanoacetylene[5] and methacrylonitrile.[6] The spectral domain of our study is from 9 to 15 eV. We present branching ratios of parent and fragment ions as a function of the photon energy, as well threshold photoelectron spectra. The experiments are associated to dedicated quantum-chemical calculations on the chemical structure of fragments formed by dissociative photoionization. All results are discussed in the light of the related molecular photodynamics as well as the astrophysical context.

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FREQUENCY COMB-STABILIZED HIGH-RESOLUTION IR-UV DOUBLE RESONANCE SPECTROSCOPY ON A COLD MOLECULAR BEAM

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Reconciling high spectral resolution and high sensitivity simultaneously is a daunting task. We have previously shown that we can transfer the precision of millimeter-wave spectroscopy to infrared-excited vibrational states using a mmW-IR double resonance experiment and therefore improve the spectral resolution by up to three orders of magnitude.

Also, we have already demonstrated IR-UV double resonance spectroscopy, limited in accuracy (∼150 MHz) and precision (∼10 MHz) by the infrared stabilization to a wavemeter.

Here we present new results of frequency comb-stabilized IR-UV double resonance experiments on acetylene (C_2H_2) conducted with the cold molecular beam apparatus in the Kassel laboratory resembling an experiment of the *Quack* group[1]. The apparatus allows high-resolution infrared, optical and UV spectroscopy of cold neutral molecules, via resonant multiphoton ionization time-of-flight (REMPI-ToF) mass spectroscopy. A pulsed nozzle is utilized to produce cold molecules in an adiabatically expanding supersonic jet. Two skimmers reduce expanding gas to a molecular beam. We use a high-power (up to 1.5 W) continuous-wave optical parametric oscillator (cw-OPO) for an IR excitation of the molecules with a subsequent REMPI-ToF detection. The narrow linewidth of the cw-OPO (10 - 20 kHz) in the mid-infrared (2.7 - 4 μm) and the frequency-stability ($<$ 1 MHz) allows to uniquely address ro-vibrational states. The excellent frequency-stability is achieved by stabilizing the cw-OPOs pump and signal radiation to a frequency comb reference.

The REMPI method provides excellent detection sensitivity even for extremely small samples and mass selectivity. In the future, we plan to additionally use monochromatic mmW radiation in a perpendicular beam configuration to distinguish the enantiomers of chiral molecules using a three-wave mixing (3WM) scheme[2,3]. Furthermore, using circularly polarized light, photoelectrons can be used for the detection of chiral molecules utilizing photoelectron circular dichroism (PECD)[4]. When working with chiral molecular species in a cold molecular beam this will allow for an enantiomer selective detection.

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LABORATORY MEASUREMENTS OF SULFUR BEARING CYCLIC HYDROCARBONS BY MICROWAVE SPECTROSCOPY

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Sulfur-bearing molecules are supposed to have played a crucial role in the biological processes that led to life on Earth, likely delivered via comets and meteorites. This hypothesis is supported by the finding of abundant organic molecules in these objects, including large sulfur-bearing organic molecules. In contrast, the variety of sulfur species detected in the gas phase of interstellar space is limited to smaller molecules, with a maximum size of nine atoms (e.g., CH_3SCH_3 [1]). This molecular-size imbalance has been approaching resolution in recent years. Following the discovery of large cyclic hydrocarbons, their sulfur-bearing counterparts are expected to exist in space. To determine their rest frequencies and facilitate their astronomical detection, we have investigated the rotational spectra of discharge products from thiophenol using a chirped-pulse Fourier transform microwave spectrometer in conjunction with a pulsed-discharge supersonic-jet system.

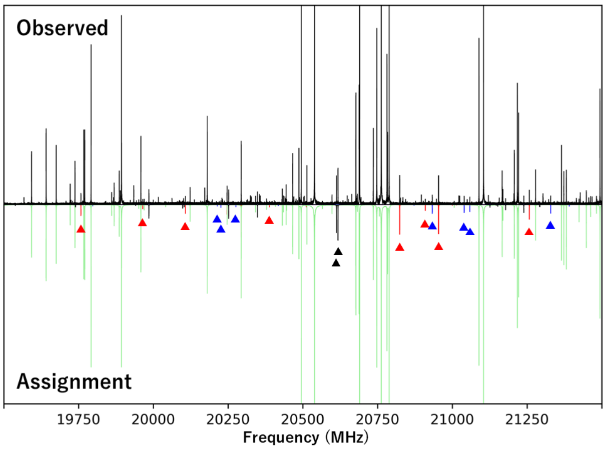

Figure 1: Observed spectrum and its assignment. Green: thiophenol, Black: ^{34}S-thiophenol, red: 2,5-cyclohexadien-1-thione, blue: 2,4-cyclohexadien-1-thione.

A lot of spectral lines corresponding to sulfur-bearing cyclic hydrocarbons have been detected in the 8–40 GHz frequency range, as shown in Figure 1. The 92 and 75 rotational lines were assigned to 2,5-cyclohexadien-1-thione and 2,4-cyclohexadien-1-thione, respectively, where the structures of them are described in Figure 2. The rotational lines cover the quantum numbers up to J=15 and K_a=7. The rest frequencies of the rotational lines, determined with a precision of about 5 kHz, have been fitted to an effective Watson-type Hamiltonian in S-reduction, including rotational and centrifugal distortion.

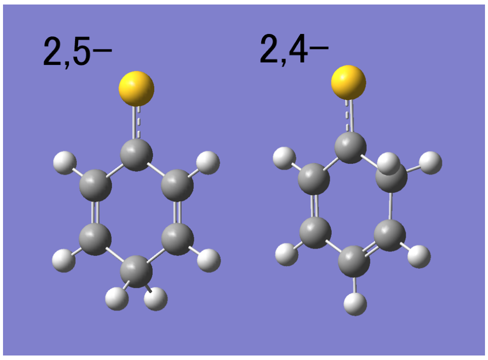

Figure 2: Molecular structures.

The fit reproduces the experimental frequencies with a root mean square deviation of 3.0 and 3.4 kHz for 2,5- and 2,4-isomers, respectively. Based on this analysis, rest frequencies for transitions are predicted with uncertainties sufficiently better than 10 kHz in the frequency ranges of several tens of GHz. These uncertainties correspond to those in velocity by less than 0.1 km s^{-1} and are small compared to the linewidths of typical molecular clouds. Furthermore, CCSD[T]/cc-pVTZ calculations performed with CFOUR revealed that both molecules have large dipole moments (>3D). The findings of this study allow us to detect these molecules in space.

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HIGH-RESOLUTION IR SPECTROSCOPY OF THE HCN$^+$ AND HNC$^+$ CATIONS

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Neutral HCN and its isomer HNC are thoroughly studied molecules, but very little is known spectroscopically about their cations, despite being of fundamental and astronomical interest. As open-shell and thus highly reactive cations, HCN$^+$ and HNC$^+$ pose significant challenges for spectroscopic detection in the laboratory.

In this work, we present the first high-resolution ro-vibrational spectra of HCN$^+$ and HNC$^+$, employing a cryogenic 22-pole ion trap combined with the novel leak-out spectroscopy (LOS) technique[1]. For HCN$^+$, the C-H ν_1 fundamental band was measured at temperatures below 10 K. Both the F_1 and F_2 spin-orbit components as well as Λ-doubling (e/f) were resolved in the recorded spectra. Additionally, we observed the $\nu_1 + \nu_2$ and $\nu_3 + 2\nu_2$ combination bands displaying Renner-Teller splitting due to the coupling of the vibrational angular momentum from the ν_2 bending mode with the total electron momentum. For HNC$^+$ the ν_1 fundamental band was recorded around 3408 cm^{-1}.

Finally, using LOS, we report the first high-resolution electronic spectrum of the $\tilde{X}^2\Pi^+$ to $\tilde{A}^2\Sigma^+$ transition located at 3250 cm^{-1}. The spectrum exhibits fine, and hyperfine structure, providing precise descriptions of the nature of these electronic states.

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COMBINING A CRYOGENIC ION TRAP WITH A 2 THZ MULTIPLIER CHAIN SOURCE: REVISITING THE $J = 1 \leftarrow 0$ FUNDAMENTAL ROTATIONAL TRANSITION OF HHe$^+$

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[b] University of Novi Sad, Faculty of Sciences, Department of Physics, Novi Sad 21000, Serbia
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The HHe$^+$ cation is a fundamental two-electron system, very similar to the hydrogen molecule H_2, and is thought to be the very first diatomic molecule formed when the early universe cooled down[1]. It has been first discovered 1925 in a laboratory mass spectrometer by Hogness and Lunn[2]. The direct measurements of the fundamental rotational transition $J = 1 \leftarrow 0$ at 2010.1839(2) GHz by Matsushima et al.[3] in 1997 laid the foundation for the later astrophysical detection of HHe$^+$ in the planetary nebula NGC 7027[4]. Now, nearly 30 years later, this transition of HHe$^+$ at 2.010 THz has been revisited by us, using a combination of a 4 K 22-pole ion trap apparatus (COLTRAP[5]) and a high-power frequency multiplied THz source. The THz radiation source is the local oscillator (LO), which was utilized for the Low Frequency Array (LFA) of the upGREAT receiver onboard the airborne telescope SOFIA, operating in the range 1.83-2.07 THz[6]. For the detection of the resonant absorption, three different action spectroscopic techniques have been applied: laser induced inhibition of complex growth (LIICG), double-resonance leak-out spectroscopy (DR-LOS) and one which is demonstrated here for the first time: ejection of the ion upon pure rotational excitation (rot-LOS). The different methods are evaluated and compared, and improve the precision of the former transition value by Matsushima et al. by one order of magnitude to 2010.183312(8) GHz as seen in Figure 1. The newly determined transition frequency may serve as a strict benchmark value for future ab initio calculations of this fundamental two-nucleus-two-electron system.

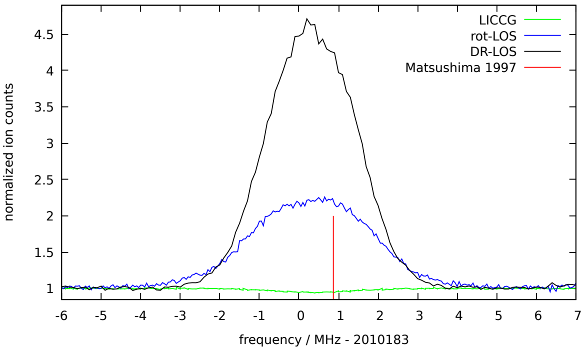

Figure 1: The $J = 1 \leftarrow 0$ fundamental rotational transition of HHe$^+$, measured with three different action spectroscopic methods: a) LIICG b) rot-LOS c) DR-LOS. The FWHM of the different measurements is in the order of 3 MHz, corresponding to ion temperatures between 16 and 27 K.

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MILLIMETER-WAVE SPECTRUM AND NUCLEAR HYPERFINE STRUCTURE OF THE (*para*)-NH_3–(*ortho*)-H_2 VAN DER WAALS COMPLEX

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The spectra of the NH_3-H_2 van der Waals complex provide detailed information on its intermolecular interaction potential, which is of astrophysical importance for accurate modelling of the collisional excitation of ammonia in the cold and warm molecular clouds and the hydrogen-abundant planetary atmospheres.[1,2] In a previous work[3] two nuclear spin isomers, (*ortho*)-NH_3–(*ortho*)-H_2 and (*para*)-NH_3–(*ortho*)-H_2, were detected by observing their pure rotational spectra. The ^{14}N nuclear spin interaction results in hyperfine quadrupole structure of the observed lines, which was well resolved for the complexes with (*ortho*)-NH_3, but not for those with (*para*)-NH_3.

The current study presents the first measurements and analysis of the hyperfine structure for (*para*)-NH_3–(*ortho*)-H_2 arising due to quadrupole interaction of the nitrogen nucleus ($I_\mathrm{N} = 1$) as well as the magnetic nuclear spin interaction of the H nuclei ($I_\mathrm{H2} = 1$) of the H_2 part. The pure rotational spectra (75-150 GHz) have been observed in a supersonic molecular jet expansion using recently developed spectrometer with coaxial propagation of the molecular beam and millimeter-waves.[4] To produce the NH_3-H_2 dimers the gas mixtures of 3% ammonia in hydrogen or 3% ammonia and 10% hydrogen in neon were prepared at pressures of 5-7 bar. The measured frequencies are consistent with the rotational line centers reported in the earlier paper,[3] but now the hyperfine components are well resolved and their frequencies can be determined with an accuracy of 3-5 kHz. As a result, the nuclear quadrupole coupling constant, spin-spin, and spin-rotation interaction constants were obtained for the first time for the (*para*)-NH_3–(*ortho*)-H_2 complex in its ground Π state. These parameters were analyzed to derive dynamical information about the orientation of the ammonia and hydrogen units within the van der Waals complex.

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THE PROGRESS ON HIGH RESOLUTION SPECTRA MEASUREMENTS OF VAN DER WAALS COMPLEXES WATER$-$CO$_2$ IN THE SECOND WATER OVERTONE RANGE

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Water and CO_2 are the most important greenhouse gases in our atmosphere. The solvation of CO_2 is a decisive process in the chemistry of clouds and oceans. A precise characterization of the interaction of these two molecules is thus of prime importance. In the present work, we recorded the set of rotationally resolved spectra associated to the multiple excitation of the OH/OD stretch in the water$-$$CO_2$ molecular complex. This represents a further step in our longstanding effort to better characterize the dynamics of the interaction of CO_2 and H_2O notably through a systematic increase of the vibrational excitation[1,2,3]. All the measurements were performed using the FANTASIO experimental setup[4,5]. The complexes were formed using an 8 cm long pulsed slit supersonic jet and probed using the CRDS technique in the spectral range of the second overtone of water. The experimental spectra, the assignment, and the improvements of the experimental setup, which allowed the recording of this spectral signature, will be presented.

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GAS PHASE VIBRATIONAL SPECTROSCOPY OF $PF_6^-(H_2O)_{0-7}$: DECODING THE ONSET OF HYDROGEN-BOND NETWORK FORMATION

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The widespread use of the hexafluorophosphate anion (PF_6^-), both as a counterion in room-temperature ionic liquids and as an electrolyte component in lithium-ion batteries, has resulted in the recent detection of PF_6^- in environmental water samples.[1,2,3] Given that PF_6^- can be hydrolysed, particularly under acidic conditions, leading to the formation of hydrofluoric and phosphoric acids, a comprehensive understanding of its local solvation environment is, therefore, essential to elucidate how surrounding chemical species influence its stability and reactivity.[4]

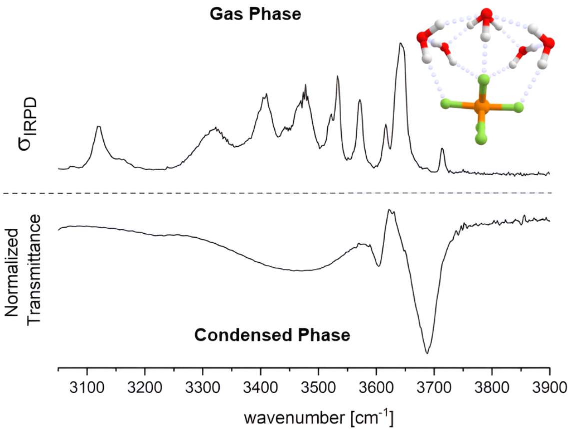

Figure 1: Comparison between a gas-phase vibrational spectrum of $PF_6^-(H_2O)_6$ (top) and a FT-IR spectrum of an aqueous PF_6^--solution (bottom).

In this study, we explore the PF_6^- solvation at the molecular level through infrared photodissociation (IRPD) spectroscopy of cryogenically cooled D_2 adducts of $PF_6^-(H_2O)_n$ complexes ($n = 0 - 7$). Spectra were recorded across vibrational regions characteristic of the solute (750–900 cm^{-1}) and solvent (1400–3800 cm^{-1}) vibrational modes. To aid spectral interpretation and structural assignment, experimental results are complemented by quantum chemical calculations and compared to the Fourier-transform infrared (FT-IR) spectrum of an aqueous PF_6^--solution.

The stepwise addition of water molecules to PF_6^- results in a distinct splitting of the O–H stretching bands, reflecting the presence of ionic and intermolecular water-water hydrogen bonds. The latter exhibits a more pronounced red shift, indicating stronger hydrogen bonding compared to the ionic hydrogen bonds with PF_6^-. Starting with $n = 6$, the IRPD spectra begin to resemble those of PF_6^- in aqueous solution. These results support a solvation motif in which PF_6^- is surface-solvated and the subsequent water molecules preferentially aggregate on one side of the anion, forming a droplet-like structure.

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EXPLORING HALOGEN EFFECTS IN THE ESTERIFICATION REACTION OF FORMIC ACID AND ETHANOL

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Esterification is a key reaction in organic and biological chemistry, typically involving the combination of a carboxylic acid and an alcohol to form an ester. Previous rotational spectroscopic studies have shown that primary and secondary alcohols readily form esters with formic acid, while tertiary alcohols tend to form stable van der Waals complexes instead.[1] Further investigation revealed that non-covalent interactions can significantly influence this reactivity.

In this study, we explored how halogen substitution affects the esterification reactivity of ethanol. Using broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy combined with a supersonic jet expansion, we examined gas-phase mixtures of halogenated ethanol and formic acid. While unsubstituted ethanol readily undergoes esterification, the halogenated analogs formed only weakly bound complexes during the experiment, with no evidence of ester products. This reduced reactivity is likely attributed to changes in the electrostatic potential caused by halogen substitution, which alters the nature of intermolecular interactions critical for reaction progression. These findings demonstrate how subtle electronic modifications can markedly inhibit reactivity, offering valuable insights into the molecular-level control of chemical reactions.

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A NEARLY COMPLETE TREATMENT OF THE EFFECT OF NON-ADIABATICITY (NO DIABATISATION) ON ROVIBRATIONAL ENERGIES OF H_3^+

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It is generally accepted that radiative association of ions with molecules plays an important role in the molecular synthesis in the super-cold, low-density environment of the interstellar medium. One of the crucial steps in the investigation of cross-sections for radiative association (and the infrared predissociation spectrum [1] of H_3^+, with ca. 100 transitions per wavenumber) is the calculation of the ro-vibrational bound states and resonances near the dissociation limit. Because H_3^+ has a binding energy of ≈ 35000 cm^{-1}, the accurate determination of the highest bound energy levels can be demanding. For the description of radiative association of a strongly bound molecule, we need a good potential energy and dipole surface, an efficient reactive scattering implementation and an efficient way of calculating high-lying bound states and resonances. But, it is already problematic to calculate with spectroscopic accuracy all rovibrational transitions < 16000 cm^{-1}.

In this report significant contributions of non-adiabaticity for the rovibrational bound states up to 25000 cm^{-1} and total angular momentum J=0 - 20 of H_3^+ are investigated. A coupled-perturbed full configuration interaction (CP-FCI) treatment is applied to calculate all couplings between electronic states caused by the nuclear motion. These derivative couplings were evaluated up to the second order by means of a perturbation treatment, and include all nuclear Cartesian first and second derivatives of the electronic wavefunctions. Especially, the coupling of special derivatives with respect to r and R in the Jacobi coordinate representation are more significant than thought. The perturbation approach is especially optimal for the treatment of weak non-adiabaticity in case of rovibrational energies in H_3^+, and had not been available before for H_3^+ or other triatomics. Using exclusively Gaussian basis functions for CP-FCI appears to be sufficient, because explicit correlated wavefunctions are already used for all other potential energy contributions.

Our work is an extension of earlier non-adiabatic investigations based on first derivative couplings of electronic states that led to the concept of geometry-dependent effective nuclear masses and which needs only a single potential energy surface for the dynamics. The implementation allows to include all non-adiabatic effects up to the order of $O(\mu^{-2})$, μ being the reduced nuclear mass. Our treatment works for any isotopologue and for the whole PES. By this treatment a further reduction of deviations to experimental data for most rovibrational levels to less than 0.1 cm^{-1} is possible. For the related transition frequencies, 1366 of 1720 known rovibrational transitions in H_3^+ have deviations less than 0.1 cm^{-1} without using any empirically adjustable parameters or optimizing the nuclear mass for a specific transition. For many questionable assignments (deviations > 0.3 cm^{-1}) of observed transitions in H_3^+ a new labeling is proposed [1].

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REINVESTIGATION OF PROPYLENE OXIDE BY FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

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Propylene oxide (in short PO), $CH_3C_2H_3O$, is an oxirane (c-C_2H_4O) with one hydrogen being substituted by a methyl group. PO is one of the smallest organic chiral molecules and has been detected in interstellar medium in 2016[2]. More than 50 years ago, Swalen & Herschbach[3] and Herschbach & Swalen[4] measured the microwave spectra of PO, and analyzed the internal rotation of the methyl group as a high barrier case. Recently, in 2017, Mesko *et al.* reported new ground state spectra of PO up to 1 THz, resulting in improved molecular parameters and a more accurate potential barrier height[5]. In 2021, the first excited torsional state of PO was investigated in millimeter up to sub-millimeter wavelengths (75-950 GHz)[6]. In addition, high-resolution infrared spectra of PO have been reported for the four C-H stretching vibrational modes[7] and the ν_{12} band[8].

Being stimulated by those works we have reinvestigated the ground-state rotational spectrum of PO; its low frequency transitions were observed and analyzed by high-resolution molecular beam Fourier transform microwave spectroscopy. We have assigned A and E torsional states of PO for $J = 0$ to 12 and $K_a = 0$ to 7 in the frequency region between 4 to 34 GHz. Because PO is a chiral molecule, the a-, b-, and c-type rotational transitions have been observed. The splittings due to the internal rotation were analyzed by the XIAM program to determine the three-fold potential barrier V_3 to be 888.956 (29) cm^{-1}. The rotational constants thus derived agree with the predictions made by quantum chemical calculations, MP2/6-311++G(d, p), within 0.1%.

The energy diagram of PO involving the transition $J_K = 12_5 \leftarrow 11_6$ in the ground state is illustrated in the textbook of Gordy & Cook[9] as Fig. 12.8, which is a reproduction of Fig. 5 of Ref.[4]. In the present study, we found several errors in the original figure which must be corrected.

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NEAR-INFRARED SPECTROSCOPY OF METHANOL AT THE 10^{-13} LEVEL FOR RADIO ASTRONOMY

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This poster showcases the application of Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) for precision spectroscopy of methanol. This approach, invented almost thirty years ago[1] and further developed as an optical precision tool[2], allows the measurement as Lamb-dips (see Figure 1 right panel) of extremely weak transitions[3], combining both sensitivity and accuracy.

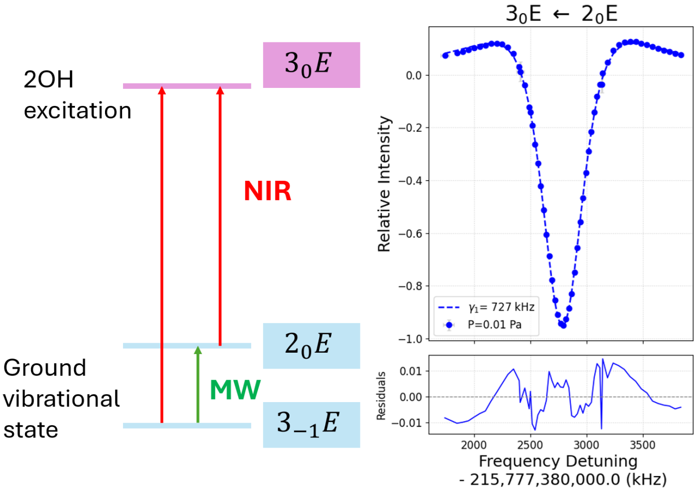

Figure 1: Left panel: Illustration of the transitions considered in methanol: three transitions, two in the near infrared and one in the microwave, form a network allowing to verify the mutual accuracy of the measurements in the two spectral ranges. Right panel: Example of one near infrared Lamb-dip measured *via* our ultrasensitive NICE-OHMS set-up.

We report sub-kHz precision measurements of three vibrational line pairs, corresponding to the $3_{-1}E$ - 2_0E combination difference (see Figure 1 left panel) in the vibrationless ground state. This allows the determination of this 12.2 GHz radio line frequency, highly sensitive to potential variations in the proton-electron mass ratios [4] [5], at kHz precision. Furthermore, having moved our NICE-OHMS setup, we will be presenting a comparison of results obtained in Amsterdam and Louvain-la-Neuve on these very accurate frequency determinations of methanol resonances.

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HIGH-RESOLUTION VUV AND VIS FT SPECTROSCOPY AND EXTENDED DEPERTURBATION ANALYSIS OF THE $^{13}C^{18}O$ $A^1\Pi(v = 2)$ LEVEL

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This study presents a spectroscopic analysis of the $A^1\Pi(v = 2)$ energy level in the $^{13}C^{18}O$ isotopologue. To achieve this goal, two comprehensive FT techniques were employed: *(i)* emission spectroscopy in the Vis region using the Bruker IFS 125HR spectrometer, and *(ii)* VUV absorption spectroscopy using the DESIRS beamline at the SOLEIL synchrotron. Spectral measurements were performed within the vacuum ultraviolet (VUV, 66,450 – 68,450 cm^{-1}) and visible (Vis, 19,100 – 25,000 cm^{-1}) ranges, achieving measurement accuracies of approximately 0.04 cm^{-1} for the VUV-FT and 0.007 cm^{-1} for the Vis-FT spectroscopy. An example spectrum is shown in Fig. 1. A total of 787 radiative transitions were analysed, involving various electronic states. A comprehensive deperturbation analysis of the $A^1\Pi(v = 2)$ level was performed using the PGOPHER program[1]. As a result, 38 floated parameters and 429 ro-vibronic term values of the states under consideration were obtained. The extra-lines involving the $a^3\Pi(v = 13)$ level in the $A^1\Pi$ – $X^1\Sigma^+(2, 0)$, $B^1\Sigma^+$ – $A^1\Pi(0, 2)$ and $C^1\Sigma^+$ – $A^1\Pi(0, 2)$ bands of $^{13}C^{18}O$ have been clearly observed. The results are part of the studies on the electronic state of $A^1\Pi$ and its interstate interactions in various isotopologues of carbon monoxide, which were undertaken by our research group[2,3,4].

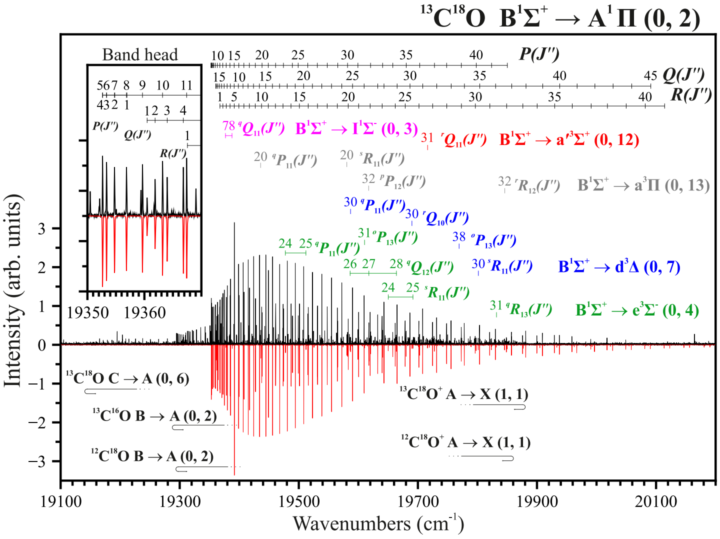

Figure 1: The $^{13}C^{18}O$ $B^1\Sigma^+$ – $A^1\Pi(0, 2)$ emission spectrum (upper, black trace) and the simulated one (lower, red trace) by using the PGOPHER program[1].

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ANALYSIS OF THE HIGH RESOLUTION INFRARED SPECTRUM OF MONODEUTERO-OXIRANE

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Monodeutero-oxirane (c-C_2H_3DO) is of fundamental interest in the context of the concept of isotopic chirality, which introduces a completely new isotope effect arising from the parity violating weak nuclear force.[1,2,3] It is also of astrophysical interest because of its recent detection towards IRAS 16293-2422B, based on our high resolution spectroscopic results.[4,5] We have previously reported the analysis of GHz and THz *c*-C_2H_3DO[4,6] and *trans*-*c*-CHD−CHDO spectra[7], and have provided a first high resolution analysis of the infrared spectra of the two *c*-C_2H_3DO fundamentals at 896.025 cm-1 and 837.36 cm^{-1}.[6] Here we report new measurements of the infrared spectrum of improved newly synthesized samples of *c*-C_2H_3DO (room temperature, Doppler-limited resolution), making possible the extension of our analysis towards the two lowest frequency fundamentals, as well as further stronger fundamentals, combination and overtone bands throughout the mid- to near-infrared range, using our Bruker IFS 125 HR ETH-SLS 2009 Prototype (MOPD=11.7m) [4,8,9]. We have used our improved molecular parameters for the ground state of *c*-C_2H_3DO [6] to carry out the rovibrational analysis in several regions of interest and shall report on the current status of our analysis, including a discussion of the tetrad of the lowest four fundamentals with possible rovibrational interactions. The results will also be discussed as they pertain to ab initio calculations [6,10], isotopic chirality, molecular parity violation, and the evolution of biomolecular homochirality [1,9,11] We thank G. Matmon for his help with the experiments, F. Merkt for his continued support, and the SNF and the EU for financial support (COST COSY, ERC advanced grant).

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(SUB-)MM AND INFRARED ANALYSIS OF VINYL CHLORIDE

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Recently, methyl chloride (CH_3Cl) was detected with ALMA toward the infant star system IRAS 16293–2422 and with the Rosetta space probe in the atmosphere of the comet 67P/C–G[1]. This gives rise to the question if vinyl chloride (CH_2CHCl) might also be present in these or other astronomical sources. Previous laboratory millimeter and sub-millimeter ((sub-)mm) wave studies were limited in quantum number and frequency coverage[2] whereas previous infrared (IR) studies did not cover ν_9, the energetically-lowest fundamental[3].

Here, we report high-resolution (sub-)mm and IR investigations of vinyl chloride performed in Cologne and at the SOLEIL synchrotron, respectively. The rotational spectrum was recorded from 170 to 1100 GHz, which resulted in more than 3000 newly assigned transitions for the ground state of $C_2H_3^{35}Cl$ while simultaneously reducing the RMS from 147 kHz to 47 kHz. In addition, the vibrational satellite spectrum of the energetically lowest deformation mode ν_9 has been assigned for the first time. The preceding rotational analysis of the ground vibrational state allowed us to speed up the analyses of the infrared bands using the Automated Spectral Assignment Procedure (ASAP)[4]. The two energetically lowest fundamentals ν_9 and ν_{12} can be readily assigned for both $C_2H_3^{35}Cl$ and $C_2H_3^{37}Cl$. These results will then greatly facilitate pure rotational analyses of the respective vibrational satellite spectra.

Based on the new ground state rotational data, highly accurate frequency predictions enable astronomical searches of both isotopologues over a wide frequency and quantum number range.

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HIGH-RESOLUTION INFRARED SPECTROSCOPIC INVESTIGATION OF THE ν_{12} BREATHING MODE OF PROPYLENE OXIDE AND ITS FERMI-TYPE RESONANCE WITH THE $2\nu_{24}+\nu_{19}$ TORSIONAL COMBINATION BANDS

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The recent detection of the chiral molecule propylene oxide in the interstellar medium has led to extensive experimental and theoretical studies, however interpreting its spectrum remains challenging due to its high spectral density, the presence of 24 vibrational degrees of freedom, and the complexity introduced by Coriolis interactions and Fermi resonances. The spectrum consists of numerous transitions arising from the excitation of fundamental vibrations as well as hot bands and combination bands involving the CH_3 torsion vibration mode $\nu_{24} \approx 199.870$ cm^{-1} and the CH_2, CH_3 rocking vibration mode $\nu_{19} \approx 894.120$ cm^{-1}, both of which appear near the breathing vibration mode $\nu_{12} \approx 1267.260$ cm^{-1}

In this study, a high-resolution infrared spectrum was recorded at room temperature using a tunable quantum cascade laser spectrometer[1]. The observed transitions, with quantum numbers $J < 19$ and $k_a < 13$, were assigned to strong b- and c-type bands. We used the PGOPHER program in combination with Loomis-Wood plots to assign 1352 lines to the combination band. We derived the molecular parameters from a least-squares fit analysis of data which also include the parameters for Fermi-type interaction.

The data analysis of the combination band is essential to identify ro-vibrational transitions of propylene oxide in the mid-IR in order to identify energy level-schemes for infrared-millimeter-wave three-wave mixing experiments (IR+mmW 3WM).[1] [2]

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PHOTODETACHMENT SPECTROSCOPY OF THE LOWEST S- AND P-WAVE THRESHOLDS OF C_2^-

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Radiofrequency ion traps are ideally suited tools for sensitive and accurate spectroscopy measurements of molecular ions. We have used photodetachment spectroscopy of negative ions near threshold to determine the electron affinity or the position of a dipole bound state near threshold [1,2]. In a recent experiments we studied the photodetachment of C_2^-, an interesting candidate for quantum-state changing collisions [3], to the two lowest electronic states of neutral carbon dimers. Detachment to the ground state occurs by p-wave detachment, while detachment to the first excited state occurs via s-wave detachment. At two different rotational temperatures of the ions in the trap, these thresholds are shown to behave very differently [4]. Using detailed fits to these measurements that take the different rotational selection rules into account, we have extracted a new value for the electron affinity of C_2 [4], which happens to deviate significantly from a recent value measured using photoelectron imaging [5].

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MACHINE LEARNING FOR ISOTOPOLOGUE EXTRAPOLATION

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Accurate isotopologue line lists are essential for modelling and interpreting high-resolution astronomical spectra, particularly for molecules like carbon monoxide (CO) that play a key role in the atmospheres of exoplanets, brown dwarfs, and cool stars. Existing approaches to isotopologue extrapolation used by ExoMol typically apply corrections based on variational calculations for the main isotopologue, assuming mass-dependent shifts and shared residuals across isotopologues.[1] While this method is effective and has proved useful,[2] it can struggle with higher accuracy requirements at elevated vibrational or rotational states, and/or for minor isotopologues. In this work a variety of machine learning (ML) techniques have been applied to improve isotopologue extrapolation for CO. Isotopologue rovibrational energy levels and transition frequencies have been predicted using ML on a combination of variational calculations, hybrid line list data, and available experimental results. By learning patterns in the residuals between computed and corrected energy levels, these models help to generalize to isotopologues with sparse experimental data, such as $^{12}C^{17}O$, $^{13}C^{17}O$, or $^{13}C^{18}O$, reducing residuals by >50% for all minor isotopologues. Further work on applying these methods to more diatomics within the ExoMol database and extending to polyatomics is also underway.

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LASER SPECTROSCOPY OF NEW UV $A^2\Pi$ - $X^2\Sigma^+$ BANDS OF CALCIUM MONOHYDRIDE

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CaH is an important astronomical molecule found in cold stars such as sunspots and brown dwarfs. Despite its simplicity, CaH has complex electronic states due to interactions between the excited states. Below 30000 cm^{-1}, there are the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $1^2\Delta$, $E^2\Pi$, and $D^2\Sigma$ states. Among them, the $B^2\Sigma^+$ excited state possesses a typical double minimum potential, and we have previously observed irregularly spaced vibrational levels of the B state [1] , [2]. The THz spectra made it possible to improve the molecular constants of the ground state[3]. In addition, we have identified the forbidden transition from the ground state to the $1^2\Delta$ state for the first time. Many bands were still left unassigned in this region[4]. We present here laser-induced fluorescence (LIF) measurements of transitions between the high vibrational levels, v = 10, 11, and 12 of the $A^2\Pi$ state and v=0 of the ground state.

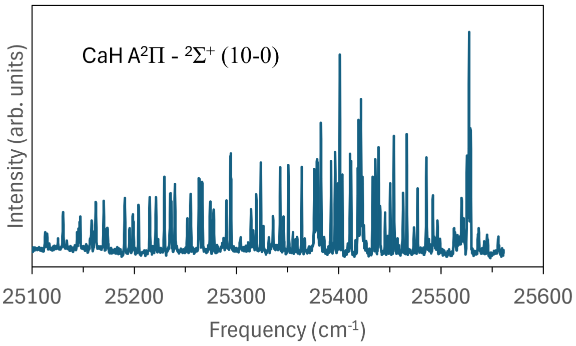

Figure 1: Broadband measurement spectra of CaH $A^2\Pi$ (v = 10) – $X^2\Sigma^+$ (v = 0).

CaH molecules were generated by laser-ablation of a Ca metal chip in a hydrogen atmosphere and were then excited by a pulse of dye laser. The subsequent LIF was detected by a PMT. The v = 10, 11 and 12 levels of the $A^2\Pi$ were observed around 25400 cm^{-1}, 26300 cm^{-1}, 27000 cm^{-1}, respectively. Figure 1 shows the $A^2\Pi$ - $X^2\Sigma^+$ (10-0) region. The rotational temperature was about 300-500 K. Each spectral line used in our analysis was measured individually to precisely determine its frequency.

The assignment was done based on the combination differences. Local perturbations were observed at all levels. We plan to identify the origin of these perturbations and report the molecular constants.

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EXOMOL EXTENSIONS: EXOATOM AND EXOPHOTO – SPECTROSCOPIC DATABASES FOR ATOMS AND MOLECULAR PHOTODISSOCIATION

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Recent advances in high-resolution spectroscopy and atmospheric modeling on exoplanet have created a growing demand for temperature-dependent high-accuracy molecular and atomic data. Therefore, we have extended ExoMol by creating two new databases.

The first extension is ExoPhoto database (`https://exomol.com/data/data-types/photo/`) [1]. It extends the ExoMol database to provide high-accuracy, temperature-dependent photodissociation cross-section data at short ultraviolet wavelengths. ExoPhoto combines theoretical models from three computational databases (ExoMol, UGAMOP, and PhoMol) with experimental datasets from two research groups, covering a broad range of wavelengths and temperatures. Currently, ExoPhoto includes photodissociation data for 20 molecules: AlH, HCl, HF, MgH, OH, NaO, MgO, O_2, AlCl, AlF, CS, HeH^+, CO, CO_2, H_2O, SO_2, C_2H_2, C_2H_4, H_2CO, and NH_3. It also provides detailed branching ratios and quantum yields for selected datasets. Data are organized in JSON-based files with a consistent naming convention, and cross sections are stored in `.photo` files for each molecule and temperature. Future developments will include additional photodissociation data and support for non-local thermodynamic equilibrium (non-LTE) conditions.

The second extension is ExoAtom database(`https://exomol.com/data/data-types/atom/`)[2]. It extends the ExoMol database by providing atomic line lists for 80 neutral atoms and 74 singly charged ions in the ExoMol format, derived from NIST and Kurucz databases. ExoAtom uses five main file types: `all`, `def`, `states`, `trans`, and `pf`. The `states` file lists energy levels with quantum numbers, uncertainties, and lifetimes; the `trans` file records transition wavenumbers and Einstein A coefficients; the `pf` file supplies partition functions over various temperatures. Future work will expand ExoAtom to include additional ionization stages.

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LINE BY LINE ANALYSIS OF THE ν_{10} AND ν_9 BANDS OF ALLENE BETWEEN 600 AND 1200 cm^{-1}

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High-resolution infrared measurements from ground- and space-based instruments are used to detect and quantify small organic molecules both on Earth and in outer atmospheres. The interpretation of these observations relies on the availability of reference spectroscopic data.

The present work aims to improve the description of line positions and intensities in the ν_{10} and ν_9 bands of allene (propadiene, C_3H_4), located respectively near 841 and 999 cm^{-1}. Spectroscopic constants for these bands are available in the litterature[1,2], line intensities have been measured[3] and a linelist containing the position, intensity and lower state energy of 31686 lines between 296 and 1192 cm^{-1} is available in the GEISA database[4]. High resolution Fourier transform spectra of pure allene were recorded at room temperature under various pressure conditions. Although comparisons with spectra calculated at the same conditions using the GEISA linelist show that the overall structures of the bands are well reproduced, some discrepancies are nevertheless observed. Results of this ongoing study will be presented.

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HIGH-RESOLUTION INFRARED SPECTROSCOPY OF N_2O AND SO_2 BROADENED BY HELIUM TO ASSIST IN ANALYSIS OF EXOPLANETARY ATMOSPHERES.

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The James Webb Space Telescope (JWST), launched in 2021, as well as the next generation telescopes like Extremely Large Telescope (ELT), ARIEL, and GRAVITY+, will collect high resolution spectral data of exoplanetary atmospheres with high sensitivity, covering the near to mid-IR, and optical regions of the electromagnetic spectrum. The interpretation of these spectra requires accurate line modeling based on reference laboratory data, including transition frequencies, line intensities, and broadening parameters along with their temperature dependence. These molecular parameters are available in databases such as HITRAN[1,2] and EXOMOL[3] to aid in modeling and interpreting the spectra of planetary atmospheres.

However, many key parameters in these spectral catalogs remain incomplete. In particular, pressure and temperature dependent broadening parameters of several molecules relevant to exoplanetary atmospheres, such as, N_2O, SO_2, and OCS, in He-, H_2-, and CO_2-dominated environments are limited. For example, previous experimental work on the pressure broadening of N_2O by He, reported by Tasinato et al.[4] and by Nakayama et al.[5], is not enough to allow a fit to build a sufficient model for it.[6]

Therefore, it becomes essential to have a complete set of pressure and temperature based broadening parameters for such molecules in foreign broadening gases. In this study, we present high-resolution infrared measurements of N_2O and SO_2 broadened by He. N_2O is a potential biosignature gas, while SO_2 is one of the photochemical products that was also recently identified in exoplanetary atmospheres, e.g. WASP39-b[7,8]. Using a Bruker IFS 120/5HR spectrometer with a spectral resolution of 0.002 cm^{-1}, we investigate the pressure broadening effects of He on N_2O, and SO_2 at room temperature, with pressures up to 1000 mbar. These measurements aim to enhance existing spectral databases and support the accurate characterization of exoplanetary atmospheres.

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SOLIS: AN ACCURATE IR/VIS LINE LIST FOR SULFUR MONOXIDE (^{32}S^{16}O) & UV PHOTOABSORPTION AND PHOTODISSOCIATION CROSS SECTION PREDICTIONS

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We present a rovibronic IR/Vis line list[1] for the transient diatomic sulfur monoxide (^{32}S^{16}O) computed through our variational code Duo[2] using a semi-empirical spectroscopic model consisting of potential energy curves, spin-orbit curves, electronic angular momentum curves, (transition) dipole moment curves as well as other couplings. The underlying *ab initio* spectroscopic model of SO was taken from Brady et al. (2022)[3] which was refined by fitting to a comprehensive experimentally derived set of energies of SO. To this end, an experimental set of 50106 transitions, 49613 of those being non-redundant, have been compiled through the analysis of 29 experimental sources. A self-consistent set of 8850 rovibronic energy levels for the $X\,^3\Sigma^-$, $a\,^1\Delta$, $b\,^1\Sigma^+$, $A\,^3\Pi$, $B\,^3\Sigma^-$, and $C\,^3\Pi$ electronic states has been generated with the Marvel algorithm[4] covering rotational and vibrational quantum numbers $J \leq 69$ and $\nu \leq 30$, respectively, and energies up to 52350.40 cm^{-1} ($\geq$ 191 nm). A large gap in our network between 12300-20500 cm^{-1} exists due to lack of vibrational data for $X\,^3\Sigma^-$, $a\,^1\Delta$, and $b\,^1\Sigma^+$ with no coverage of the $c\,^1\Sigma^-$, $A'^3\Delta$, and $A''^3\Sigma^+$ states. Our refined spectroscopic model reproduces the $X\,^3\Sigma^-$, $a\,^1\Delta$, $b\,^1\Sigma^+$, and $A\,^3\Pi$ MARVEL energies with a weighted root-mean-square error of 3.13×10^{-3} cm−1, 1.08×10^{-3} cm^{-1}, 0.27 cm^{-1}, and 0.24 cm^{-1}.

We are currently refining the UV region of the spectroscopic model, which was not done originally because of the many perturbations in the $B\,^3\Sigma^-$ and $C\,^3\Pi$ electronic state energies due to their overlapping potentials and large coupling. However, we present novel predicted UV absorption cross sections for the SO radical, highlighting specific wavelengths for its potential detection. Furthermore, we provide initial photodissociation cross sections, crucial for understanding SO's behaviour in astrophysical environments, particularly the atmospheres of hot Jupiter exoplanets.

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AB INITIO SPECTROSCOPIC INVESTIGATION OF HYDROGEN FLUORIDE

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Hydrogen fluoride (HF) is a chemically simple molecule, yet it holds significant importance in astrophysics due to its strong rovibrational signatures, which make it an effective tracer in planetary and exoplanetary atmospheres[1]. HF has been observed in diverse astronomical environments, including sunspots[2], the atmosphere of Venus[3], red giant stars[4], and the interstellar medium[5].

In this work, we present a detailed ab initio study of the rovibronic spectroscopy of HF. High-level quantum chemical methods are employed to compute the electronic structure, including potential energy curves, transition dipole moments, and key couplings between relevant excited states. These data are integrated with accurate nuclear motion calculations to model the rovibronic energy levels and spectral transitions of the molecule.

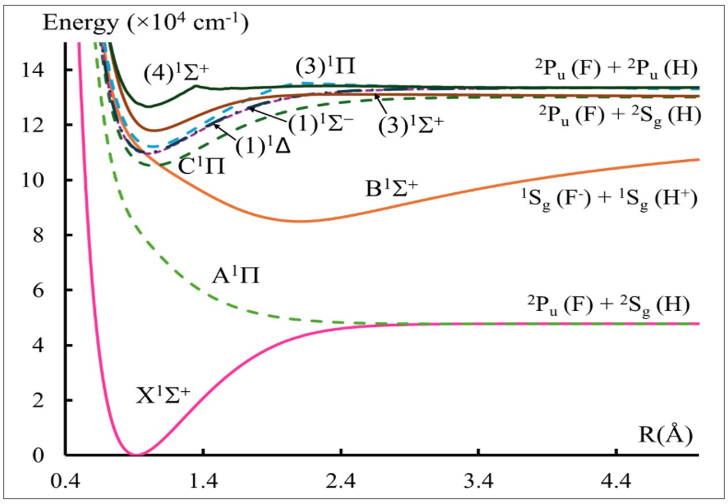

Figure 1: Calculated lowest level Potential Energy Curves of the HF molecule

The resulting theoretical spectra provide high-quality molecular data relevant to astrophysical applications, particularly in modeling exoplanetary atmospheres and interstellar chemistry. This study enhances our understanding of HF's spectroscopic behavior in the ultraviolet (UV) region and supports the interpretation of observational data from current and future space-based missions.

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LINE PARAMETERS MEASUREMENTS OF THE $2\nu_3$ BAND OF CH_3F : LINE INTENSITIES AND LINE AIR-BROADENING COEFFICIENTS

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Among the HFCs, methyl fluoride (CH_3F) is a molecule found naturally in the atmospheres of the Earth and Venus[1]. Its use as a nonflammable aerosol propellant makes it particularly interesting. In atmospheric and combustion chemistry, chemical reactions involving CH_3F are fundamental; it is also well known to be a powerful inhibitor of methane oxidation and production[2].

High-resolution infrared spectra of the $2\nu_3$ band of CH_3F were recorded using a Fourier-transform spectrometer in the GSMA laboratory in Reims. The focus of this study is the determination of line parameters, specifically line intensities and air-broadening coefficients. Approximately 600 isolated and blended transitions were processed in total to obtain line intensities, based on a set of six spectra collected at pressures between 0.1 and 1.5 mbar of CH_3F. Only well-separated lines were considered to determine the line broadening, reducing the number of observable transitions to around 300. Seven additional sets of spectra were collected for this purpose, with a constant CH_3F pressure of 0.7 mbar and varying air pressure between 2 and 45 mbar. All spectra were analysed using Voigt profile fitting with the `Wspectra` software[3, 4]. These data include precise spectroscopic information that is crucial for modelling the spectroscopy and atmospheric occurrence of CH_3F.

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[1] K. Narahari Rao and C. W. Mathews, *Molecular Spectroscopy: Modern Research*, Academic Press, New York and London, 1972.

[2] P. Frenzel and U. Bosse, "Methyl fluoride, an inhibitor of methane oxidation and methane production", *FEMS Microbiol. Ecol.*, **21**, 25–36 (1996).

[3] M. R. Carleer, "WSpectra: A Windows program to accurately measure the line intensities of high-resolution Fourier transform spectra", in *Remote Sensing of Clouds and the Atmosphere V*, Proc. SPIE **4168**, 337–343 (2001), eds. J. E. Russell, K. Schäfer, and O. Lado-Bordowsky.

[4] M. Tudorie, T. Foldes, A. C. Vandaele, and J. Vander Auwera, "CO_2 pressure broadening and shift coefficients for the 1–0 band of HCl and DCl", *J. Quant. Spectrosc. Radiat. Transf.*, **113**, 1092–1101 (2012).

EXOMOL LINE LISTS FOR 12 ISOTOPOLOGUES OF CO_2

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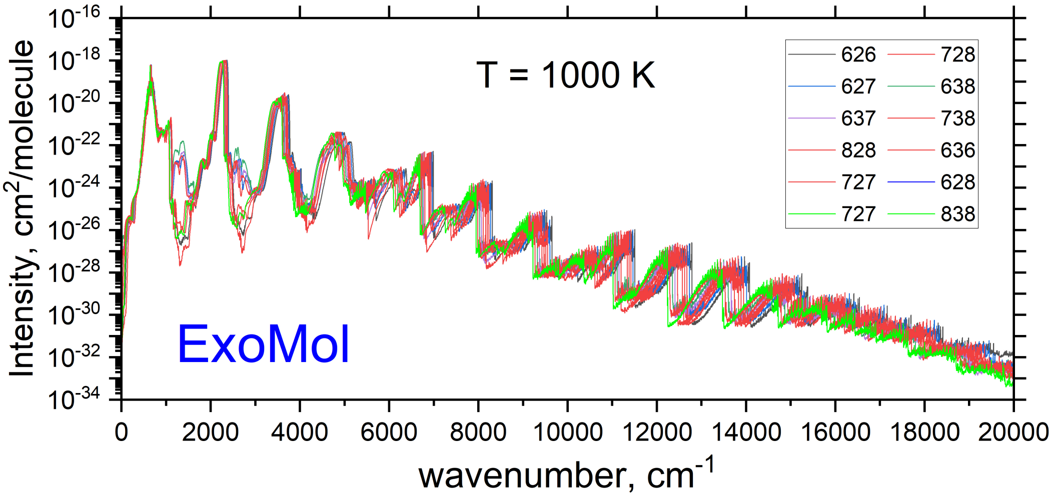
Extensive rovibrational line lists for 12 isotopologues of carbon dioxide, $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{17}O_2$, $^{13}C^{17}O_2$, $^{12}C^{18}O_2$, $^{13}C^{18}O_2$, $^{16}O^{12}C^{17}O$, $^{16}O^{12}C^{18}O$, $^{16}O^{13}C^{17}O$, $^{16}O^{13}C^{18}O$, $^{17}O^{12}C^{18}O$, $^{17}O^{13}C^{18}O$, called "Dozen" have been constructed for hot exoplanetary applications. We used accurate empirical potential energy surfaces Ames-2[1] and Ames-X01d[2], accurate *ab initio* dipole moment surface Ames-2021–40K by Huang et al. and the variational rovibrational program TROVE to solve the Schrödinger equation and generate associated Einstein A coefficients. We then applied empirical energies from the most recent MARVEL[3], HITRAN2020[4] and CDSD-2024-PI[5] studies of CO_2 to replace the calculated energies where available. We used a combination of Machine learning algorithms handled by a separate estimator built as a VotingClassifie to assign the AFGL quantum numbers where they are not available. The line lists and all associated data will be provided at `www.exomol.com`.



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[1] X. Huang, D. W. Schwenke, R. S. Freedman, T. J. Lee, *J. Quant. Spectrosc. Radiat. Transf.*, **203**, 224 (2017)

[2] X. Huang, R. S. Freedman, S. Tashkun, D. W. Schwenke, T. J. Lee, *J. Mol. Spectrosc.*, 392, 111748 (2023)

[3] M. T. I. Ibrahim, D. Alatoom, T. Furtenbacher, A. G. Csáaszár, S.N Yurchenko, A. A. A. Azzam, J. Tennyson, *J. Comput. Chem.*, 45, 969 (2024); A. A. A. Azzam, Azzam S. A. A., Aburumman K. A. A., J. Tennyson, S.N Yurchenko, A. G. Csáaszár, T. Furtenbacher, *J. Mol. Spectrosc.*, 405, 111947 (2024); A. A. A. Azzam, et al., *Sci. Data*, **12**, 532 (2025); A. A. A. Azzam, J. Tennyson, S.N Yurchenko, T. Furtenbacher, A. G. Csáaszár, *J. Comput. Chem.*, **46**, e27541 (2025); A. A. A. Azzam, AlAlawin J. M. A., J. Tennyson, S.N Yurchenko, T. Furtenbacher, A. G. Csáaszár, *J. Quant. Spectrosc. Radiat. Transf.*, **343**, 109485 (2025); S. A. M. Obaidata, A. A. A. Azzam, J. Tennyson, S.N Yurchenko, T. Furtenbacher, A. G. Csáaszár, *J. Mol. Spectrosc.*, **340**, 109444 (2025); M. H. I. Mansour, A. A. A. Azzam, J. Tennyson, S.N Yurchenko, T. Furtenbacher, A. G. Csáaszár, *Mol. Phys.* (2025)

[4] I. E. Gordon, et al., *J. Quant. Spectrosc. Radiat. Transf.*, **277**, 107949 (2022)

[5] R. Kochanov, V. Perevalov, *J. Quant. Spectrosc. Radiat. Transf.*, **341**, 109428 (2025)

C: Minisymposium on Interstellar Astrophysics

Monday, August 25, 14:00
Hörsaal I

Chair: Sandra Brünken

INTERSTELLAR CHEMISTRY: WHAT MOLECULES TELL US ABOUT THE UNIVERSE

A. M. Jacob [a,b]

[a] I. Institute of Physics University of Cologne, Cologne, Germany
[b] Max Planck Institute for Radio Astronomy, Bonn, Germany

Throughout much of human history, the space between stars collectively known as the interstellar medium (ISM) was thought to be empty. It was only toward the end of the 19th century that scientists began to discover the existence of a gaseous ISM, with the first direct evidence provided by the discovery of spectral lines in the optical spectra of emission nebulae, such as the Orion Nebula by Huggins and Miller (1864) and later Huggins and Huggins (1889). Today we understand the ISM to be a highly complex and inhomogeneous mixture with it's baryonic component comprised of gas and dust permeated by energetic particles, exposed to intense radiation fields and violent shocks. Although the warm and hot ionised phases of this medium occupy much of the volume, they account for only a small portion of the total gas mass, with the bulk of this material residing in cooler and denser neutral regions. These neutral regions serve as a fascinating laboratory for investigating a wide array of astrophysical processes, forming the raw material for star formation and bridging the physical scales between stars and galaxies.

Despite being composed of only trace abundances of elements heavier than helium, the ISM has proven to be a surprisingly rich environment for molecular formation and complexity. Against expectations, scientists have discovered a wide variety of molecules in space, ranging from simple diatomic species to complex structures such as fullerenes with up to 60 carbon atoms (Sellgren et al., 2010). These molecules have been identified toward a broad range of astronomical environments–including comets, exoplanetary atmospheres, interstellar clouds, circumstellar envelopes, and even external galaxies–leading to the cataloguing of nearly 300 distinct molecular species over the past eight decades. Such discoveries have been driven by advances in receiver technology, particularly in sub-mm and radio astronomy, as well as breakthroughs in laboratory spectroscopy. The resulting field of astrochemistry has become a truly interdisciplinary science, engaging astronomers, physicists, and chemists, alike.

But what do we learn from these molecules?

Owing to the complexity of their energy level structures–and the resulting distinct chemical fingerprints observed in emission or absorption–molecules serve as powerful diagnostic tools for probing the physical conditions of their environments. Beyond their role as tracers, molecules actively shape their surroundings by influencing the thermal balance and ionisation state of interstellar gas. They can trigger condensations and instabilities that lead to star formation, thereby playing a crucial role in regulating the evolution of the regions in which they reside. Although astronomical spectra offer a wealth of information, interpreting them requires a detailed understanding of the underlying chemistry, often informed by theoretical models and laboratory experiments. However, such studies are frequently limited to simpler molecular systems. In this context, small molecules–whose chemistry is relatively well understood and which form the foundation for the synthesis of more complex species–hold the greatest promise for advancing our understanding of the chemical Universe. This talk will journey through a renaissance of astronomical observations detailing the puzzling discoveries of certain simple molecules and the chemical mysteries they hold, with special a focus on hydrides.

FROM LILLE TO THE STARS: THE QUEST FOR MOLECULES IN THE INTERSTELLAR MEDIUM

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Lille, France

To date, approximately 330 molecules have been detected in the interstellar medium (ISM), the majority of which have been identified through their rotational transitions in the centimeter and millimeter wavelength domains. Until 2019, the average rate of new molecular detections outside the solar system was about 3.7 per year [1]. However, this rate has significantly accelerated in recent years, with 108 new molecular species identified since early 2021.

This rapid growth highlights the need for continued improvements in both detection capabilities and astrochemical modeling to better understand the formation pathways of complex organic molecules. Addressing these challenges requires a multidisciplinary approach involving astrophysicists, spectroscopists, and chemists.

In this context, the spectroscopy group in Lille has developed advanced instrumentation, including the FLASH spectrometer (Fast Lille Absorption emiSsion High resolution). FLASH is a unique, high-performance system capable of operating up to 1.5 THz in absorption mode [2] and up to 0.5 THz in chirped-pulse mode [3]. This contribution will present recent spectroscopic studies and the latest technological developments that support the identification of new molecular species in space.

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[1] McGuire et al., **2018**, *ApJS*, 239, 17)

[2] Zakharenko et al., **2015**, J. Mol. Spectrosc., 317, 41

[3] L. Zou, et al. **2020**, *Rev. Scien. Inst*, 91, 063104

HIGHLY CORRELATED AB INITIO CALCULATIONS APPLIED TO THE CHARACTERIZATION OF ASTROPHYSICAL SPECIES

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Ab initio and DFT procedures have an indisputable application for the assignment of molecular spectra, and for this reason, their use has become widespread. Some methods are very popular due to their computational efficiency and accessibility (i.e., B3LYP, MP2, etc.). However, some molecular species can pose complex problems that require the use of more sophisticated levels of theory. Calculations of rotational constants for medium-sized species can be an example.

In the case of gaseous astrophysical sources, unstable species that are difficult to treat in the laboratory can play a fundamental role in chemical evolution. This is the case of unsaturated carbon chains such as C_3H or C_5H. [1]

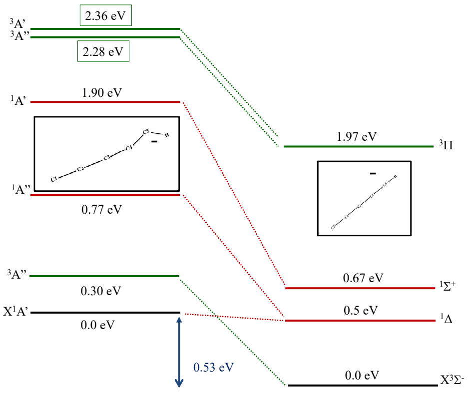

Figure 1: Low-lying electronic states of carbon chains

Furthermore, new large-scale facilities allow observing species in diverse vibrational states. This is the case for many organic molecules that exhibit large-amplitude motions (LAMs).

The spectra of these molecules can be studied in the laboratory and assigned with effective operators. However, most models are designed for species with one or two LAMs. Examples such as methoxymethanol [2] are proposed , in which three or more LAMs interact and are not separable. High-level calculations can shed light on these problems. [3]

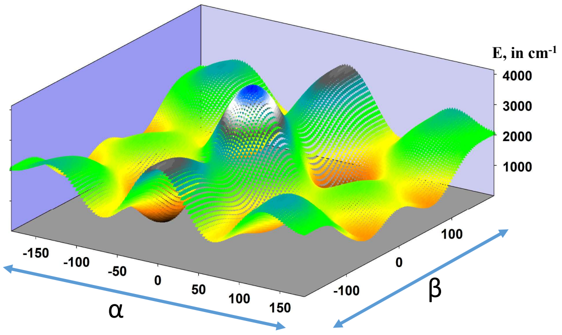

Figure 2: methoxymethanol

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[1] Bennedja, S.C., Hammoutène, D., and Senent, M.L., **2019** *Astrophys.J.*, 871, 255.

[2] Missaoui,D., Brahem, S., Najar, F., Yazidi, O., and Senent, M.L., **2024** *ACS Earth and Space Chemistry*, 8, 1236.

[3] This research was supported by the Ministerio de Ciencia, Innovación y Universidades and the Agencia Estatal de Investigación of Spain and the European Regional Development Fund through the grant PID2023-147545NB-I00 /MCIU/AEI/10.13039/501100011033/FEDER EU.

HIGH-RESOLUTION SPECTROSCOPY OF MOLECULES OF ASTROPHYSICAL IMPORTANCE

S. Spezzano[a]

[a] Center for Astrochemical Studies (CAS), Max Planck Institute for Extraterrestrial Physics (Germany)

To use molecules as astrophysical tools, a multidisciplinary approach is mandatory. Only with a concerted effort of laboratory work, observations, and theoretical work, we can address fundamental questions about the formation of stars and planets, and about the inheritance of material within the star formation process. In order to interpret the steadily increasing amount of high-resolution astronomical data, high-resolution laboratory spectroscopy data are necessary. In my talk, I will present our most recent results on the spectroscopy of deuterated complex organic molecules and their link with the development of molecular complexity in star-forming regions. I will also present the first results on our measurements of pressure broadening coefficients for studies of exoplanetary atmospheres.

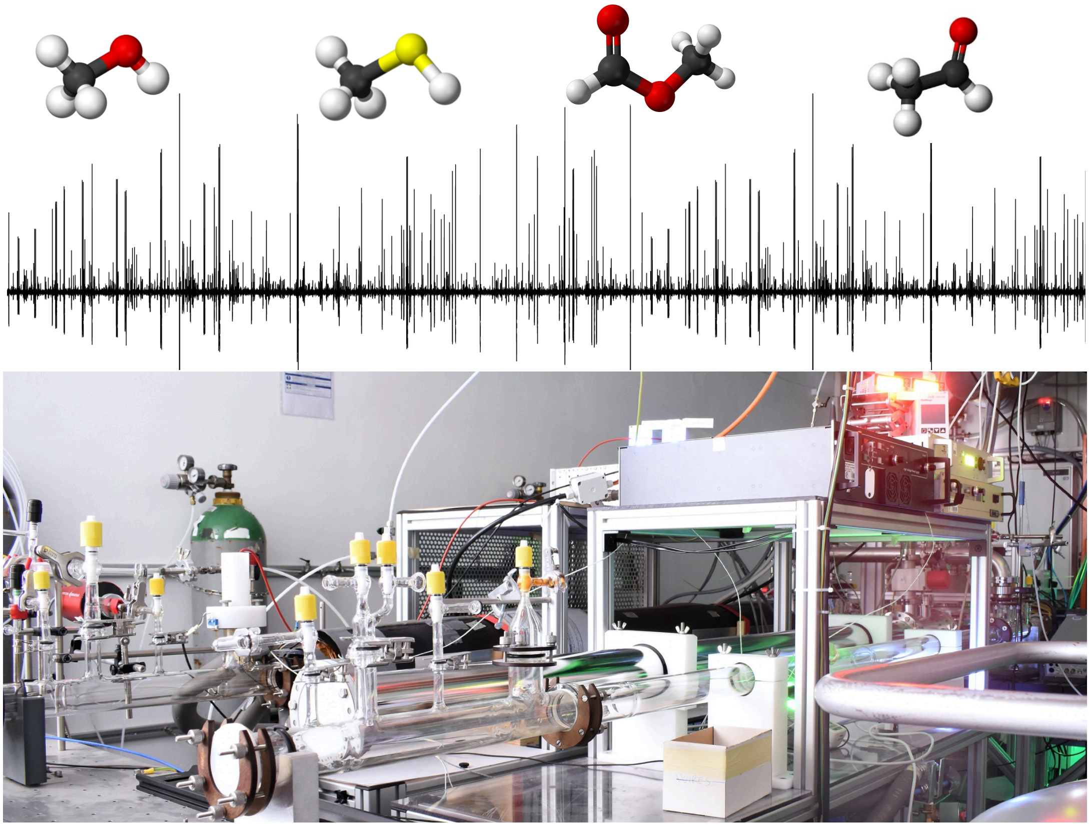

Figure 1: The absorption spectrometers in the CAS Labs shown in the figure are used to measure the rotational spectrum of molecules of astrophysical importance. Complex spectra are routinely analyzed in the CAS Labs to allow the detection of new molecules in space (e.g. the molecules shown at the top of the figure).

D-I: Contributed Talks

Monday, August 25, 16:30
Hörsaal I

Chair: Marie-Aline Martin-Drumel

SHEDDING LIGHT ON SiC$^+$: FIRST LABORATORY SPECTRA OBTAINED BY ELECTRONIC PHOTODISSOCIATION

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Silicon carbide ions ($Si_nC_m{}^+$) are thought to form in carbon-rich circumstellar environments, such as those around Asymptotic Giant Branch (AGB) stars.[1,2] While small neutral Si_nC_m molecules have been identified in the interstellar medium by radioastronomy,[3] the detection of their expected cationic counterparts remains elusive due to the absence of experimental spectroscopic data.[4] As a potential contributor to interstellar ion–molecule chemistry and silicon carbide dust formation, knowledge of the spectroscopic signatures of $Si_nC_m{}^+$ are crucial for future astronomical identification.

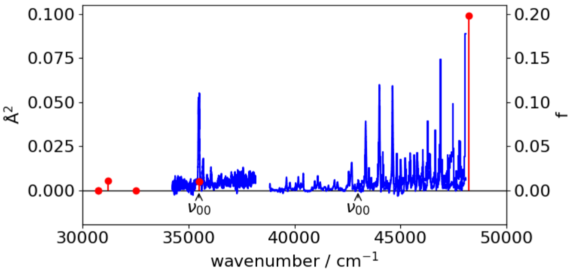

Figure 1: Measured photodissociation spectrum of SiC$^+$ (cross section) compared to vertical excitation spectra computed by TD-DFT calculations (oscillator strength f).

We present herein the first laboratory spectrum of SiC$^+$. Its optical spectrum is obtained by vibronic photodissociation of mass-selected ions recorded in a quadrupole/time-of-flight tandem mass spectrometer coupled to a laser vaporization source. The obtained spectrum (Figure 1) exhibits distinct vibrationally resolved excited states that reflect its asymmetric bonding character. The derived spectroscopic parameters are in good agreement with available predictions of high-level quantum chemical calculations.[5]

These results offer the first direct spectroscopic fingerprint of SiC$^+$ and thus the basis for the potential identification of this fundamental diatomic cation in interstellar space. In addition, it provides new insights into the complex excited-state landscape of small cosmic ions.

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[1] Chen, Tao, et al. "Where have all the interstellar silicon carbides gone?." Monthly Notices of the Royal Astronomical Society 509.4 (2022): 5231-5236.

[2] C. McCarthy, Michael, et al. "Building blocks of dust: A coordinated laboratory and astronomical study of the archetype AGB carbon star IRC+ 10216." Journal of Molecular Spectroscopy 356 (2019): 7-20.

[3] Massalkhi, Sarah, et al. "Abundance of SiC_2 in carbon star envelopes-Evidence that SiC_2 is a gas-phase precursor of SiC dust." Astronomy & Astrophysics 611 (2018): A29.

[4] Förstel, Marko, et al. "Structure and photochemistry of a potential precursor of circumstellar dust: The optical spectrum of $Si_4C_2{}^+$." Journal of Molecular Spectroscopy 377 (2021): 111427.

[5] Zhou, Dan, et al. "Spectroscopic properties and transition probabilities of SiC$^+$ cation." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 204 (2018): 164-173.

HIGH-RESOLUTION RO-VIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF THE OPEN-SHELL, LINEAR CCH$^+$ ION

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[a] HFML-FELIX, Nijmegen, The Netherlands
[b] Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands
[c] I. Physikalisches Institut, Universität zu Köln, Köln, Germany
[d] Max-Planck-Institut für extraterrestrische Physik, CAS, Garching, Germany
[e] Photon Science Division, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

The ethynyl radical cation, CCH$^+$ ($^3\Pi$), is very interesting from an astrochemical point of view, since it is proposed to be a key intermediate in interstellar hydrocarbon chemistry. However, due to its extremely reactive nature, experimental spectroscopic data, which is needed for its detection in space, was lacking. Here, we report on the high-resolution infrared spectrum of CCH$^+$ recorded in the range 3066−3184 cm^{-1} by means of leak-out spectroscopy (LOS)[1]. This spectral range covers the fundamental of the CH stretching mode and a highly excited bending vibrational mode with Π symmetry. Based on this data (385 lines), accurate spectroscopic descriptions of the ground and two vibrationally excited states of CCH$^+$ were obtained. This effective Hamiltonian analysis allowed a search for pure rotational lines of CCH$^+$ in its electronic and vibrational ground state using a double-resonance mm-wave - infrared scheme[2]. We observed all rotational transitions from $J'' = 2$ up to $J'' = 6$ within the $\Omega = 2$ lowest energy fine structure component with resolved hyperfine splittings. This data has already guided the first detection of CCH$^+$ in space and has the potential to support further astronomical searches for CCH$^+$ either through radio or infrared spectroscopy, e.g., with the recently launched James Webb Space Telescope.

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[1] P. C. Schmid, O. Asvany, T. Salomon, S. Thorwirth, S. Schlemmer, *J. Phys. Chem. A* **126** (2022) 8111-8117

[2] O. Asvany, S. Thorwirth, P.C. Schmid, T. Salomon, S. Schlemmer, *Phys. Chem. Chem. Phys.* **29** (2023) 19740-19749

HIGH-RESOLUTION ELECTRONIC AND THRESHOLD PHOTOELECTRON SPECTROSCOPY OF C_{70}^+

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Fullerenes are present in several types of regions in space and the C_{60}^+ cation has been identified as a carrier of five of the Diffuse Interstellar Bands (DIBs).[1] Although initially its fullerene family member C_{70}^+ was not estimated to be a DIB carrier,[2] recent analyses show some favoritism to the strongest bands of C_{70}^+ correlating with DIBs.[3] In this work we combine two state of the art experimental techniques to obtain complementary spectroscopic information about C_{70}^+ that could be of use to identify the cation in interstellar environments. In Innsbruck, a high-resolution electronic spectrum of one of the electronically excited states of C_{70}^+ was recorded using He nanodroplet technology. At the SOLEIL synchrotron, we recorded the first high-resolution threshold photoelectron spectrum (TPES) of C_{70} which contains the ground state and several excited states of the cation. We provide tentative vibrational assignments to the complex vibrational structure in the electronic spectrum and comment on the symmetry breaking involved in the vibrational structure. We then utilize the electronic spectrum as a benchmark to identify excited states in the TPES and we use previous theoretical methods to build a model spectrum that accounts for a complicated pattern of hot bands in the TPES.

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[1] Linnartz, H. et al. **2020** *J. Mol. Spec.*, 367, 111243.
[2] Campbell, E. et al. **2016** *Astrophys. J.*, 822, 17.
[3] Majaess, D. et al. **2025** *MNRAS*, 538 (4), 2392.

NON-LTE MOLECULAR OPACITIES AND RADIATIVE TRANSFER FOR EXOPLANETS

C. A. Bowesman[a], S. N. Yurchenko[a]

[a] Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom

A new tool for solving radiative transfer and computing molecular opacities in non-LTE exoplanet atmospheres is presented. The ultra-hot Jupiter KELT-20 b is used as a case study to test the wavelengths at which non-LTE effects may be detectable. It is shown that upper atmospheric hydroxyl radicals (OH) in vibrational non-LTE should be observable via hot bands in the mid-infrared and through stimulated emission. Using recent calculations for the photodissociation cross sections of OH it is shown that non-LTE effects can increase the total photodissociation rate by over three orders of magnitude, which is likely to have a significant impact on atmospheric modelling. Enhanced continuum absorption in non-LTE may significantly impact retrieved atmospheric abundances.

ROTATIONAL SPECTRA OF ASTROPHYSICALLY RELEVANT CYANO ALIPHATIC COMPOUNDS: MOLECULAR STRUCTURE AND PUCKERING TUNNELLING IN CYCLOPENT-1-ENECARBONITRILE

D. Heras[a], Y. Li[b], N. Osseiran[a], C. Bermúdez[a],
G. Feng[b], C.Pérez[a] and A. Lesarri[a]

[a] *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias – I.U. CINQUIMA, Universidad de Valladolid, Paseo de Belén 7, 47011, Valladolid (España)*
[b] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing (China)

Among the growing inventory of interstellar molecules, nitrile-bearing compounds play a key role due to their strong dipole moments and their prevalence in chemically rich environments such as TMC-1[1]. In this context, 1-cyclopent-1-enecarbonitrile (CPCN) emerges as an attractive astrochemical candidate: it combines a polar nitrile group with a compact, unsaturated five-membered ring, offering a structural motif commonly found in interstellar chemistry. Although not yet detected in space, its spectroscopic characterization is a necessary step toward enabling future astronomical searches.

We have recorded the rotational spectrum of CPCN using chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW) in a supersonic jet expansion over the 2–18 GHz range. A single conformer is observed, but transitions are doubled, revealing a tunneling splitting. This behaviour is attributed to a large-amplitude motion between two equivalent ring-puckered structures. Similar tunneling phenomena have been reported in structurally related five-membered ring systems, such as cyclopentene and tetrahydrofuran[2]. In addition, we assigned all ^{13}C isotopologues in natural abundance, permitting the determination of an experimental structure. Quantum chemical calculations (including B3LYP, MP2, CCSD among others) support the spectral assignment and reproduce both the observed rotational constants and the shallow double-well potential associated with the puckering coordinate. Further measurements in the 75–110 GHz range are currently in progress. More details will be presented at the conference.

These results establish CPCN as a spectroscopically well-characterized and astrophysically relevant molecule, ready for inclusion in spectral catalogs for future radioastronomical surveys.

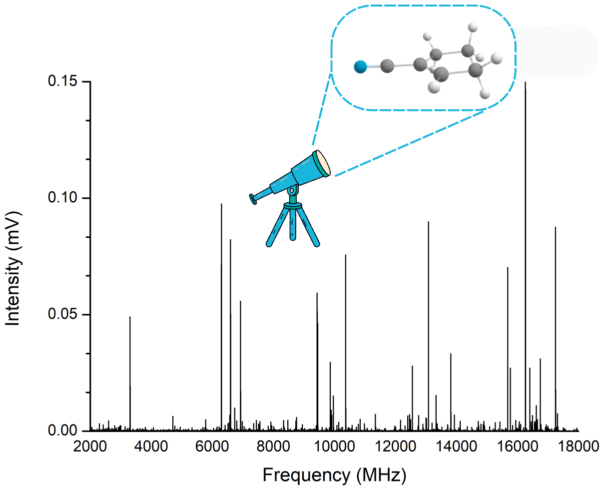

Figure 1: Experimental spectrum and molecular structure of CPCN

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[1] Wenzel, G., Speak, T.H., Changala, P.B. et al. **2025** *Nat. Astron.*, 9, 262-270.
[2] López, J. C., Alonso, J. L., Charro, M. E., Wlodarczak, G. & Demaison, J. **1992** *J. Mol. Spec.* 155, 143-157.

MILLIMETER-WAVE SPECTROSCOPY OF TRANS-METHYL FORMATE.

C. P. Endres[a], M. Araki[a], V. Lattanzi[a], M. Sanz-Novo[b], V. M. Rivilla[b], I. Jimenez-Serra[b], and P. Caselli[a]

[a] Max-Planck-Institut für extraterrestrische Physik, Garching, Germany
[b] Centro de Astrobiología (CAB), INTA-CSIC, Madrid, Spain

Methyl formate (CH_3OCHO) is an abundant molecule in the interstellar medium (ISM) and has been detected in its most stable (*cis*) isomeric form, in numerous star-forming regions. In recent observations towards the Galactic Center molecular cloud G+0.693-0.027 and the protostellar shock L1157-B1[1], also the higher-energy *trans*-conformer was unambiguously identified, confirming its presence in the ISM, which had previously been only tentatively detected[2].

The rotational spectrum of methyl formate is quite complex, because the rotational transitions are split into A- and E-substates due to the internal rotation of the methyl group. In comparison to the *cis*-conformer, the torsional barrier of the *trans*-conformer is much lower ($V_3^{cis} \approx 12$ cm^{-1} & $V_3^{trans} \approx 380$ cm^{-1}). So far, only transitions of the A-substate have been detected in the astronomical observations (30 - 170 GHz), due to the limited spectroscopic information available, particularly for the E-substate.

Therefore, we extended the laboratory investigations of *trans*-methyl formate to encompass the frequency range of 80-110 GHz, using a Chirped-Pulse Fourier Transform spectrometer coupled to a pulsed DC - supersonic jet experiment. In the spectra, that cover the entire frequency range, several tens of *trans*-methyl formate lines were identified, assigned and analysed using a torsion-rotation Hamiltonian. A catalog of rest frequencies has been compiled to support the analysis of the astronomical observations. Besides the laboratory study also a comparison with astronomical data will be presented.

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[1] Sanz-Novo, M., Molpeceres, G., Rivilla, V. M., Jimenez-Serra, I. **2025** *Astron. Astrophys.*, 698, A36

[2] Neill, J. L., Muckle, M.T., Zaleski, D. P., Steber, A. L., Pate, B. H. , Lattanzi, V., Spezzano, S., McCarthy, M. C., and Remijan, A. J. **2012** *Astrophys. J.*, 755, 153

D-II: Contributed Talks

Monday, August 25, 16:30
Hörsaal II

Chair: Jeremy Harrison

TIME-RESOLVED ROTATIONAL SPECTROSCOPY OF TRANSIENT SPECIES PRODUCED BY UV PHOTOLYSIS

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Reactive intermediates and radicals are commonly present in atmospheric, combustion, and astrophysical environments, but their study in the laboratory remains challenging due to their short lifetime and low concentration. Many methods have been used to produce unstable molecules for spectroscopic study, but pulsed laser photolysis is less common with rotational spectroscopy, even though it allows for the study of dynamics as well as spectra. In this study UV pulsed laser photolysis has been implemented in a new room-temperature flow cell with the Fast Lille Absorption emiSsion Hybrid (FLASH) spectrometer to probe transient molecular species. High-energy photons (typically 266 nm) break stable molecules creating products with significant internal energy. This energy is sufficient to populate small molecules in excited vibrational states, enabling rotational spectroscopic measurements of the ground and the vibrationally excited states. In addition, dynamics can be monitored in time domain using Fourier transform spectroscopy experiments. Using this new setup, we successfully generated the simplest Criegee intermediate (CH_2OO) via photolysis of the CH_2I_2 precursor in the presence of oxygen (O_2). As shown in Figure 1, a spectral transition and its temporal dynamics are illustrated. A rise in the signal is observed within approximately 1000 μs after the laser pulse, followed by a gradual decay. To study the mechanism of its formation and consumption, we also explored the spectra of the CH_2I and IO radicals, as well as those of other stable products in the system, such as H_2CO. The results are promising for further studies, demonstrating the capability of this new setup to probe reactive molecules and their dynamics.

Additionally, we successfully observed vibrationally excited photolysis products, such as vibrationally excited CO formed via the photolysis of benzaldehyde. This confirms the potential of our system to investigate vibrationally excited states of photolysis intermediates. Preliminary results concerning the rotational transitions observed for the vibrational CH_2OO will also be presented.

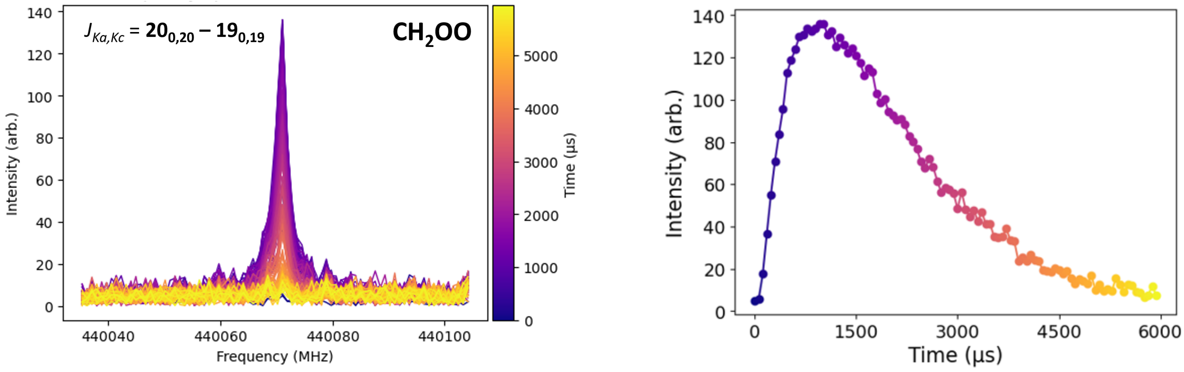

Figure 1: Spectral transition (left) and temporal dynamics (right) of CH_2OO.

LINE SHAPE PARAMETER STUDY OF HELIUM-BROADENED METHANE LINES IN THE ν_4 BAND BY A HIGH-RESOLUTION DUAL-COMB SPECTROMETER

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Methane is a molecule of great importance due to its large global warming potential and its presence in a significant amount in Earth. $^{12}CH_4$ is also found in outer planets' atmospheres such as Saturn or Jupiter, exoplanets and other celestial objects. This molecule appears in a multitude of physical and chemical processes, some of which occur in the atmospheres of Jovian planets where helium is also present. In order to obtain precise monitoring of temperature, concentration and pressure profiles of planetary atmospheres, it is necessary to know the spectroscopic parameters of methane with great accuracy.

In this work, the line shape parameters of methane lines broadened by helium in the ν_4 vibrational band were determined at room temperature. Seven experimental spectra, with total pressure ranging from 26 to 536 mbar, were recorded using a high-resolution dual-comb spectrometer based on quantum cascade lasers[1]. Recent improvements to this instrument have resulted in high quality spectra and fast measurements. The Voigt, Nelkin-Ghatak, speed-dependent Voigt and speed-dependent Nelkin-Ghatak theoretical line profiles were adjusted to the experimental methane line shapes to precisely determine spectroscopic parameters such as broadening and collisional narrowing coefficients. The first-order line-mixing effect was included using Rosenkranz's approximation in addition to each theoretical profile. To our knowledge, line shape parameters were determined for the first time for multiple ν_4 band CH_4 lines diluted in helium. The results are in good agreement with previous literature data when available.

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TEMPERATURE DEPENDENCE OF THE SELF AND FOREIGN WATER VAPOR CONTINUA IN THE 1.6 μm WINDOW

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The work presented here aims to better characterize the temperature dependence of both the self and foreign water vapor absorption continua in the atmospheric window centered at 1.6 μm. This characterization will provide valuable tests for the MT_CKD model [1], which serves as a reference for radiative transfer calculations.

To this end, absorption spectra of pure water (for the self-continuum) were recorded at various temperatures between 285 and 332 K using a cavity ring-down spectrometer (CRDS) equipped with a high-finesse, temperature-controlled cavity [2].

An example of a spectrum recorded for water vapor in air around 5752 cm^{-1} (at 333.33 K) is shown in the Fig. 1. The contributions from the local monomer absorption, the self-continuum, and the foreign-continuum are distinguished. The strong temperature dependence of the self-continuum was measured at about thirty wavenumbers between 5700 and 7000 cm^{-1}. This new dataset improves the accuracy of previous measurements [3], which were used to adjust the MT_CKD model since its version 3.2[1] in this spectral region.

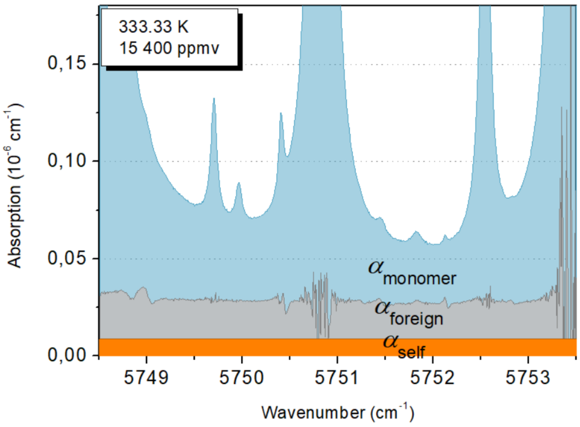

Figure 1: CRDS spectrum of water vapor recorded around 5752 cm^{-1} at a total pressure of 670 Torr with a dry air mixture containing 15,400 ppmv of water vapor, at 333.33 K.

While no temperature dependence is assumed for the MT_CKD foreign-continuum, from our measurements a slight positive temperature dependence is evidenced for water vapor in air, O_2 and N_2.

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HIGH-RESOLUTION SPECTROSCOPIC INSIGHT INTO METHYL FORMATE DEHYDROGENATION: DETECTION AND CHARACTERIZATION OF CH_2OCHO AND CH_3OCO RADICALS

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The depletion of fossil fuel reserves, driven by increasing human consumption, coupled to the ongoing environmental crisis, has raised the question of alternative fuels. In this context, biodiesels are emerging as promising alternatives to conventional diesel fuels, offering similar performance while significantly reducing atmospheric CO emissions[1,2]. Among the various biodiesel options, fatty acid methyl esters (FAMEs) are of particular interest due to their straightforward production via the transesterification of vegetable or animal fats with methanol [3].

Consequently, understanding the combustion chemistry of the simplest ester, methyl formate (MF; CH_3OCHO), is crucial to better model the oxidation mechanisms of FAMEs, especially through the identification of key intermediate species formed during combustion. In this context, kinetic investigations using various pressure flow reactors and shock tube ignition experiments have been performed [4]. These studies reveal that hydrogen abstraction is a dominant pathway in the oxidation of MF. As such, characterizing the radicals produced from MF dehydrogenation — namely the vinyloxy radical (CH_2OCHO) and the methoxy carbonyl radical (CH_3OCO) — is essential for gaining deeper insight into MF combustion mechanisms. However, because of their relatively large reactivity, no spectroscopic data in the gas phase is available.

In this presentation, we will describe the first high-resolution spectroscopic characterization of the vinyloxy (CH_2OCHO) and methoxy carbonyl (CH_3OCO) radicals performed in the sub-millimeter wave range. These radicals were generated via hydrogen abstraction from MF through collisions with fluorine atoms, and their rotational spectra were recorded using our sub-millimeter frequency multiplication chain spectrometer in combination with the Faraday rotation (FR) modulation technique [5]. The analysis of the CH_2OCHO and CH_3OCO rotational spectra has been performed exploiting results from high-level quantum chemical calculations, in association with graphical tools for spectral assignments (Loomis-Wood plots) and dedicated Hamiltonians to model their rotational structure. While the rotational structure of CH_2OCHO can be modeled using a standard semi-rigid Hamiltonian including spin-rotation coupling, CH_3OCO shows a more complicated internal dynamics where the overall rotation is coupled to the methyl group internal rotation and to the electron spin.

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COLLISIONAL LINE BROADENING FOR (EXO)PLANETARY ATMOSPHERES

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Exoplanet atmospheres are characterized by high fluxes of stellar radiation and elevated temperatures, leading to formation of molecules and molecular ions whose spectroscopic line-shape parameters are very poorly known or simply unavailable. Contrary to typical atmospheric molecules collected in several spectroscopic databases (HITRAN,[1] GEISA,[2] etc.) with their extensive line lists of positions and intensities, "exotic" molecular systems have been specifically addressed solely by the ExoMol database.[3] The question on line-broadening parameters (i.e. pressure-broadened line widths and pressure-induced line shifts) has come into focus of the modern research due to a new generation of high-resolution space missions, since pressure-broadening line-shape parameters were identified as the most important need for experimental and theoretical studies.[4]

Figure 1: ColLine database.

This question has been addressed recently in the framework of the European-Research-Council-funded ExoMol-HD project via a new line-broadening section created in the ExoMol database.[5] Because of “exotic” molecules needed as optically active species and a wide range of required perturbers, we provided as a first step rotationally independent estimates of pressure line-broadening parameters with their temperature dependence for infrared/microwave transitions of 52 absorbers and 12 perturbers (Ar, CH_4, CO, CO_2, H_2, H_2O, He, N_2, NH_3, NO, O_2 and self)[6] with one-value “default values” included in the ExoMol and complete datasets gathered in the specifically created for this purpose ColLine (Collisional Line broadening) database.[7]

In the present work we consider the last updates and extensions of ColLine, focusing at robust theoretical approaches to calculations of rotationally-dependent line-shape parameters over wide temperature ranges. Such data will be essential for developing appropriate database structures, including opacities, k-tables and precomputed atmospheric models.

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[7] https://colline.u-bourgogne.fr/

CARS THERMOMETRY OF BURNED C_2H_4: CALCULATION OF COLLISIONAL BROADENING COEFFICIENTS

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[a] Institut UTINAM - UMR CNRS 6213, Université Marie et Louis Pasteur, Besançon, France

Modern spectroscopic techniques, such as Coherent Anti-Stokes Raman Scattering (CARS) thermometry, provide non-invasive, high-spatial-resolution diagnostics of reactive media. However, their performance depends on the quality of the input spectroscopic data, particularly the collisional line-broadening coefficients.

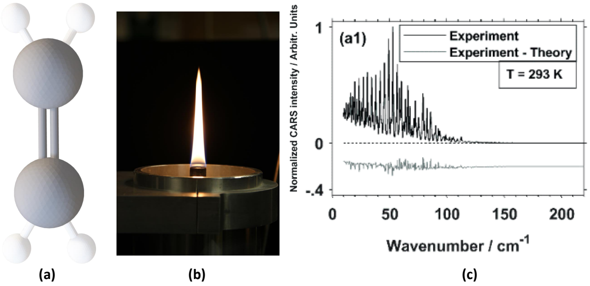

Figure 1: Geometry of C_2H_4 (a), ethylene flame (b), recorded spectrum [3] (c).

Ethylene C_2H_4 is one of the key molecules in combustion diagnostics. However, its asymmetric top structure results in dense and complex spectral signatures, complicating the experimental determination of these coefficients. In this context, theoretical approaches present promising alternatives to the paucity of measurements. The present work focuses on the calculation of broadening coefficients using a semi-empirical method [1]. This approach, being less CPU-expensive than rigorous semi-classical methods typically employed [2], is particularly well-suited for the requirements of high-temperature diagnostics, since it relies on a limited number of experimental measurements available at room temperature to generate extensive data at desired temperatures.

The calculated coefficients are integrated into existing thermometry codes to evaluate their impact on the accuracy of thermal diagnostics [3]. Finally, this study represents an initial step towards more advanced theoretical modeling, aimed at incorporating the effects of line overlapping, a phenomenon particularly pronounced in the C_2H_4 spectra.

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D-III: Contributed Talks

Monday, August 25, 16:30
Hörsaal III

Chair: Jennifer van Wijngaarden

METHYL INTERNAL ROTATION AND NUCLEAR QUADRUPOLE COUPLING EFFECTS IN THE MICROWAVE SPECTRUM OF 1-BROMOPROPENE

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Although bromine-containing organic compounds are relatively scarce in the Earth's atmosphere, accounting for only ≈ 20 ppt of total organic content, they play a significant role in stratospheric ozone depletion, including the formation of the ozone hole and wintertime ozone loss at mid and high northern latitudes.[1] However, few high-resolution spectroscopic studies have been conducted on brominated species, including 1-brompropene, probably due to the inherent complexity of their spectra and the lack of appropriate spectral assignment tools. This complexity arises from the interplay between a large nuclear quadrupole coupling constant associated with the bromine nucleus and the internal rotation of the methyl group.

1-bromopropene exists in two isomer forms, *E* and *Z*. A non-bonded intramolecular interaction between the in-plane methyl hydrogen and the bromine substituent is responsible for the higher stability of the *Z* isomer and the lowering of its methyl torsional barrier compared to the *E* isomer. To date, only the spectrum of the *E* isomer of 1-bromopropene has been reported in the literature.[2] To complete our ongoing investigations on halogenated propene derivatives, we have measured the microwave spectra of both *Z*- and *E*-1-bromopropene, including both the ^{79}Br and ^{81}Br isotopologues, in the 4−20 GHz range using the recently developed Passage And Resonance In Synergy (PARIS) spectrometer.[3] The analysis of bromine hyperfine splittings were more challenging than the chlorine analogous due to the larger nuclear quadrupole coupling constants. The barrier hindering the methyl internal rotation were determined, with the Z isomer exhibiting a significantly lower barrier than the E isomer. Spectral assignments were carried out using a new version of the *XIAM* program,[4] *XIAM-NQ*,[5] which enables an exact treatment of nuclear quadrupole coupling effects. The results were further validated by comparison the A species fit with the *SPFIT* program.[6] A comparative analysis of the methyl torsional barriers in 1-bromopropene and other 1-substituted propene derivatives offers insights into the role of non-bonded intramolecular interactions in shaping the internal dynamics of such systems.[7]

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[7] This research has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skodowska-Curie Grant Agreement No. 872081.

METHYL INTERNAL ROTATION AND NUCLEAR QUADRUPOLE COUPLING EFFECTS IN THE MICROWAVE SPECTRUM OF 2-FLUORO-3-PICOLINE

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Large amplitude motion (LAM) exhibited by methyl groups within isolated molecules constitutes a fundamental phenomenon in molecular physics. The methyl internal rotation is highly sensitive to both steric hindrance and electrostatic effects from the surrounding environment, making the methyl group an effective probe for molecular structures. To investigate this effect, the microwave spectra of 2-fluoro-3-methylpyridine, one of ten isomers of fluoromethylpyridine and a volatile organic compound (VOC) whose volatility and structural properties make it of potential interest in atmospheric processes linked to air quality and climate, was measured in the frequency range from 2 to 20 GHz using the chirp-excitation mode of the Passage And Resonance In Synergy (PARIS) spectrometer.[1] Due to internal rotation of the methyl group, doublets containing an A and an E torsional species were observed for all rotational transitions. Hyperfine structures arising from the nuclear quadrupole coupling of the ^{14}N nucleus were fully resolved. The spectral assignment and modeling were performed using the *XIAM*[2] and the *BELGI* programs,[3] giving a root-mean-square deviation of 3.9 kHz for a data set of 627 lines. The torsional barrier of the methyl group was determined to be 288.0 cm^{-1}.[4]

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A CHLORINE, A NITROGEN, AND A METHYL ROTOR: 2-CHLORO-5-PICOLINE ANALYZED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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The microwave spectroscopic analysis of molecules containing ^{14}N hyperfine splittings and methyl internal rotation is challenging, but the number of studied molecules are steadily increasing, i.a. 2,4-dimethylpyrrole[1] and 4-methyl-2-nitrophenol.[2] Molecules containing two nitrogen atoms and one methyl rotor such as 4-methylpyrimidine[3] and methylimidazoles[4] have also been studied. On the other hand, there are very few analyses containing nuclei with strong quadrupole coupling such as chlorine or bromine in combination with methyl internal rotation, such as 2-fluoro-4-chlorotoluene[5] and 2-chloro-4-fluorotoluene.[6] This is partly due to the difficulties in spectral analysis, but also the lack of programs being able to deal with exact treatment of the strong nuclear quadrupole coupling and internal rotation. In terms of molecules containing two quadrupole coupling nuclei with at least one requiring exact hyperfine treatment, several molecules have been analyzed using *SPFIT*,[7] such as 1,1-dichloro-1-silacyclohex-2-ene[8] and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene.[9] However, none of these molecules contains internal rotation.

We will present the first microwave spectroscopic study on a molecule presenting one chlorine atom, one nitrogen atom, and one low barrier methyl internal rotation, 2-chloro-5-picoline. The spectrum was recorded in the range of 4 to 20 GHz using the PARIS (Passage and Resonance In Synergy) spectrometer.[10] The analysis allowed the assignment of both isotopologues of chlorine, ^{35}Cl and ^{37}Cl, with very satisfactory results. The barrier to internal rotation was determined for both isotopologues to be approximately 96.8 cm^{-1}. The hyperfine splittings arising from the nuclear quadrupole coupling of both the ^{14}N and the ^{35}Cl or ^{37}Cl nuclei were fully resolved. The assignments were performed with the newly modified *XIAM* program, *XIAM-2NQ*.[11,12] The experimentally deduced torsional barriers were compared to those of other picoline derivatives, such as 3-picoline, 2-fluoro-5-picoline, and 2,5-lutidine.

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BROADBAND ROTATIONAL SPECTRUM OF 2,2,3,3,4,4,4-HEPTAFLUORO-1-BUTANOL AND ITS 1:1 COMPLEXES WITH WATER AND HELIUM

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[b] University of the Basque Country (UPV/EHU) and Instituto Biofisika (CSIC-UPV/EHU)

Interest in fluorinated compounds has been growing in recent years because of their presence in the environment resulting from their extensive use in industry [1]. Within this large family of compounds, fluorinated alcohols are particularly interesting due to the simultaneous presence of a polar hydroxyl group and a fluorinated carbon chain. This combination can lead to the presence of intramolecular interactions that drive the conformational stability of these molecules. It also allows for competitive intermolecular interaction sites that act as hydrogen bond donors and acceptors, influencing interactions with other molecules and resulting in distinctive properties in the condensed phase. Understanding the conformational landscape of fluorinated alcohols is essential for predicting their intramolecular hydrogen-bonding patterns and donor/acceptor roles, and for explaining why fluoroalcohols exhibit unique behaviors such as unusual solvent effects [2] and self-assembly tendencies [3].

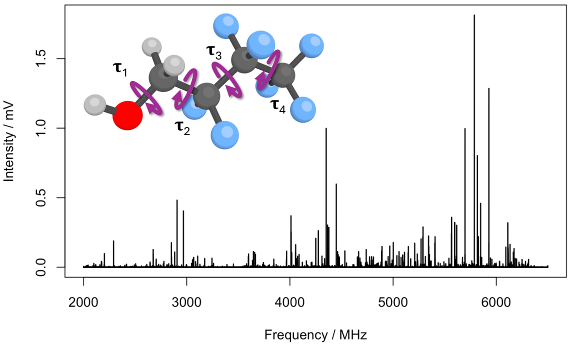

Figure 1: Molecular structure of 2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB) with its rotational spectrum recorded in the 2-6.5 GHz region.

Here we present our preliminary results on the rotational spectroscopy study of 2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB) investigated by chirped-pulse molecular beam Fourier transform microwave spectroscopy (UPV/EHU) coupled with *ab initio* and DFT calculations. Computational results indicate that the conformers of HFB are stable only when the HOCC dihedral angle adopts a *gauche* or *gauche'* orientation. In contrast, *trans* configurations do not correspond to local minima. This behavior differs from what has been observed for 2,2,2-trifluoro-1-ethanol[4] and 2,2,3,3,3-pentafluoro-1-propanol[5], where *trans*-HOCC conformers are high-energy local minima. The rotational spectrum is intense and extremely dense. Seven out of eleven non-equivalent conformers of the monomer have been identified, one of which displays the typical splitting due to the tunnelling motion of the hydroxyl group. For the global minimum conformer, the spectra of the ^{13}C and ^{18}O isotopologues were recorded at natural abundance, allowing the determination of the substitution structure (r_s) of the heavy atom skeleton. Five 1:1 complexes with water have been observed and assigned. The assigned structures involve different conformers of HFB where the hydroxyl group acts as a hydrogen bond donor, and a fluorine atom bound to $C2$ acts as a proton acceptor. Interestingly, also two 1:1 helium complexes have been detected and are currently under characterization.

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2,6-LUTIDINE: OVERCOMING THE CHALLENGE OF TWO EQUIVALENT LOW-BARRIER METHYL INTERNAL ROTATIONS AND ^{14}N QUADRUPOLE COUPLING

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2,6-Lutidine is a molecule featuring two equivalent methyl internal rotors and a ^{14}N nucleus. Each rotational transition splits into a quartet due to methyl internal rotation, corresponding to the torsional species (σ_1,σ_2)=(00), (01), (11) and (12), where σ_1 and σ_2 denote the symmetry of the first and second methyl rotors, respectively. The low barrier to internal rotation introduces significant complexity in spectral analysis. Furthermore, each torsional transition further contains a hyperfine structure due to the nuclear quadrupole coupling of the ^{14}N nucleus. 2,6-lutidine was first analyzed in 1990 by Caminati and Di Bernardo.[1] The work was extended in 1993 by Thomsen and Dreizler, where a total of 165 hyperfine transitions including 69 (00) species lines, 57 (01) species lines, 15 (11) species lines and 24 (12) species lines were assigned.[2] In the present work, we extend and refine these earlier studies using high-resolution microwave spectroscopy combined with quantum chemical calculations.
The rotation spectrum of 2,6-lutinde was recorded between 2 and 20 GHz using the PARIS (Passage And Resonance In Synergy) spectrometer,[3] in both chirp- and tone- (resonator-based) excitation modes. A total of 1628 transitions including 387 (00) species lines, 491 (01) species lines, 341 (11) species lines, and 409 (12) species lines were assigned, analyzed, and fitted using the *XIAM* program.[4] The assignement was checked by separately fitting the four torsional species, each fit achieving measurement accuracy (approximately 4 kHz). The barrier to internal rotation of the two equivalent rotors was determined to be 120 cm^{-1}. The global *XIAM* fit yielded a standard deviation of 3.19 MHz, which was significantly reduced up to 0.0029 MHz (2.9 kHz) using a new version of the program *PAM-C$_{2v}$-2tops*[5] that incorporates a pertubative treatment of the ^{14}N nuclear quadrupole coupling.

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SPECTROSCOPIC QUALITY AND VARIATIONAL VIBRATIONAL STATES OF METHANOL AND ENHANCEMENT OF PARITY-VIOLATING SHIFT IN SUBSTITUTED METHANOLS

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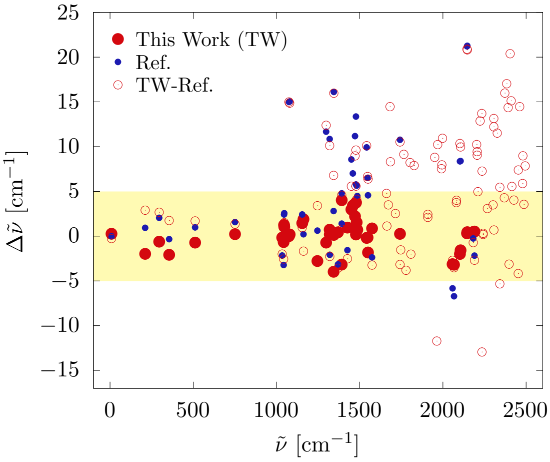

Figure 1: Variational vibrational band origins, computed with the newly developed PES and the GENIUSH-Smolyak program, reproduce experimental data with a difference ($\Delta\tilde{\nu}$) less than ±5 cm^{-1} (TW) [7]. They significantly improve upon earlier results (Ref.) reported in Ref. [1], which were computed with the PES developed in Ref. [5]. The vibrational band origins are referenced to the ZPVE of each computation.

The theoretical prediction of (ro-)vibrational spectra of methanol has been challenging due to the torsional motion of the methyl unit. The harmonic oscillator approximation qualitatively fails to describe torsional motions. We solved the vibrational Schrödinger equation of methanol in full dimensionality on an *ab initio* potential energy surface (PES) [1]. We used the numerical kinetic energy operator approach as implemented in the GENIUSH program [2]. The harmonic oscillator basis functions were employed for the small-amplitude motions (SAMs) and Fourier functions for the torsional degree of freedom. The direct-product basis and integration grid for the SAMs are truncated according to the Smolyak approach [3], which was combined with GENIUSH to tackle systems with several large-amplitude motions [4]. We have converged the vibrational states up to the C-O stretching overtone, 2190 cm^{-1} beyond the zero-point vibrational energy (ZPVE), using the PES of Ref. [5] at the CCSD(T)-F12b/aug-cc-pVDZ level of theory. The maximum theory-experiment deviation was more than 20 cm^{-1}. The limitation of the accuracy was suspected to be due to the imperfections in the underlying PES, because the vibrational energies were converged within 2 cm^{-1} in the variational vibrational procedure [1]. We developed a new PES at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory and fitted it with the permutationally invariant polynomial (PIP) approach. The geometry set for the PES was generated with the Robosurfer code [6], which follows an active-learning approach. The computed vibrational energies agree within 5 cm^{-1} with the available experimental energies up to the C-O stretching overtone and nearby combination bands as shown in Figure 1 [7]. The maximum error of the combination bands decreased from 21.3 cm^{-1} [1] to 3.2 cm^{-1} [7]. This result is an important milestone towards the rovibrational computations of methanol and its substituted derivatives; in the latter case, a substantial enhancement of the parity-violating frequency shift has been reported [8].

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E: Plenary

Tuesday, August 26, 9:00
Hörsaal I

Chair: Wolfgang Jäger

EXPLORING CONFORMATIONS AND NON-COVALENT INTERACTIONS IN COMPLEX MOLECULAR SYSTEMS WITH ROTATIONAL SPECTROSCOPY

S. Melandri[a]

[a] University of Bologna, Department of Chemistry "G. Ciamician", via Gobetti, 85 40129 Bologna, Italy

Flexibility in molecular systems gives rise to complex conformational potential energy surfaces influenced by the presence of internal degrees of freedom and different non-covalent interactions occurring within the molecules or with their surroundings. The study of molecules and small molecular complexes in isolation allows insight into the intrinsic molecular properties, their changes upon complexation and the interaction process at the molecular level, bridging the gap between gas-phase and bulk properties. Accurate data on structures, energies, and dynamics of complex organic molecules and small molecular complexes can be obtained by rotational spectroscopy performed under the cold isolated conditions of a free jet expansions and these properties can be directly compared to the results of accurate quantum-mechanical calculations obtained under the same isolated conditions. Important questions which can be addressed regard, the binding sites, the kind of established interactions, the conformational and energetic changes caused by the interactions and finally the driving forces of the interactions and how they can be influenced, for example by the substituents. Through chosen results on flexible organic molecules and molecular complexes formed in supersonic expansions and characterized by rotational spectroscopy, we will show how non-covalent interactions (hydrogen bonds, halogen bonds, lp-π-hole interactions . . .) compete to shape the conformational potential energy surface of the molecular systems and determine their shapes and dynamics. We also show how these interactions can be drastically changed through substitution (in particular, with halogen atoms) or complexation with solvent molecules.

COLLISIONAL EXCITATION OF MOLECULES IN ASTROPHYSICAL ENVIRONMENTS: RECENT ADVANCES AND CHALLENGES

J. Loreau[a]

[a] KU Leuven, Department of Chemistry (Leuven, Belgium)

Molecular spectroscopy is extensively used to probe the physics and chemistry of astrophysical environments. The observed spectra often show significant deviations from the local thermodynamic equilibrium assumption, and their complete interpretation thus requires an understanding of the collisional excitation of molecules by the background gas mainly composed of He atoms and H_2 molecules. However, the collisional properties of many molecules observed in astrophysical environments remain unknown due to the complexity of the underlying calculations and measurements, coupled with the rapid increase in the number of detected species.

In this talk I will review some recent developments in the field of molecular collisions and discuss the current theoretical and computational challenges. I will illustrate these through several examples ranging from the rotational excitation of complex organic molecules, including aromatic species, to the ro-vibrational excitation of small molecules and ions induced by collisions with He or H_2. I will also discuss the impact of these collisional data on the interpretation of observations for various environments such as the interstellar medium, protoplanetary disks, comets, or the circumstellar envelope of evolved stars.

F-I: Contributed Talks

Tuesday, August 26, 11:00
Hörsaal I

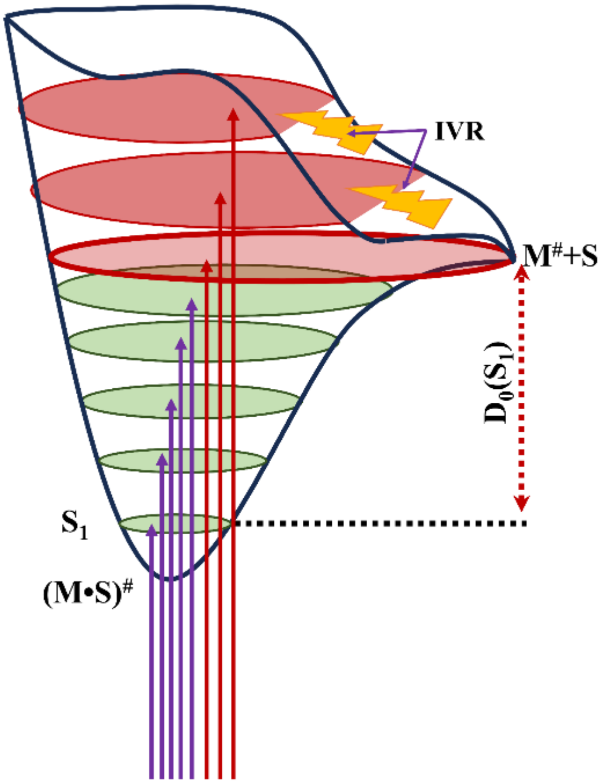
Chair: Lucile Rutkowski

LASER SPECTROSCOPIC INVESTIGATION OF DESORPTION ENERGY OF CO_2 FROM THE DISPERSION-DOMINATED CO_2 COMPLEXES: ROLE OF N-SUBSTITUTION AND -OH FUNCTIONAL GROUP COLLISIONAL LINE BROADENING FOR (EXO)PLANETARY ATMOSPHERES

Muhammed Shabeeb Surajit Maity

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy,
PIN-502285, India

We have developed a versatile spectroscopic methodology to accurately measure the desorption energy of adsorbate molecules from the aromatic surface of adsorbents. Here, naphthalene (Np), naphthol (NpOH), and 2-(2' pyridyl) benzimidazole (PBI) were used as the aromatic surfaces and the dispersion-dominated Np-CO2, NpOH-CO2, and PBI-CO2 complexes are isolated in the gas phase were used to demonstrate methodology. The complexes were characterized using resonant two-photon ionization (R2PI) spectroscopy and UV-UV hole-burning spectroscopy. The disappearance of Franck-Condon active intramolecular vibrational modes in the R2PI spectra and of the complexes was utilized to determine the desorption energies. The formation of multiple isomers was verified using UV-UV and IR-UV hole-burning spectroscopy. The study revealed higher desorption energies in the excited state of the complex than those measured in the ground state, which implied an efficient adsorption process upon UV irradiation of the system. Additionally, a substitution of an N atom in the aromatic ring can enhance the adsorption efficiency rather than the incorporation of an electron-withdrawing functional group.



HIGH-RESOLUTION VIBRATION-ROTATIONAL SPECTRA AND ABSOLUTE LINE STRENGTHS OF HO_2 RADICAL IN THE ν_1, ν_2 AND ν_3 FUNDAMENTAL BANDS

P.-L. Luo[a], I-Y. Chen[a], and C.-W. Chang[a]

[a] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

The hydroperoxyl radical (HO_2) plays a critical role in atmospheric chemistry, and its spectroscopic characterization is essential for both laboratory kinetic studies and field observations. Herein, we report high-resolution spectral measurements and absolute line strength determinations of the HO_2 radical using mid-infrared time-resolved dual-comb spectroscopy.[1][2][3] By simultaneously probing the byproduct HCl near 3.3 μm and the HO_2 radical near 7.1 or 8.9 μm in the $Cl_2/CH_3OH/O_2$ flash photolysis system, the absolute line intensities of the HO_2 ν_2 or ν_3 fundamental transitions could be accurately determined by referencing the well-known line strength of HCl. In addition, the line intensities of the HO_2 ν_1 transitions near 2.9 μm were determined relative to the measured line intensities of the HO_2 ν_2 or ν_3 transitions. Broadband high-resolution spectra were also recorded to further derive the vibration–rotational parameters of HO_2 and estimate the strengths of its fundamental bands. Based on high-resolution spectral analysis, the HO_2 band strengths were determined with uncertainties of 5–8% and compared with previous experimental and theoretical results. Our work provides precise experimental data to support the refinement of HO_2 spectral databases and to validate computational methods for improving the prediction of infrared intensities of radical vibrational bands.

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INFRARED SPECTRA OF ACETALDEHYDE AND ITS AGGREGATES IN HELIUM NANODROPLETS

R. Hamidi Mejlej[a], S. Parshotam[a], W. Jäger[a] and Y. Xu[a]

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We have recently incorporated an electrospray ionization (ESI) source and an ion trap into our existing helium nanodroplet isolation (HENDI) spectrometer[1] to enable study of a broad range of chemical species. HENDI spectroscopy provides a weakly perturbative, ultracold matrix and offers noticeable advantages[2] over conventional cold matrix isolation techniques. Acetaldehyde (CH_3CHO) was selected as a test molecule to verify the performance of the HENDI setup.

Acetaldehyde is commonly found in cigarette smoke, industrial emissions, and the atmosphere, and is also a well-known interstellar molecule. Although its rotational spectrum has been extensively studied, its infrared spectrum was only recently investigated using matrix isolation spectroscopy[3], with tentative band assignments. In our experiments, by varying the acetaldehyde pressure in the pick-up chamber, we recorded infrared spectra of the acetaldehyde monomer, dimer, and larger aggregates in superfluid helium nanodroplets. Two continuous-wave (CW) optical parametric oscillator (OPO) lasers were used to probe the CH and OH stretching regions. More infrared bands were observed than in the previous matrix study within the same frequency region. Using Poisson plots, we identified mass peaks corresponding to the monomer, dimer, and larger aggregates, and recorded the corresponding mass-selected infrared spectra. To aid spectral assignment, conformational searches and DFT calculations at the B3LYP-D3(BJ)/def2-TZVP level of theory were carried out for the acetaldehyde monomer, dimer and trimer. We present our ongoing assignments and discuss the preferred conformations of each acetaldehyde cluster and the associated non-covalent interactions.

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TWO-DIMENSIONAL FLUORESCENCE AND MASS-SELECTIVE SPECTROSCOPY OF SMALL SILICON CARBIDES: SiC_2, l-SiCCSi, AND c-SiC_6H_4

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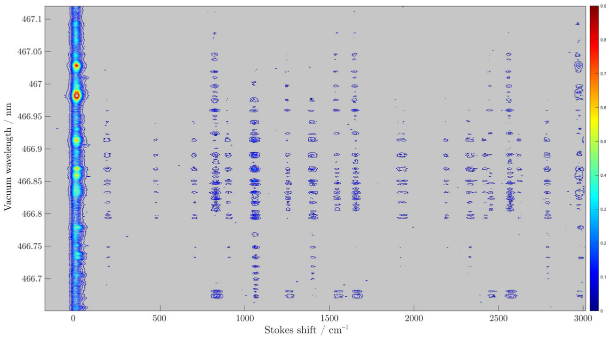

Figure 1: Excitation/emission spectrum of the $2^2_0 3^1_0$ and $2^1_0 3^2_0$ Merrill-Sanford bands of SiC_2

We present recent results from an on-going optical investigation of small silicon carbides using resonant two-colour two-photon ionization (R2C2PI) and two-dimensional (excitation/emission) laser-induced fluorescence with intensified array detection (2DF). Measurement of the $\tilde{A}\,^1B_2 \leftarrow \tilde{X}\,^1A_1$ Merrill-Sanford bands of SiC_2 by 2DF exposes several complex features that have been overlooked or have escaped discovery in previous fluorescence and mass-resolved studies (an example of the possibly Coriolis-coupled $2^2 3^1$ and $2^1 3^2$ levels, distinguished by a-type (respectively, b-type) excitation profiles and emission to odd (respectively, even) quanta of the ν_3 pin-wheel mode is shown in Fig. 1). A pronounced J-dependence of the $\tilde{A}$-state lifetime for higher vibronic levels is tentatively ascribed to a triplet state interaction. For l-SiCCSi, a thorough analysis of its $\tilde{C}\,\Sigma_u^- \leftarrow \tilde{X}\,\Sigma_g^-$ transition from single-vibronic-level emission spectra is described. The change in the Si-C bond length and rotational constant that we infer by fitting Franck-Condon activity in ν_2 (the Si-C stretch) is in excellent agreement with a previous rotationally resolved study[1] (both yielding $B'/B'' = 0.966$) but departs significantly from theory ($B'/B'' = 0.942$), as does the observed $\tilde{C}$-state ν_2 frequency ($348\,\mathrm{cm}^{-1}$ *vs.* $434\,\mathrm{cm}^{-1}$ calc.). Measurement of the same electronic transition using 193 nm radiation (6.42 eV) for ionization results in remarkably different relative intensities for the same spectral features in comparison with LIF and near-threshold R2C2PI, as well as a relative insensitivity to the delay between resonant and ionizing photons. This difference is reconciled in terms of internal conversion from the $\tilde{C}$-state to vibrationally hot levels of lower electronic states that lie ~ 6.3 eV below the cation vibrationless level, thereby admitting favorable overlap with similarly vibrationally excited levels of the cation at 193 nm and presenting an unusual example of an action spectrum revealing features that a direct absorption spectrum would not. It is suggested that the preponderance of the tropyl motif in IR-UV depletion experiments of reactive hydrocarbon mixtures may have a similar explanation. Results for other reactive $Si_nC_mH_x$ species including SiC_6H_4 will be discussed if time permits.

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THE R-INDEX METRIC FOR EVALUATING OAM CONTENT AND MODE PURITY IN OPTICAL FIELDS

Monika Bahl[a], Georgios M. Koutentakis[b], Mikhail Maslov[b], Tom Jungnickel[a], Timo Gassen[a] and Oliver H. Heckl[a]

[a] Optical Metrology Group, Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria
[b] Institute of Science and Technology Austria (ISTA), Am Campus 1, 3400 Klosterneuburg, Austria

Light fields can carry orbital angular momentum (OAM), enabling rotational motion through light-matter interactions. Manipulating this momentum has driven major technological advances [1]. Recent work by Maslov et al. on OAM interactions with molecules has renewed interest in using spectroscopy to observe otherwise forbidden transitions [2]. We aim to identify optical fields with optimal OAM that could induce quadrupole transitions in cold molecules. This work introduces the R-index, a novel metric that quantifies the intrinsic canonical energy or OAM content in optical fields. The index is also used to assess the purity of a field, offering insight into the fidelity and robustness of OAM generation.

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HIGH-RESOLUTION TWO-PHOTON DOPPLER-FREE UV SPECTROSCOPY OF XENON WITH DIRECT MEASUREMENT OF THE AC-STARK SHIFT

M. H. Rayment, R. Stech, and F. Merkt

Institute for Molecular Physical Science, ETH Zürich, 8093 Zürich, Switzerland

One of the main systematic uncertainties in Doppler-free two-photon laser spectroscopy, and more generally in multiphoton spectroscopy, arises from the AC-Stark shift induced by the laser intensities required to drive the transitions. Here, we present a technique for performing precision Doppler-free two-photon UV spectroscopy with direct measurement of the AC Stark shift. This was achieved using the frequency-upconverted output of long-pulse-length narrow-bandwidth (FWHM $\sim$ 15 MHz) Ti:Sa bow-tie amplifiers,[1] that exhibits large shot-to-shot pulse-energy fluctuations. A single-shot detection method was used to simultaneously but separately record spectra over the entire range of laser intensities. This method was demonstrated by performing (2+1) REMPI spectroscopy of the $(5p)^6\,{}^1S_0 \rightarrow (5p)^5\,6p\,[1/2]_0$ transition in Xe, with uncertainties of down to ~ 0.7 MHz achieved for transition wavenumbers around 80118.9 cm^{-1}. These measurements, when combined with recent precision[2−4] and historic[5−11] data, allowed for a new determination of the isotopic-abundance-weighted first ionisation wavenumber of Xe, which was found to be 97833.7644(14) cm^{-1}. This new value resolves the ~ 1 GHz discrepancy of recent measurements from the metastable $(5p)^5 6s\,[3/2]_2$ state with the previously determined ionisation limit.[2]

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F-II: Contributed Talks

Tuesday, August 26, 11:00
Hörsaal II

Chair: Stefan Willitsch

PRECISION TIME-DOMAIN SPECTROSCOPY OF THE 12.2 GHz MASER TRANSITION IN METHANOL

S. Collignon[a], B. M. Hays[b], D. Lederer[c], M. Daman[a] and C. Lauzin[a]

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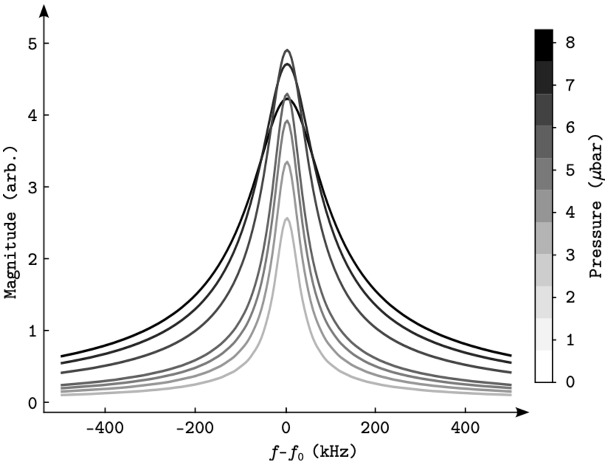

Figure 1: Fourier transform of the 12.2 GHz methanol free induction decay captured at various pressures.

The relative precision $\delta\nu/\nu$ achieved in the near-infrared region today reaches the 10^{-12} level [1,2], whereas the state of the art in coherent-emission microwave spectroscopy remains several orders of magnitude lower, around 10^{-6}. Here, we aim to surpass this limit through time-domain analysis of the $2_0\ E \leftarrow 3_{-1}\ E$ torsion-rotation transition of methanol. Located at approximately 12.2 GHz, this transition is responsible for the second brightest class II maser emission observed in the interstellar medium [3]. Accurate laboratory determination of its rest frequency is critical for using this line to probe physical quantities near stellar objects, such as magnetic fields [4] or variations in the proton-to-electron mass ratio [5]. Measurements were performed using a new experimental setup combining a Ku-band waveguide cell with a Fourier-transform microwave spectrometer. Methanol molecules were maintained in the gas phase at pressures between 0.8 μbar and 8 μbar and probed within the waveguide cell. The spectrometer offers a high signal-to-noise ratio through the acquisition and averaging of large numbers of free induction decays (FIDs). The line center of the $2_0\ E \leftarrow 3_{-1}\ E$ transition is extracted via least-squares fitting of the FID using a time-domain, speed-dependent Voigt profile [6,7]. Comparisons with alternative line-shape models are presented. Full automation of the setup enables statistical analysis of the line center and investigation of systematic experimental effects. In particular, we assess the impact of unresolved hyperfine structure on the measured rest frequency. The final value of the line center and its associated uncertainties are reported.

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PRECISION MEASUREMENTS IN THE MOLECULAR HYDROGEN IONS FROM RYDBERG-STATE SPECTROSCOPY

I. Doran[a], L. Jeckel[a], M. Beyer[b], Ch. Jungen[c], and F. Merkt[a]

[a] Institute of Molecular Physical Science, ETH Zürich, Switzerland
[b] Department of Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands
[c] Université Paris-Saclay, Centre National de la Recherche Scientifique, Laboratoire Aimé Cotton, Orsay, France

Precision measurements of spin-rovibrational energies in molecular hydrogen ions provide access to fundamental constants such as the proton-to-electron mass ratio or the proton charge radius, by comparison with theoretical results [1]. These ionic energy intervals can be determined precisely by Rydberg-series extrapolation [2] of series converging to different spin-rovibrational states in the ion. Measurements of Rydberg-Stark manifolds at varying electric field strengths and comparison with precise calculations of the field-induced Stark shifts [3] enable the determination of the zero-quantum-defect positions $-R_{\mathrm{H}_2}/n^2$, which yield precise ionization thresholds. The use of this procedure has recently been demonstrated in determining the fundamental vibrational interval of H_2^+ with sub-MHz uncertainty [4].

This contribution focuses on the extension of the zero-quantum-defect method to molecular hydrogen ions which have a fine or hyperfine structure. We present precision measurements and calculations of Stark manifolds in Rydberg states of molecular hydrogen including interactions involving the rotational angular momentum and the nuclear spin of the ion. Focusing on the spin-rotation splitting in para-H_2^+ $(v^+ = 1, N^+ = 2, I = 0)$ and the hyperfine splitting in ortho-D_2^+ $(v^+ = 1, N^+ = 0, I = 0, 2)$, we show that these calculations accurately describe the experimentally measured Rydberg-Stark manifolds quantitatively. Finally, the comparison between experiment and calculations is used to determine the hyperfine splitting in ortho-D_2^+ with an uncertainty in the low-kHz range.

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ULTRA-PRECISE LINE-INTENSITY RATIOS REDEFINING PRIMARY OPTICAL THERMOMETRY WITH PARTS-PER-MILLION ACCURACY

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Accurate quantification of molecular transition intensities remains a critical challenge in quantum chemistry and metrology, with conventional approaches for diatomic systems historically constrained to 0.1% uncertainty. We present a paradigm-shifting methodology employing dual-wavelength cavity mode dispersion spectroscopy, achieving relative intensity ratio determinations with 0.003% statistical uncertainty – a two-order-of-magnitude improvement over absolute intensity benchmarks. This advancement exposes systematic discrepancies of 0.02% between experimental data and state-of-the-art *ab initio* calculations, directly implicating higher-order electron correlation effects in dipole moment curve perturbations. Applied to line-intensity ratio thermometry (LRT), our technique establishes gas temperature determinations with 0.5 mK statistical uncertainty, surpassing prior LRT precision by two orders of magnitude. The methodology enables SI-traceable metrology for combustion diagnostics and isotopic analyses. Observed deviations in transition probability ratios challenge existing theoretical frameworks to further refine computational models. By establishing intensity ratios as a new benchmark for molecular spectroscopy, this work bridges the gap between experimental observables and first-principles predictions while advancing optical gas metrology into the sub-10-ppm precision regime.

ACCESSING ALL VIBRATIONALLY EXCITED STATES OF THE $X^+\ {}^2\Sigma_u^+$ ELECTRONIC GROUND STATE OF He_2^+

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Precise spectroscopic measurements in small molecular systems such as He_2 and He_2^+ are of interest as benchmarks for high-accuracy *ab-initio* quantum-chemical calculations in few-electron molecules[1,2,3]. In the case of He_2^+, only the lowest ($v^+ = 0-2$)[4,5] and highest ($v^+ = 22-23$)[6] vibrational levels of the $X^+\ {}^2\Sigma_u^+$ electronic ground state have been characterized experimentally.

We describe methods to access and study all vibrational states of He_2^+ $X^+\ {}^2\Sigma_u^+$ from $v^+ = 0$ to $v^+ = 19$ using a multi-steps excitation scheme. The approach involves the production of a supersonic beam of He_2 in the long-lived metastable a ${}^3\Sigma_u^+(v = 0-3)$ states using a cryogenic pulsed valve coupled to an electric discharge.[7] A pulsed laser promotes the system to a selected excited rovibrational level of the c ${}^3\Sigma_g^+$ electronic state with v' and N' in the range $3-4$ and $0-18$, respectively. These states either decay radiatively to vibrationally excited levels of the a ${}^3\Sigma_u^+$ state or by quantum mechanical tunneling through a barrier in the c-state potential. A second laser is then employed to induce transitions from these vibrationally excited a ${}^3\Sigma_u^+(v)$ metastable states to vibrationally excited He_2^+ $X^+\ {}^2\Sigma_u^+(v^+)$ states with $v^+ \leq 5$. High-resolution photoelectron spectra of these ionizing transitions are recorded using the technique of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. To study even higher vibrational levels of He_2^+, the second laser is used to directly photoionize the selected intermediate c ${}^3\Sigma_g^+(v', N')$ states and record PFI-ZEKE photoelectron spectra of the $X^+\ {}^2\Sigma_u^+(v^+, N^+)$ levels. With these excitation schemes, spectra of $X^+\ {}^2\Sigma_u^+(v^+, N^+)$ rovibrational levels of He_2^+ could be measured for the first time up to the $v^+ = 19$ rovibrational level.

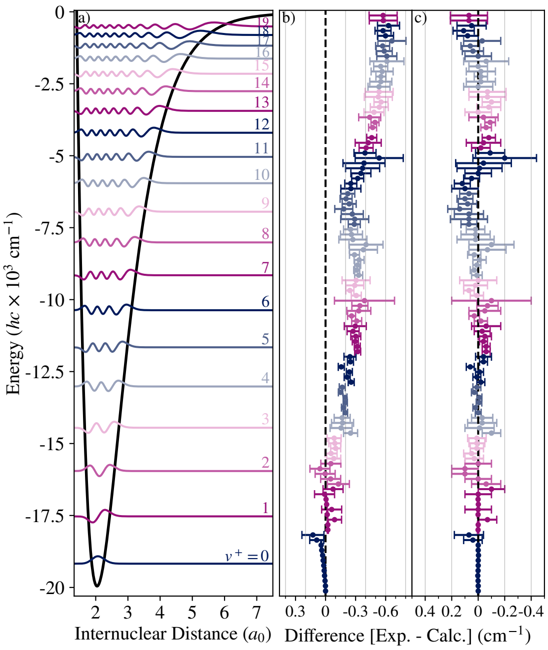

Figure 1: (a) Energy-level diagram of all $X^+\ {}^2\Sigma_u^+(v^+, N^+ = 1)$ levels of He_2^+. (b)-(c) Experimental minus calculated term values: (b) *ab initio*[2], (c) empirical potential (this work).

These new results will be compared with the predictions of *ab-initio* quantum-chemical calculations and are used to determine an empirical potential-energy function for the $X^+\ {}^2\Sigma_u^+$ ground electronic state of He_2^+ that reproduces all experimental data within their experimental uncertainties.

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PROBING FUNDAMENTAL CONSTANTS AND TESTING QED THEORY OF MOLECULES THROUGH HIGH-PRECISION SPECTROSCOPY OF MOLECULAR HYDROGEN IONS

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Molecular hydrogen ions (MHIs) are the simplest molecules. They offer unique opportunities to probe fundamental physics: determination of fundamental constants (FCs), searches for physics beyond the Standard Model, and precision tests of CPT invariance [1]. Among the MHIs, the heteronuclear species HD^+ has been the most extensively investigated, yielding highly precise values of rovibrational and rotational transitions. In general, the measured transition frequencies have shown agreement with ab initio theoretical predictions [2].

We have recently extended high-precision spectroscopy of MHIs to the homonuclear H_2^+, which presents experimental challenges due to the absence of electric-dipole transitions. We have overcome this difficulty by successfully measuring an electric-quadrupole transition. This represents the first demonstration of Doppler-free rovibrational laser spectroscopy in H_2^+ [3]. We resolved the spin structure of a first-overtone transition, which enabled the determination of a spin Hamiltonian coefficient with an uncertainty of 150 Hz, improving on values that have remained unchanged for over five decades [4]. From the resolved spin structure we extracted the spin-averaged transition frequency, and by combining with theoretical calculations, we obtained an independent determination of m_p/m_e. It is consistent with the CODATA 2022 value, and has comparable uncertainty [5]. Our experiment lays the foundation for future tests of CPT symmetry via comparisons of rovibrational transitions in H_2^+ and anti-H_2^+ [6] [7].

Complementary to this, we are reinvestigating the hyperfine structure of HD^+, where some experimental-theoretical discrepancies appear to exist [8]. Here, we present recent progress in accurately determining the hyperfine structure of HD^+ in the rovibrational ground state and compare with theory.

A long-term perspective in the field is the determination of the set m_p/m_e, m_d/m_e, m_d/m_e, and the triton charge radius with 100-fold reduced uncertainty compared to CODATA 2022 [9]. Using a model calculation, we have shown that this should be possible by measuring a moderately large set of transitions (e.g. 10) on at least 5 of the 6 isotopologues, all with 1-Hz-level experimental uncertainties. New theoretical computations are required, but they do not appear to pose fundamental challenges. In addition, using only data from electronic systems, the proton and deuteron charge radii should become accessible with uncertainties competitive to the results from muonic H/D. This would enable a test of lepton universality.

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QUANTUM-LOGIC SPECTROSCOPY OF FORBIDDEN ROVIBRATIONAL TRANSITIONS IN SINGLE MOLECULAR IONS

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Ultranarrow, electric-dipole forbidden transitions between rovibrational states in molecules and molecular ions with expected natural linewidths on the Hz level present intriguing opportunities for the development of highly precise mid-infrared frequency standards and for the exploration of fundamental physical problems such as possible time variations of fundamental constants.[1] The molecular nitrogen ion N_2^+ has been proposed as an attractive system for precision molecular spectroscopy because, as an apolar diatomic ion, it features small systematic shifts and transitions with low sensitivity to magnetic fields in its electronic ground state.[2,3] However, the experimental detection of pure rovibrational transitions in systems like N_2^+ and their precision spectroscopy is challenging on several levels.[4] Besides the weak line strengths, which require highly sensitive detection methods, the positions of the lines are usually known only with substantial uncertainties based on spectroscopic constants determined through indirect methods. Moreover, theoretical predictions of the line strengths are also affected by significant uncertainties.

Here, we report the first observation of electric-quadrupole rovibrational transitions in single molecular ions using a highly sensitive quantum-logic detection protocol.[5] We studied individual hyperfine-Zeeman components of the $|v=1, N=2\rangle \leftarrow |v=0, N=0\rangle$ rovibrational transition in the $X^2\Sigma_g^+$ electronic ground state of single N_2^+ ions confined in a radiofrequency ion trap with a co-trapped Ca^+ ion used for sympathetic laser cooling and quantum-logic state detection. The transitions were directly driven by rapid adiabatic passage using a frequency-chirped laser pulse from a mid-infrared quantum cascade laser. This approach enabled the effective, fully reversible transfer of the rovibrational populations even without precise knowledge of the transition frequencies and at the same time allowed the recycling of the same single molecule in sequential spectroscopic experiments. Thus, line positions could be detected with a 2 MHz uncertainty limited by the frequency sweep of the laser pulse. The present approach represents a powerful methodology for coherently manipulating single molecules on ultranarrow spectroscopic transitions for precision measurements and quantum technologies applications. It can readily be adapted for other diatomic and polyatomic species, provided suitable laser sources for excitation and quantum-logic detection of transitions are available.

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F-III: Contributed Talks

Tuesday, August 26, 11:00
Hörsaal III

Chair: Iouli Gordon

MACHINE LEARNING PRESSURE BROADENING PARAMETERS FOR EXOPLANETARY STUDIES

E. R. Guest, J. Tennyson, and S. N. Yurchenko

University College London

Correct pressure broadening is essential for modelling radiative transfer in atmospheres, however data are lacking for the many exotic molecules expected in exoplanetary atmospheres. Here we explore modern Machine Learning methods to mass produce pressure broadening parameters for the molecules in the ExoMol database.

In this work, Large Language Models were tested for use in collecting large volumes of published literature data. Machine Learning models were used to fit to existing literature pressure broadening data. A computationally cheap method was developed for large-scale production of pressure broadening parameters between unseen molecule-perturber pairs. This method was used to augment the previously insufficient ExoMol line broadening diet, giving the ExoMol database a full and more accurate treatment of line broadening.

AIR-PERTURBED OXYGEN B-BAND LINE-SHAPE PARAMETERS FOR THE HITRAN2024 DATABASE

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The oxygen molecule plays a key role in atmospheric spectroscopy. It is used to determine pressure and temperature profile, as well as total air column density[1] as its content is constant, independent of the altitude. Thus, the accuracy of reference oxygen line-shape parameters is crucial, and it affects remote sensing applications such as the determination of greenhouse gases and air pollutants concentrations, as well as energy transfer dynamics investigations. The B band $\left(b^1\Sigma_g^+\,(v=1) - X^3\Sigma_g^-\,(v=0)\right)$, centered in the spectral range near 690 nm, is the second strongest atmospheric band of the O_2 molecule and it is approximately 15 times weaker than the strongest A band. For that reason it is significantly less saturated on atmospheric path lengths, thus being convenient for use in satellite measurements. It is already being used for example by EPIC-DISCOVR and ESA Sentinel 5&5P instruments.

Relatively low line intensities in the B band caused that, until recently, there were no accurate line-shape parameters available for the air-broadened lines. The first high-resolution and high signal-to-noise-ratio measurements were only recently performed and analyzed with speed-dependent Nelkin-Ghatak profile. Measurements performed in the range of pressures and temperatures for limited number of lines resulted in first beyond Voigt line-shape parameters set and enabled also to determine temperature dependencies of the parameters for the B band[2].

Here we present J''-dependence modeled for all lines from the measured range[3], where J'' is the total angular momentum quantum number for the lower state. That dataset can be extended towards higher J''-lines based on the A-band trend. That data will be included in the 2024 edition of the HITRAN database[4]. In case of some of the parameters we find that the dependence varies between P and R branches, and sometimes it is different also for different subbranches, like for the a_s, a dimensionless parameter for the speed dependence of the collisional line shift, see Fig. 1.

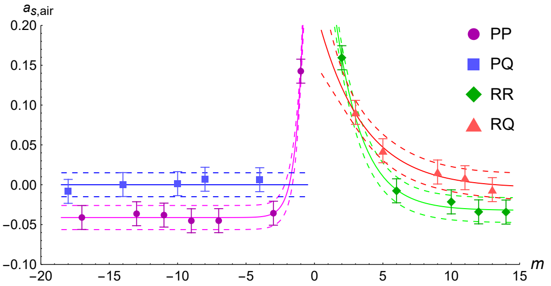

Figure 1: The speed dependence of the collisional shift, a_s, different for each subbranch, versus line index, m. $m = -J''$ for P branch, $m = J'' + 1$ for R branch. Points show measured values, solid lines show functional dependencies and dashed lines show limits of their standard uncertainty.

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SPECTROSCOPY OF TRITIATED WATER SPECIES: NEW RESULTS ON THE $\nu_2 + \nu_3$ AND $\nu_1 + 2\nu_2$ BANDS OF HTO AND THE ν_3 BAND OF DTO

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Tritiated water species, such as HTO and DTO, are of high relevance in environmental monitoring, fusion research, and quantum theory of molecules. However, their infrared spectroscopic characterisation remains incomplete, especially in the mid-IR.

To expand the data base for these isotopologues, we developed two tritiated water vapour samples with a total activity of 1 and 10 GBq [1] from which high-resolution FTIR spectra ranging from 2450 to 6440 cm^{-1} have been obtained. Analysis of these spectra previously delivered high-precise line lists of HT^{16}O, DT^{16}O and T$_2^{16}$O with a total number of 5177 lines and precision up to 5.6×10^{-5} cm^{-1} including its acquisition and validation [2,3,4,5].

This talk presents new high-resolution FTIR results that significantly extend the known line lists for the $\nu_2 + \nu_3$ and $\nu_1 + 2\nu_2$ bands of HTO and the ν_3 band of DTO. Also, for the first time, a set of DTO transitions between vibrationally excited states will be presented. The increased number of lines assigned provides an improved experimental basis for line list generation and potential refinement of the potential energy surface.

In addition, the next steps of the research programme will be outlined: the establishment of a systematic measurement campaign using a newly acquired FTIR setup within the within the radiation-supervised tritium laboratory of KIT, and a collaboration with a theoretical group to model the spectra. Together, these developments aim to advance our understanding and spectroscopic description of tritiated species.

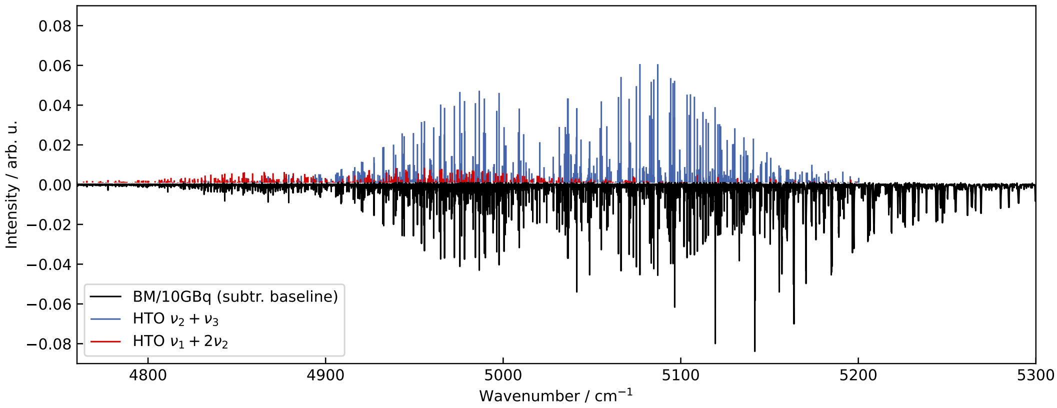

Figure 1: Visualization of the assigned lines of HTO from the $\nu_2 + \nu_3$ and $\nu_1 + 2\nu_2$ band and the baseline-subtracted FTIR spectrum

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LINE POSITIONS AND INTENSITIES OF THE SILANE MOLECULE (SiH_4) FOR ITS FUNDAMENTAL BANDS AND SOME COMBINATION AND OVERTONES

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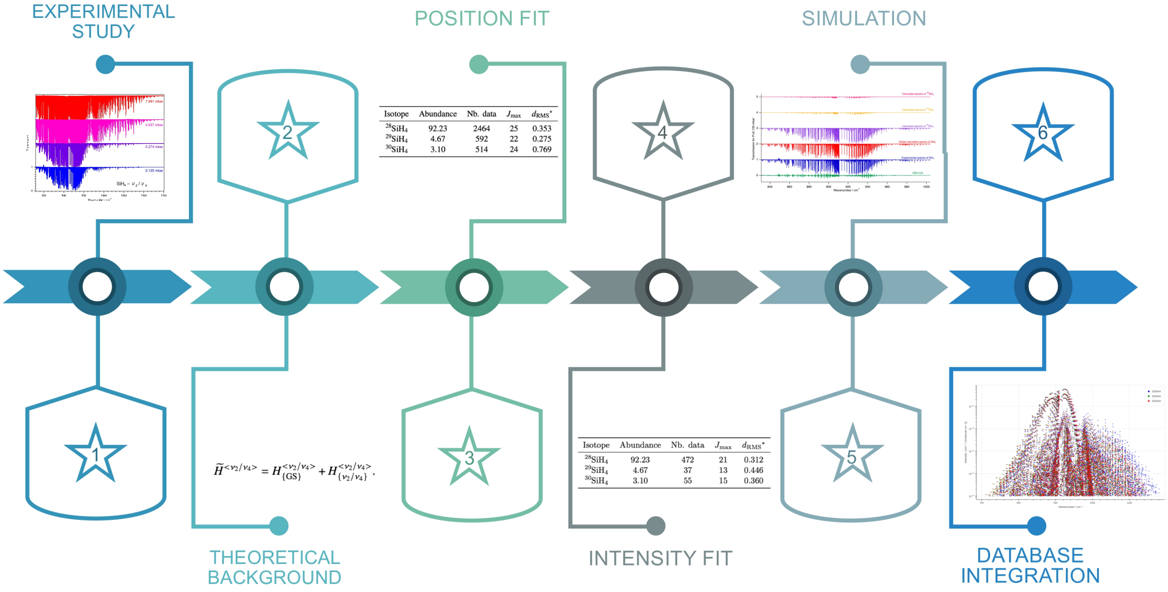
In the context of quantum computer development, silicon ^{28}Si is essential for ensuring sufficient coherence time of qubits. Laser separation of ^{28}Si using a supersonic cold molecular jet is being considered with SiH4. To initiate this study, we have chosen to work on the silane molecule SiH_4 and 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.

The first results concerning the initial dyad ν_2/ν_4 are included in the new SiCaSDa database[1] at the link: `https://vamdc.icb.cnrs.fr/PHP/SiH4.php`. 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.



Isotope	Abundance	Nb. data	$J_{\max}$	$d_{\mathrm{RMS}}{}^*$
$^{28}SiH_4$	92.23	2464	25	0.353
$^{29}SiH_4$	4.67	592	22	0.275
$^{30}SiH_4$	3.10	514	24	0.769

$$\widetilde{H}^{<\nu_2/\nu_4>} = H^{<\nu_2/\nu_4>}_{\{\mathrm{GS}\}} + H^{<\nu_2/\nu_4>}_{\{\nu_2/\nu_4\}}.$$

Isotope	Abundance	Nb. data	$J_{\max}$	$d_{\mathrm{RMS}}{}^*$
$^{28}SiH_4$	92.23	472	21	0.312
$^{29}SiH_4$	4.67	37	13	0.446
$^{30}SiH_4$	3.10	55	15	0.360

Figure 1: Methodology used for spectra analysis[2].

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

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Parameters associated with the collisional perturbation of spectral lines are essential for modeling the absorption of electromagnetic radiation in gas media. The HITRAN molecular spectroscopic database provides these parameters, although originally they were associated only with the Voigt profile parameterization. However, in the HITRAN2016 and HITRAN2020 editions, Voigt, speed-dependent Voigt and Hartmann-Tran (HT)[1] profiles have been incorporated, thanks to the new relational structure of the database. The HT profile was introduced in HITRAN in 2016 as a recommended profile for the most accurate spectral interpretations and modeling. It was parameterized with a four-range temperature dependence. Since then, however, some features of the HT profile were revealed to be problematic from a practical perspective[2]. These are: the singular behavior of the temperature dependencies of the velocity-changing parameters when the shift parameter crosses zero and the difficulty in evaluating the former for mixtures. In this talk, we will summarize efforts to eliminate the above-mentioned problems that led us to recommend using the quadratic speed-dependent hard-collision (qSDHC) profile with double-power-law (DPL) temperature dependencies. We refer to this profile as a modified Hartmann-Tran (mHT) profile. The computational cost of evaluating it is the same as for the HT profile. We will give a detailed description of the mHT profile (also including line mixing) and discuss the representation of its parameters, together with their DPL temperature parametrization adopted in the HITRAN database. We will discuss an efficient algorithm for evaluating this profile and provide corresponding computer codes in several programming languages: Fortran, Python, MATLAB, Wolfram Mathematica, and LabVIEW. Associated Python libraries for working with HITRAN Application Programming Interface (HAPI) will also be discussed.

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AB INITIO SPECTROSCOPY OF METHANOL CH_3OH

O. Smola[a], S. N. Yurchenko[a], and J. Tennyson[a]

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Methanol is highly abundant in the interstellar medium, where it acts as a so-called weed, owing to the fact it obscures other species of interest with its dense spectrum. With 12 vibrational degrees of freedom, variationally computing ro-vibrational spectra for methanol remains a daunting task, although in recent years some progress has been made in computing vibrational energies using both older[1] and newly computed PESs (potential energy surfaces)[2]. Obtaining spectroscopically accurate potential energy surfaces using ab intio methods is extremely challenging, and often requires consideration of higher order corrections. We present a new 12-dimensional PES computed using the explicitly correlated CCSD(T)-f12b method, and using the aug-cc-pVQZ-f12b basis set using the quantum chemistry code MOLPRO[3]. To obtain the best ab initio surface possible we consider contributions from core-valence correlation, as well scalar relativistic corrections, higher-order electronic correlation, and the diagonal Born-Oppenheimer correction, the latter three of which are computed using the coupled cluster code CFOUR[4]. The nuclear motion problem is then treated with a numerically exact kinetic energy operator derived from the full symbolic expression, represented in sum of products form, such that it can be input into the variational nuclear motion code TROVE[5]. These developments pave the way for the development of a high-resolution ExoMol line list for methanol, as we intend to empirically refine the potential energy surface to empirical data in the future.

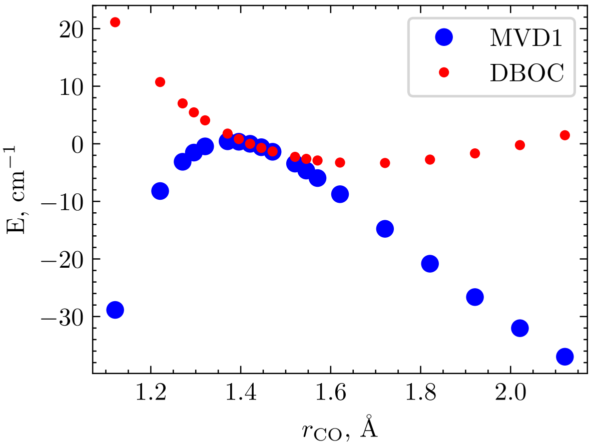

Figure 1: Scalar relativistic correction and diagonal Born-Oppenheimer correction, computed along a 1D cut of the r_{CO} bond stretch, using the CFOUR coupled cluster code.

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[2] A. Sunaga, T. Győri, G. Czakó, and E. Matyus, Vibrational Quantum States of Methanol, *arXiv 2505.16262.* `https://arxiv.org/abs/2505.16262`

[3] Werner H-J, Knowles PJ, Knizia G, Manby FR, Schütz M; Molpro: a general-purpose quantum chemistry program package; *WIREs Comput. Mol. Sci.* **2**, 242–253 (2012) `https://doi.org/10.1002/wcms.82`

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G: Minisymposium on Non-Covalent Interactions

Tuesday, August 26, 14:00
Hörsaal I

Chair: Yunjie Xu

MOLECULAR AGGREGATION: LESSONS I LEARNED FROM MOLECULAR SPECTROSCOPY IN JETS

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The study of molecular aggregation is decades old. The intermolecular forces that govern such process are small in module but big in importance, as they model the world around us. They also control key processes in the cell, such as docking or protein folding. For many years, there has been an intense activity in the field of spectroscopy in jets to characterize molecular aggregates of different nature and increasing size, to understand the above-mentioned process. The use of jets is required to create the necessary conditions for the molecules to aggregate. A cold environment ensures the survival of the species created during the cooling process at the exit of the valve's nozzle. Then, several spectroscopic techniques have been developed to extract physical observables from the system, which are afterwards compared with high-level quantum-mechanical calculations, but the most popular ones are laser spectroscopy with mass-resolved detection and microwave spectroscopy. Both offer complementary data over the same systems. Using this methodology, many systems have been characterized. Here, we will review some of them and the lessons learned from their study, trying to create general rules of broad application.

THE ROLE OF π-π INTERACTION IN DRIVING DIELS-ALDER CYCLOADDITION: INSIGHTS FROM ROTATIONAL SPECTROSCOPY

Q. Gou[a]

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The Diels–Alder (DA) reaction is a fundamental transformation in synthetic chemistry, widely utilized for its regio- and stereoselectivity in constructing cyclic frameworks. High-resolution rotational spectroscopy enables direct characterization of weakly bound pre-reactive intermediates (PRIs) in the gas phase, offering structural precision in revealing non-covalent interactions that precede transition states.

In a broader investigation into π–π interactions as a governing force in DA cycloadditions, three representative systems have been reported in this talk, evidenced by rotational spectroscopy and complementary quantum chemical calculations. For the furan–maleic anhydride system, the PRI was experimentally detected and shown to adopt a π–π stacked geometry that selectively stabilizes the endo channel. The influence of carbonyl groups on stacking interactions was found to contribute significantly to the conformational preference [1]. In the furan–acrolein system, multiple isomeric PRIs were characterized, with π–π stacking prevailing over hydrogen bonding. The relative stabilities and solvent effects were explored through microsolvation theoretical models, which indicated that solvents such as hexafluoro-2-propanol reinforce exo-selectivity while preserving π–π stacked conformations via cooperative hydrogen bonding [2]. For the oxazole-maleic anhydride complex, experimental evidence revealed that incorporation of small solvent molecules like H_2O and CO_2 induces substantial conformational changes in the PRI. These changes arise from combined hydrogen-bond and tetrel-bond interactions, leading to solvent-specific modulation of the endo/exo preference and reshaping the reaction energy landscape.

Taken together, these results demonstrate that π–π interactions are not only prevalent but also tunable features in pre-reactive configurations of Diels–Alder reactions. Solvent environments, whether modeled computationally or observed experimentally, play a critical role in modulating PRI geometries and selectivity. Rotational spectroscopy provides a powerful tool for revealing such subtle yet decisive non-covalent forces, offering new insights into reaction stereocontrol at the molecular level.

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INTERMOLECULAR INTERACTIONS REVEALED WITH ROTATIONAL SPECTROSCOPY: STRUCTURE, DYNAMICS & CHIRALITY

Melanie Schnell[a,b]

[a] Deutsches Elektronen-Synchrotron DESY
[b] Institut für Physikalische Chemie, CAU Kiel

Rotational spectroscopy is a coherence technique known to determine the structures of molecules and molecular complexes in the gas phase in great detail – ranging from fundamental topics like proton transfer in microsolvated acids to molecular recognition and astrochemistry. The structural information that can be deduced from the spectroscopic data provides an unprecedented molecular view on chemical processes, such as solvation and molecular recognition, governed by hydrogen bonding.

A first example addresses polycyclic aromatic hydrocarbons (PAHs), which are omnipresent in interstellar space, complexed with an increasing number of water molecules to understand the initial steps of ice formation. Because of the high symmetry of the PAHs, rich intermolecular dynamics can occur, including a large-amplitude motion of a single water molecule across the entire PAH surface. Secondly, a fascinating example where intermolecular interactions can shape molecular structures concerns chirality induction, as in the case of achiral tetraethyllead interacting with chiral trifluoromethyloxirane. In this complex, the latter induces a handedness in the highly flexible, initially achiral tetraethyllead compound. This chirality induction causes an increase in the predicted energy difference between the two enantiomers of this complex because of parity violation. Last but not least, the usefulness of nuclear quadrupole coupling to sense differences in the electronic environment of a particular molecular moiety will be addressed by using the example of water-driven dissociation of a single HCl molecule. In rotational spectroscopy, the nuclear spin of a quadrupolar nucleus like chlorine is a sensitive probe of its electronic environment and thus its bonding situation. Consequently, it was possible to precisely determine how many water molecules are needed for HCl to dissociate. This approach is quite general and can be applied to other molecular species containing atoms with nuclear spin, such as nitrogen.

H: Posters

Tuesday, August 26, 16:30
Foyer

HIGH-RESOLUTION ROTATIONAL SPECTRUM ANALYSIS OF HETEROCYCLIC COMPOUNDS FOR FUTURE ATMOSPHERIC APPLICATIONS

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Heterocyclic compounds, a group of volatile organic compounds (VOCs) abundant in smoke from biomass combustion, are potential sources of brown carbon aerosol formation. The main unsaturated heterocyclic compounds are known to react rapidly at night with NO_3 radicals, leading to the formation of secondary organic aerosols (SOAs). These SOAs affect the climate both directly and indirectly, but significant uncertainties remain regarding their contribution to radiative forcing.

Thiophene and its derivatives are heterocyclic organic compounds containing a sulfur atom. A study of 3-methylthiophene (3-MT) was conducted in 1972 between 7.6 and 25 GHz[1] and more recently the 2-methylthiophene (2-MT) was studied from 2 to 26.5 GHz.[2] To be able to detect these compounds in the atmosphere or in simulation chambers in the future, we need to extend the studies to higher frequencies where rotational lines are observed at room temperature. The spectra of 2- and 3-MT were recorded from 70-100 GHz with the amplified multiplication chain of the LPCA at Dunkirk, and the splittings due to internal rotation were analyzed using the BELGI code. A unitless standard deviation of the fit of 0.89 for 989 transitions (537 lines in $v_t = 0$, 440 lines in $v_t = 1$ and 12 lines in v_t=2) for 3-MT was obtained, close to the experimental precision. Nineteen parameters were determined, including the torsional barrier height ($V_3 = 279.15(97)\ \mathrm{cm}^{-1}$). The spectra of 2-methyl pyrrole was also recorded in Dunkirk and its analysis is under course.[3]

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[1] Ogata, T., Kozima, K. **1972** *J. Mol. Spectrosc.*, 42, 38–46.

[2] Koziol, K. J., Hadki, H. E., Lüchow, A., Vogt, N., Demaison, J., Nguyen, H. **2023** *Spectrosc. J.*, 1, 49.

[3] This research has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skodowska-Curie Grant Agreement No. 872081.

ROTATIONAL SPECTROSCOPY AND STRUCTURE OF BORNYL ACETATE

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[b] Institute of Physical Chemistry, Christian-Albrechts-Universität zu Kiel, 24118 Kiel (Germany)

Bornyl acetate is a chiral component of many coniferous oils. It is widely used in food, cosmetics, and medical industries and has a variety of biological functions, such as anti-inflammatory and antimicrobial effects[1] . In-depth study of the relationship between the molecular structure of bornyl acetate and its biological activity helps to reveal its mechanism of action and provides guidance for designing and synthesizing more effective natural bioactive compounds.

Herein, we employed a combination of rotational spectroscopy and quantum-chemical methods to investigate the conformational space of bornyl acetate. 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 package [3] was employed to predict energetically low-lying conformers. The rotational spectrum of bornyl acetate has been observed and assigned in the 2.0-8.0 GHz range using the chirped-pulse Fourier transform microwave spectrometer COMPACT. Only one isomer was determined corresponding to the global minimum of the monomer predicted theoretically, which is stabilized by an intramolecular C-H···O hydrogen bond. Each transition was divided into two components due to internal rotation of the single methyl group attached to the acetate group described by a three-fold potential. We determined the precise value of the V_3 barrier height of methyl group internal rotation, which is 1.19240(2) kJ/mol. The rotational spectra of twelve ^{13}C substituted isotopologues were also measured and analyzed. The structural characteristics of the detected isomer were ascertained using the experimental spectroscopic parameters.

Additionally, due to its chirality, the two enantiomers of bornyl acetate exhibit significant differences in odor perception and biological interactions. We are currently using styrene oxide as a chiral tag to form diastereomeric complexes with the (-)-bornyl acetate in the gas phase. This is the basis of chiral tag rotational spectroscopy[4], which can be used to determine absolute configuration, enantiomeric excess, and to gain deeper insight into its stereochemical characteristics, like chiral molecular recognition.

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PRESSURE-BROADENING LINE-SHAPE PARAMETERS OF CO ROVIBRONIC TRANSITIONS

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The crucial role played by carbon monoxide in studies of atmospheric composition and chemical reactions occurring in exoplanetary atmospheres initiated an increase of interest to its various spectroscopic characteristics. In particular, line-shape parameters of rovibronic transitions have become a subject of increasing study since they are needed for modeling of visible and ultraviolet radiation transport. Getting their experimental values represents however a formidable task, so that a very limited number of measurements is available in the literature for CO self-perturbed and perturbed by N_2 and CO_2.

In the present work we analyse transitions in the $a^3\Pi$ – $X^1\Sigma^+(1, 0)$ band of pure $^{12}C^{16}O$ recorded in SOLEIL Synchrotron at 300 K.[1] The broadening and shift coefficients obtained for different values of the rotational quantum number J in different P-Q-R-branches are compared to the measurements of Q-branch transitions in the $B^1\Sigma^+$ - $X^1\Sigma^+(0,0)$ band by Di Rosa et al.[2] who reported no observed dependence on rotational quantum state. Whereas quite close values are obtained for line-shift coefficients, the broadening-coefficient results differ approximately by a factor of two. Theoretical computations are in progress to establish the origins of this discrepancy.

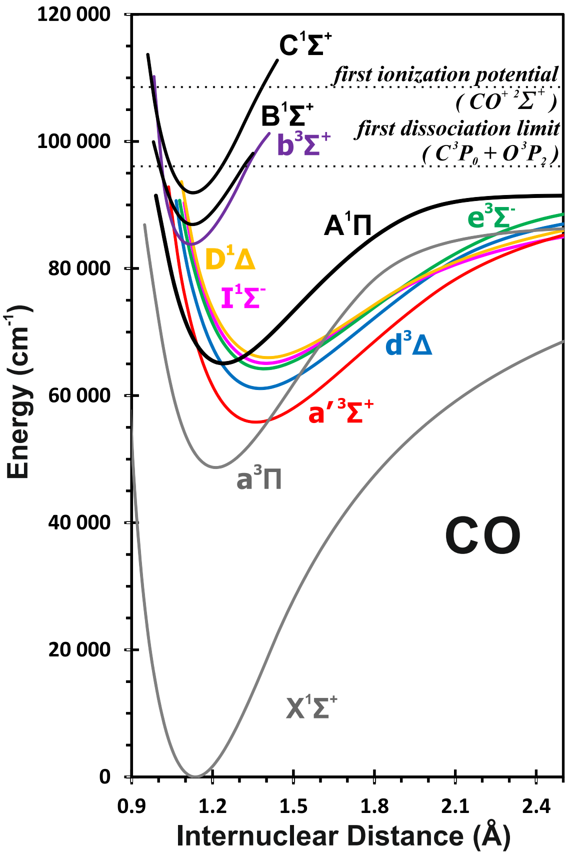

Figure 1: Electronic states of CO molecule.

Our measurements represent an alternative way to obtaining rovibronic line-shape parameters at room and elevated temperatures (above 1000K) needed for exoplanets. They enable also probing of various buffer gases. The J-dependence of broadening and shift coefficients opens a prospective of more advanced theoretical calculations going beyond the traditional "phase-shift" theory previously applied to NO and OH.[3]

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[3] Buldyreva, J., et al., **2024** *JQSRT*, 313, 108843.

LINE-SHAPE PARAMETERS OF METHANE BROADENED BY DRY AND HUMIDIFIED AIR FROM THE R(0) TO R(10) MANIFOLDS OF THE $2\nu_3$ BAND

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[b] Institute of Life, Earth and Environment (ILEE), University of Namur (UNamur)

The R-branch manifolds of the $2\nu_3$ band of methane broadened by dry and humidified air have been studied by cavity ring-down spectroscopy (CRDS) to improve the retrieved atmospheric CH_4 concentration from satellite missions like MERLIN and GOSAT-2. For this purpose, high-resolution spectra were recorded using a set of DFB laser diodes coupled to a high-finesse cavity. The frequency scale was accurately determined by beating to an optical frequency comb locked to a GPS-referenced rubidium clock. A coherence transfer method was employed to generate a sideband corrected from the jitter of the laser source using an electro-optic modulator. This sideband is coupled to the high-finesse cavity and tuned by a RF synthesizer from 2 to 18 GHz to scan and record the absorption spectra. Several hundred ring-down events were averaged for each spectral point to reach a noise level of 2×10^{-11} cm^{-1}. For each manifold, 5 spectra were recorded at pressures of 50, 100, 250, 500 and 750 Torr. Experimental spectra were fitted using a multispectrum fitting procedure with the Hartmann-Tran line-shape model, with the first and second order line-mixing approximations. The fitting residuals are reduced down to the noise level for the first few manifolds, but not for lines that strongly mix with each other. To our knowledge, this is the first time that rotational dependencies of all parameters of the Hartmann-Tran profile are determined for the methane-air molecular system.

ACCURATE INTENSITIES AND LINE PARAMETERS FOR THE $2\nu_3$-BAND OF METHANE BASED ON COORDINATED FOURIER-TRANSFORM AND CAVITY RING-DOWN SPECTROSCOPY MEASUREMENTS FROM THREE INDEPENDENT LABORATORIES

R.-H. Yin[1a], J.-K. Li[1a], Z. D. Reed[1c],J. Wang[b], A.-W. Liu[b], J. T. Hodges*[c], M. Birk[d], Y. Tan*[a,b], S.-M. Hu[a,b]

[a] Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, 230026, Anhui, China; [b] Hefei National Laboratory, University of Science and Technology of China, Hefei, 230088, Anhui, China; [c] Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, 20889, Maryland, USA; [d] Remote Sensing Technology Institute, German Aerospace Center (DLR), Wessling, D-82234, Germany

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A quantitative understanding of methane (CH_4) spectra in the 6050 cm^{-1} – 6250 cm^{-1} region is essential for atmospheric remote-sensing applications (e.g., TCCON, GOSAT-2, MERLIN) based on both solar- and laser-based absorption methods. This region corresponds to the $2\nu_3$ vibrational band, consisting of manifolds and multiplets with two or more transitions exhibiting strong spectral congestion, causing up to 10% uncertainties in HITRAN data, limiting methane retrieval precision. Here we report the combined results of a two-part study of the R(0) through R(10) manifolds of this methane vibrational band, Reed *et al.*[1], and Yin *et al.*[2], involving independent Fourier-transform spectroscopy (FTS) and cavity ring-down spectroscopy (CRDS) measurements made in three laboratories over a wide range of pressure. In Part I, measurements were made at relatively low pressures by DLR (using FTS) and NIST (with CRDS), while in Part II, N_2-broadened methane spectra were acquired at USTC using CRDS. The lines were nearly Doppler-broadened in Part I, with collisional line-shape parameters and line-mixing informed by the Part II study entering only as small correction. For these measurements, the zero-pressure line positions were constrained to the high-accuracy (kHz-level) values reported by Votava *et al.*[3]- thus largely eliminating correlations between blended lines retrieved from multispectrum fits. The ratio of the summed manifold intensities was 0.6‰ with a standard deviation of 1.4 ‰. In Part II, spectra were modeled using the speed-dependent Voigt profile, with first-order line mixing and using the line intensities determined in Part I, for atmospheric applications, air-broadened values for the line-shape parameters were determined using scaling rules. The resulting line-shape parameters had uncertainties of less than 1 %, which when combined with the line intensities from Part I, represents a significant improvement over the previous HITRAN2020 data. These results serve as an important benchmark for theoretical calculations and future measurements, thereby improving methane spectral line lists.

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HIGH-RESOLUTION FT SPECTROSCOPY OF THE ^{12}C^{16}O a$^3\Pi$ – X$^1\Sigma^+$ SYSTEM

A. Stasik[a,b], W. Ubachs[c], R.W. Field[d], N. de Oliveira[e], W. Szajna[a], S. Ryzner[a,b], M. I. Malicka[f], S. Mahmoud[g], N. El-Kork[g], N. Abu Elkher[g], M. Al Mehairbi[h], R. Al Abdallah[i], T. Furtenbacher[j], O. P. Yurchenko[k], S. N. Yurchenko[k], J. Tennyson[k] and R. Hakalla[a]

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[b]Doctoral School of the University of Rzeszow, Poland [c]Department of Physics and Astronomy, and LaserLaB, Vrije Universiteit, Amsterdam, Netherlands
[d]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, USA
[e]Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, France
[f]Faculty of Mathematics and Applied Physics, Rzeszow University of Technology, Poland
[g]Department of Physics, Khalifa University, Abu Dhabi, United Arab Emirates
[h]Department of Chemistry, Khalifa University, Abu Dhabi, United Arab Emirates
[i]Department of Mechanical and Nuclear Engineering, Khalifa University, Abu Dhabi, UAE
[j]HUN-REN-ELTE Complex Chemical Systems Research Group, Budapest, Hungary
[k]Department of Physics and Astronomy, University College London, UK

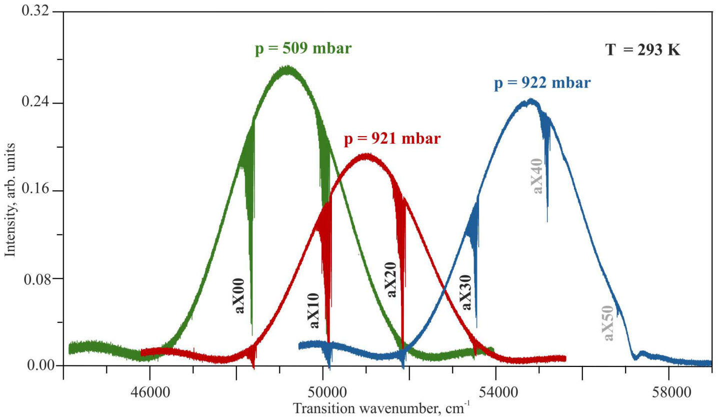

Figure 1: Synchrotron VUV-FT absorption spectra of the Cameron (a$^3\Pi$ – X$^1\Sigma^+$) system of ^{12}C^{16}O

Carbon monoxide (CO) is one of the key molecules in the study of planetary and exoplanetary atmospheres, as well as processes occurring in the outer space. The accurate determination of the positions of energy levels and the description of the processes governing them is crucial for modeling astrophysical phenomena and the dynamics of astronomical environments and objects. Research performed at the University of Rzeszow focuses on high-precision measurements of the ro-vibronic frequency of diatomic molecules of great astronomical and astrophysical importance[1,2]. As a result of our studies, we obtained 806 spectral lines of the ($v' - 0$) progression of the forbidden Cameron system (a$^3\Pi$ – X$^1\Sigma^+$). The spectra were obtained using VUV absorption spectroscopy at the SOLEIL synchrotron. The MARVEL algorithm was employed to merge a wide range of experimental terms of the ^{12}C^{16}O molecule in order to contribute to the ExoMol database for carbon monoxide molecule[3].

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FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF THE FCS AND ClCS RADICALS

Cheng-Han Tsai[a] and Yasuki Endo[b]

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[b]Department of Applied Chemistry, National Yang Ming Chiao Tung University

Over the past decades, formyl and halogen-substituted formyl radicals have been studied using spectroscopic techniques, and their properties are now well understood. In contrast, their sulfur analogues have received less attention. On the other hand, extensive microwave spectroscopic studies on FOO,[1] ClOO,[2] FSO,[3] ClSO,[4] FSS[5] and ClSS[6] radical, which belong to the nineteen-valence electron group, have been reported. For the seventeen-valence electron group, since only the FCO[7] and ClCO[8] radical have been studied, we decided to replace the oxygen atom with a sulfur atom in FCS and ClCS to study their rotational spectra.

In the present study, the rotational spectra of FCS and ClCS were measured by Fourier-transform microwave (FTMW) spectroscopy, using a discharge plasma of CF_4/CS_2 and CCl_4/CS_2 gaseous mixtures diluted in Ar or Ne, respectively. All the observations were conducted in the 10-35 GHz frequency region. Since both FCS and ClCS have large rotational constant A, it is unrealistic to observe transitions other than a-type transitions by our spectrometer, which covers frequencies below 40 GHz. Three a-type transitions, only for $K_\mathrm{a} = 0$, were observed for each radical. Although only a few parameters were able to be determined in this work, we are still able to discuss their hyperfine coupling constants comparing them with those of FCO and ClCO.

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MAGNETO OPTICAL TRAPPING OF ALUMINUM MONOFLUORIDE

J. E. Padilla-Castillo[1], J. Cai[1], P. Agarwal[1], P. Kukreja[1], R. Thomas[1], B. G. Sartakov[1], S. Truppe[2], G. Meijer[1] and S. C. Wright[1]

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Ultracold polar molecules have aroused great interests for their applications in testing fundamental physics and chemistry. Whilst there has been considerable success in associating ultracold diatomic molecules from laser-cooled atoms, these species are weakly bound (∼1 eV) and scarce in nature. A complementary approach is to laser cool molecules directly. So far, all diatomic and polyatomic species loaded into a magneto-optical trap (MOT) are spin-doublet molecules, and therefore chemically reactive. Moreover, their electronic structure only supports simple optical cycling from the first rotationally excited ($N = 1$) level, and all molecular MOTs thus far have operated from this single rotational level.

Here, we demonstrate the first magneto optical trap (MOT) of a molecule with a spin-singlet $^1\Sigma^+$ electronic ground state, aluminum monofluoride (AlF)[1]. AlF is among the most deeply bound molecules known (6.9 eV), is collisionally stable against bimolecular reactions, and both naturally abundant ^{27}AlF and the radioactive ^{26} AlF isotopolgue have been detected in space. Laser cooling is implemented using the intense $\mathrm{A}^1\Pi \leftarrow \mathrm{X}^1\Sigma^+$ transition near 227.5 nm, whose Q(J) lines are all rotationally closed. We demonstrate a MOT of about 6×10^4 molecules for the $J = 1$ level, and extend the molecular MOTs to the J=2 and 3 levels for the first time, taking advantage of the distinct electronic structure of AlF as compared to spin-doublet molecules. Laser cooling and trapping of AlF is a key to leveraging its spin-forbidden $\mathrm{a}^3\Pi \leftarrow \mathrm{X}^1\Sigma^+$ transition[2] for precision spectroscopy and control of the molecule. Here, a direct analogy can be drawn with laser-cooled alkaline earth elements which today serve as powerful tools within cold atom physics.

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SHAPED LIGHT IN SPECTROSCOPY: HOW USING LIGHT CARRYING OAM CAN ENHANCE MOLECULAR SPECTROSCOPY

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Tailoring light to spectroscopic applications is common practice in the field of high-performance molecular spectroscopy. Examples of altering the properties of light are shifting the frequency or shortening the pulse duration of a light source, which relate to changes in the frequency and time domain, respectively. Experiments based on these changes are for example spectrometers employing a modulated tunable diode laser or a frequency comb as laser source. However, changing the properties of light in the spatial domain, i.e. its structure in space, is a practice underutilized in modern spectroscopy. Spatially shaped light could therefore open up a new avenue in spectroscopy enabling the study of fundamental light-molecule interactions.

One such interaction was proposed in a publication of Maslov et al.[1] in which they discuss how structured light modifies the underlying selection rules of molecular quadrupole transitions. While the general formalism draws it's power from being a general description, allowing for differently shaped fields interacting with all kinds of matter, a particular focus is given to light carrying orbital angular momentum (OAM) and the possibility of transferring its OAM to a molecule trough a particular quadrupole transition channel.

The interaction in question is a transition that not only changes the rotational number but also the projection of $\vec{J}$ onto the laboratory axis, m_Z, resulting in the modified selection rules for an S-branch transition: $\Delta\nu = +1$, $\Delta J = +2$, $\Delta m_Z = \pm 2$. In the aforementioned publication, a prototypical experiment was described to investigate the proposed transition channel, including cryogenic cooling and strong electric fields to separate the different projection states.

Verifying the feasibility of transferring the angular momentum quantum, M, associated with light carrying OAM to the molecule, could open up new perspectives in spectroscopy and further the understanding of the interaction of OAM with matter, which has been lacking ever since Allen[2] first described the concept of OAM.

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HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY OF THE X^+ $^2\Sigma^+$ GROUND STATE OF $CaAr^+$

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We report on the characterization of the structure of the X^+ $^2\Sigma^+(v^+)$ ground state of $CaAr^+$ by high-resolution pulsed-field-ionization zero-kinetic-energy photoelectron (PFI-ZEKE-PE) spectroscopy. Rotationally cold (T_{rot} = 0.7 K) CaAr molecules in the a $^3\Pi_{0^\pm}(v'' = 0)$ metastable states are generated in a supersonic expansion of a 1:5 Ar:He carrier gas following laser ablation of a calcium (Ca) rod. The spectra were recorded from the CaAr metastable a $^3\Pi_{0^\pm}(v'' = 0)$ states using a resonance-enhanced $(1+1')$ two-photon excitation scheme via the intermediate Ca(4s5s)Ar $^3\Sigma^+(v' \leq 9)$ state, previously characterized by Kaup *et al.* [1]. The adiabatic ionization energy of the metastable a $^3\Pi_{0^-}$ and $^3\Pi_{0^+}$ states of CaAr, corresponding to the $CaAr^+$ X^+ $^2\Sigma^+$ $(v^+ = 0, N^+ = 0) \leftarrow$ CaAr a $^3\Pi_{0^\pm}$ $(v'' = 0, J'' = 0)$ ionization threshold, was determined to be $E_I/(hc) = 33432.86(20)$ cm^{-1} and $E_I/(hc) = 33428.66(20)$ cm^{-1}. Vibrational levels of the X^+ $^2\Sigma^+$ ground electronic state of $CaAr^+$ in the range $v^+ = 0 - 15$ have been characterized with partial resolution of the rotational structure. These states cover more than 80% of the potential-well depth and are used to accurately determine the potential-energy function of the $CaAr^+$ ground electronic state which takes into account long-range interactions. This work is carried out in the context of the rovibronic structure characterization of diatomic molecules MRg consisting of alkaline-earth metal (M) and rare gas (Rg) atoms, as well as the characterization of their singly-charged [2] MRg^+ and doubly-charged MRg^{2+} cations [3]. This study represents a significant extension of previous work on the characterization of the X^+ $^2\Sigma^+$ ground state of $CaAr^+$ by photoionization spectroscopy of CaAr [4] and photodissociation spectroscopy of $CaAr^+$ [5].

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HIGH-RESOLUTION LASER AND MILLIMETER-WAVE SPECTROSCOPY AND MQDT ANALYSIS OF HIGH RYDBERG STATES IN Kr, Xe, AND Yb

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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 physical constants and atomic properties. High-resolution spectroscopy is essential for characterizing the electronic structure and the fundamental properties of these atomic systems. These properties include, but are not limited to, their ionization energies, their hyperfine structures, and isotopic shifts.

High-resolution spectra of high np and nf Rydberg series of Kr and Xe were measured by single-photon excitation from the Rg $(n\mathrm{p})^5((n{+}1)\mathrm{s})^1\ {}^3\mathrm{P}_2$ metastable state to study bound Rydberg states located below the $\mathrm{Rg}^+(n\mathrm{p})^5\ {}^2\mathrm{P}_{3/2}$ ionization threshold, and autoionizing Rydberg states located between the $\mathrm{Rg}^+(n\mathrm{p})^5\ {}^2\mathrm{P}_{3/2}$ and $\mathrm{Rg}^+(n\mathrm{p})^5\ {}^2\mathrm{P}_{1/2}$ ionization thresholds with $n{=}4$ and 5 for Kr and Xe, respectively. 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 [1].

The fine and hyperfine structures of np and nf Rydberg states of the nine and six natural isotopes of xenon and krypton, respectively, have been analyzed in the range of principal quantum number n between 60 and 75 using multichannel quantum-defect-theory (MQDT). For the analysis of the fine and hyperfine structure we followed the formalism introduced for the $I{=}0$ isotopes by Lu and Lee [2], and Lu [3] and its extension in our group [4,5,6] to treat the hyperfine structure in ^{83}Kr, ^{129}Xe and ^{131}Xe. Improved values of the ionization energies, the isotopic shifts and hyperfine coupling constants of $^{83}\mathrm{Kr}^+$, $^{129}\mathrm{Xe}^+$ and $^{131}\mathrm{Xe}^+$ were derived from the MQDT analysis.

The same approach can be used to study the Rydberg states of Yb, both for the $I{=}0$ isotopes and $^{171}\mathrm{Yb}^+(I{=}1/2)$ and $^{173}\mathrm{Yb}^+(I{=}5/2)$. Low-lying excited electronic configurations of Yb^+ necessitate the inclusion of many more channels in the MQDT treatment [7,8,9]. We will present the current status of our studies of the Rydberg spectrum of Yb, which includes both experimental work of the Rydberg series accessible from the metastable 6s6p $^3\mathrm{P}_0$ and 6s6p $^3\mathrm{P}_2$ states and the MQDT analysis of the (ns), (np), (nd) and (nf) Rydberg series.

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LETOKHOV-CHEBOTAYEV TRAPPING SPECTROSCOPY OF H_2

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The hydrogen molecule and its isotopologues are benchmark systems to test advanced calculations of quantum electrodynamics in molecules. Via the NICE-OHMS technique[1] precision measurements were performed on the dipole-allowed overtone spectra of the HD[2] and HT molecules[3]. In these studies the line shape appeared dispersive, thus limiting the extracted frequency accuracy of the rovibrational transitions. In a measurement of the very weak S(0) transition of the (2-0) overtone band of para-H_2, of quadrupole nature, a single symmetric Lamb dip could be observed yielding a transition frequency accurate to 8 kHz, the most accurately measured line in the hydrogen molecules so far[4]. While it was anticipated that in molecular saturation spectroscopy always a recoil doublet should appear[5] in this case of H_2 only a single blue-shifted recoil component is observed in the Lamb dip measurement. This is now attributed to the very weak level of saturation, insufficient to excite the red recoil component.

The NICE-OHMS technique is applied in a non-trivial way, by which the typical sidebands are employed for inducing the resonance and the central carrier frequency (at 2 kW intracavity circulating power) is used to trap molecules in the high-intensity standing-wave light field. We observe, for the first time, a phenomenon of 1-dimensional trapping as was predicted in the early days of laser spectroscopy by Letokhov and Chebotayev[6] with typical spectral features displayed in Fig. 1. The reversal from a Lamb-dip to a linear absorption feature at very narrow width (250 kHz, much narrower than the expected 1 GHz Doppler width at 72 K) and its position at zero recoil form the proofs that this feature is observed.

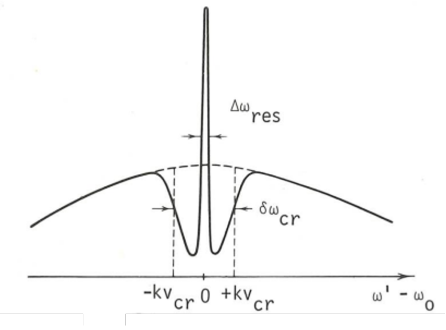

Figure 1: 1-D trapping feature as predicted by Letokhov and Chebotayev[6].

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ON THE TUNNELLING DYNAMICS OF PROTONATED ACETYLENE: THE C-H-C STRETCHING BAND OF ITS BRIDGED CONFIGURATION

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Protonated acetylene ($C_2H_3^+$) is a prototypical carbocation for which (ro)vibrational spectra [1] as well as pure rotational spectra [2] have been recorded previously. In particular, the feasibility of proton tunneling in its ground and vibrationally excited states has attracted much interest. In the minimum energy configuration, the proton is believed to be in a bridged position between the two carbon atoms of acetylene. The classical H_2CCH^+ structure belongs to a transition state, posing a substantial energy barrier which separates the three equivalent minima of the respective bridged configuration. Here we report on (ro)vibrational spectra of the C-H-C stretching vibration, which is present only for the bridged configuration. For these measurements, we employ leak-out spectroscopy in a cryogenic 22-pole ion trap using a quantum cascade laser in the 5 µm regime. Despite the richness of the spectrum, characteristic patterns of the $K = 1 \to 0$ component have been identified, which helped the assignment of the spectrum to the perpendicular band of the bridged configuration. In addition, an infrared–mm-wave double resonance excitation scheme has been applied to link these transitions to the ground state rotational transitions reported by Bogey *et al.*, thus confirming the assignment of the (ro)vibrational spectrum. Apparently, every second (ro)vibrational transition is missing in the observed spectral pattern. This finding is consistent with proton tunneling in the torsional motion of all three protons, as proposed by Hougen [3] as well as by Escribano and Bunker [4] for this system. This is another proof for the equivalence of the three protons in protonated acetylene and the feasibility of proton tunneling in this fluxional carbocation.

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LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER

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It is widely believed that in the protonated water dimer, the central proton is equally shared between the two water molecules (Zundel structure). Although this complex is subject to a variety of tunneling and large amplitude motions, it is commonly assumed that the central proton won't exchange with the outer ones due to substantial barriers. This assumption is seemingly consistent with previous partially rotationally resolved spectra of the antisymmetric O-H stretching band, reported by Yeh et al. [1]. However, a clear experimental proof of the localization of the central proton is still missing.

The fundamental property closely related to this question is the underlying molecular symmetry group. For a complex in which the central proton won't be subject to tunnelling, the symmetry group is $G_{16}^{(2)}$. But when all five protons can swap places, the underlying group is G_{240}. For these two situations, the nuclear spin statistical weights are different. In a trap experiment where a finite ensemble of cold and mass-selected ions is stored, it is possible to determine the fractions of nuclear spin species by kicking out all ions belonging to one nuclear spin configuration using leak-out spectroscopy (LOS). Results from these measurements are much more reliable than comparing line intensities, which is a traditional approach to determining those fractions. This is because the fractions are directly determined from the temporal evolution of the number of ions in the trap. This contribution presents results for such LOS depletion experiments in the symmetric O-H stretching band of the protonated water dimer. Based on a detailed analysis of our findings, we infer information about the mobility of the central proton in this fundamental complex.

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THE GROUND STATE SUPERMULTIPLET OF NiD

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Experimental data on the main isotopologues of NiH (^{58}Ni, ^{60}Ni and ^{62}Ni) may be found in many studies[1]. Recently a coupled channels model for the group of three lowest electronic states $X^2\Delta$, $V^2\Sigma^+$ and $W^2\Pi$ was published[2]. It includes all known experimental data and reproduces energy levels to within about 0.01 cm^{-1}, comparable to their experimental uncertainty. In Ref.[1] the same approach was used with the ExoMol Hamiltonian model, predicting transitions for higher rotational levels and predicting absorption linestrengths in extensive line lists for NiH isotopologues.

The data for NiD are more sparse[3]. After the analyses of NiH [1,2] the same models were applied to NiD and it transpired that simple mass scaling of the coupling functions is not sufficient to achieve experimental accuracy. It is not surprising, because the substitution of H by D may lead to additional non-adiabatic effects which need to be additionally accounted in the model.

In this contribution we report a new analyses of all available experimental data on NiD within the coupled channels formalism from Ref. [2]. It is independent from the results from the NiH model, i.e. all model functions are fitted and not simply mass scaled. We compare the fitted NiD functions and the mass-scaled NiH ones and discuss whether they can be attributed to non-adiabatic effects.

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HIGH-POWER, LOW-NOISE MID-INFRARED OPTICAL FREQUENCY COMB FOR CAVITY-ENHANCED LAMB-DIP SPECTROSCOPY

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Recent applications like human breath analysis[1] or spectroscopy in the "fingerprint region"[2] have introduced the need for more and more accurate reference data in the mid-infrared spectral region. However, precision spectroscopy methods like cavity-enhanced Lamb-dip spectroscopy with optical frequency combs[3] have rigorous demands on the used light source, requiring excellent frequency stability, very high beam quality to efficiently couple to the cavity, and several watts of average power to be able to reliably saturate several transitions simultaneously. Such sources remain technologically challenging and are currently unavailable.

Here, we present an optical frequency comb system based on an optical parametric oscillator operating in the 3 µm to 5 µm region, which reaches a record-high average power of up to 10.3 W at 3.1 µm while maintaining a near-diffraction limited beam ($M^2 < 1.3$) at up to 2.4 W. Additionally, we provide an extensive investigation of the frequency stability of the system, yielding an optical linewidth of 300 kHz in free-running operation[4]. This combination of record-high average power[5], excellent beam quality, and frequency stability is fully adequate for a first-time performance of broadband cavity-enhanced Lamb-dip spectroscopy in the mid-infrared.

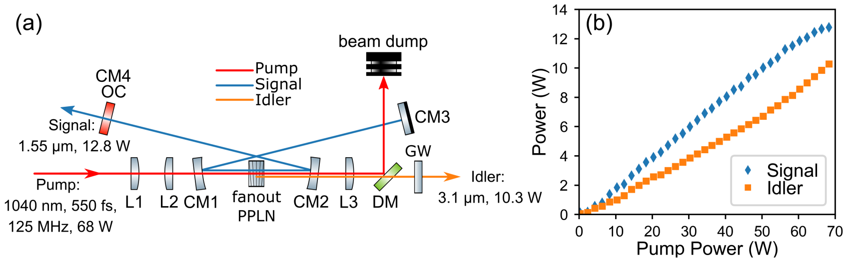

Figure 1: (a) Scheme of the OPO setup: L1-3, lenses; CM1-4, cavity mirrors; OC, 15% output coupler; DM, dichroic mirror; GW, Germanium window; PPLN, periodically-poled $LiNbO_3$ crystal. (b) Pump power slope of signal at 1.55 µm and idler at 3.1 µm.

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HIGH-RESOLUTION ROVIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF THE $C_2H_2N^+$ ISOMERIC SYSTEM

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Astronomical observations have revealed approximately 350 distinct molecules and molecular ions in the interstellar medium (ISM). Potentially, many more species remain undiscovered, for which high-resolution laboratory data is needed. Ions, in particular, are long known to be key intermediates driving molecular complexity of the ISM, and their presence and abundance are tightly connected to the process of star and planet formation. Many astrochemically relevant ions belong to isomeric systems, and distinguishing individual isomers and their corresponding abundances is crucial to understanding the underlying chemical pathways.

One such isomeric family of interest is $C_2H_2N^+$, which is isostructural to C_3H_2 and isoelectronic to both C_3H_2 and $C_3H_3{}^+$. The open-chain isomer of $C_3H_3{}^+$ was recently detected in the cold molecular cloud TMC-1[1], while c-$C_3H_3{}^+$ is proposed as a precursor of cyclopropenylidene, c-C_3H_2, which has been observed in many astrophysical environments. The open-chain isomer of C_3H_2 is also detected in the ISM.[2] The cyclic isomer, c-$C_2H_2N^+$, is particularly interesting as no N-containing aromatic ring has been observed in the ISM so far.[3]

Here, we report on the high-resolution spectra of the two lowest energy $C_2H_2N^+$ isomers, c-$C_2H_2N^+$ and H_2CCN^+ (Fig. 1). The measurements were performed using leak-out spectroscopy (LOS)[4] in a cryogenic ion trap at 4 K and 12 K. For both isomers, we recorded several vibrational bands in the infrared range. In addition, we obtained their pure rotational spectra using a millimetre wave-infrared (mmw-IR) double-resonance technique[5], allowing for the precise determination of rotational constants in the vibrational ground state. Our results provide essential spectroscopic data to support future astronomical searches for this molecular system.

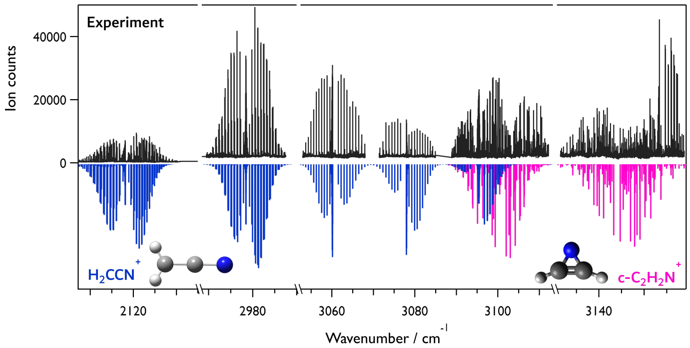

Figure 1: Rovibrational spectra of H_2CCN^+ (in blue) and c-$C_2H_2N^+$ (in pink) recorded in the present study.

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LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE JET-COOLED SiNSi RADICAL: ROTATIONAL ANALYSIS OF THE ELECTRONICALLY FORBIDDEN $\tilde{D}\ ^2\Sigma_g^+ - \tilde{X}\ ^2\Pi_g$ TRANSITION

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We have generated SiNSi in supersonic free jet expansions, and measured the laser induced fluorescence (LIF), which is observed both in ultra-violet (UV) and visible regions. The LIF excitation spectra in the UV region were recorded, and exciting vibronic bands observed in the spectra, dispersed fluorescence (DF) spectra from the single vibronic levels (SVL's) were recorded too. On the basis of rotational analyses, five vibronic bands, both $^2\Pi_u - {}^2\Pi_g$ and $^2\Sigma_u^+ - {}^2\Pi_g$, in the LIF excitation spectra have been identified to those of the electronically forbidden $\tilde{D}\ ^2\Sigma_g^+ - \tilde{X}\ ^2\Pi_g$ transition of SiNSi. Herzberg-Teller (H-T) vibronic coupling with $\Delta\Lambda = \pm 1$ and $\Delta l = \mp 1$ is concluded to induce the intensity borrowing of the vibronic bands. The electronic transition moment of the two $^2\Pi_u - {}^2\Pi_g$ bands, $\tilde{D}$ $(01^10)\ ^2\Pi_u$ – and $(03^10)\ ^2\Pi_u - \tilde{X}\ ^2\Pi_g$, can be interpreted as the one brought from the $1^2\Pi_u - \tilde{X}\ ^2\Pi_g$ electronic transition by H-T, where the $1^2\Pi_u$ state lies at ~ 13500 cm^{-1} above the $\tilde{X}\ ^2\Pi_g$ state [3]. In contrast, the electronic transition moment of the three $^2\Sigma_u^+ - {}^2\Pi_g$ bands, $\tilde{D}$ $(00^01)\ ^2\Sigma_u^+$ –, $(02^21)\ ^2\Sigma_u^+$ –, and $(10^01)\ ^2\Sigma_u^+ - \tilde{X}\ ^2\Pi_g$, can be explained as the one brought from $\tilde{E}\ ^2\Sigma_u^+ - \tilde{X}\ ^2\Pi_g$ [3,4] by H-T. The DF spectra from the SVL of the $\tilde{D}\ ^2\Sigma_g^+$ state clearly have UV and visible dual-fluorescence. The UV fluorescence corresponds to the photo-absorption induced by H-T, while the visible fluorescence is attributed to the electronically allowed $\tilde{D}\ ^2\Sigma_g^+ - 1^2\Pi_u$ transition. Fluorescence lifetime of the $\tilde{D}\ ^2\Sigma_g^+$ state, ~ 40 ns, is much shorter than that of $\tilde{C}\ ^2\Delta_u$, ~ 150 ns [5]. Contrastingly, transition dipole moment of $\tilde{D}\ ^2\Sigma_g^+ - 1^2\Pi_u$ is predicted to be 0.4 D on the MC-SCF/cc-pVTZ level, which is smaller than the other transitions, such as 1.3 D for $\tilde{C}\ ^2\Delta_u - \tilde{X}\ ^2\Pi_g$. The contradictive results on the lifetime and moment for the electronically forbidden $\tilde{D}\ ^2\Sigma_g^+ - \tilde{X}\ ^2\Pi_g$ transition are consistent with the dual-fluorescence; the dual-fluorescence is interpreted as one caused from the characteristics; (1) relatively long radiative lifetime of the allowed $\tilde{D}\ ^2\Sigma_g^+ - 1^2\Pi_u$ transition, 4 μs (0.4 D), in the visible region, (2) the relatively short radiative lifetime, ~ 40 ns, of the UV fluorescence, and (3) the inefficient door way to the UV fluorescence, due to H-T.

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LINE PARAMETERS MEASUREMENTS AND SPECTROSCOPIC MODELING OF CH_3F IN THE 20–100 cm^{-1} AND 1900–2400 cm^{-1} SPECTRAL REGIONS

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This study presents a comprehensive spectroscopic analysis of methyl fluoride (CH_3F), focusing on both *rotational* and *vibrational transitions* across distinct spectral regions. The investigation includes high-resolution modeling of line positions in the $\nu_3 + \nu_6$ and $2\nu_3$ vibrational bands, as well as in the 20–100 cm^{-1} range, corresponding to ure rotational transitions in the ground vibrational state.

The rotational spectra in the 20–100 cm^{-1} region were recorded using *Fourier Transform (FT) spectroscopy* at the **SOLEIL Synchrotron** (AILES beamline, Paris), while the *vibrational spectra* of the $2\nu_3$ and $\nu_3 + \nu_6$ bands were acquired at the **GSMA laboratory** (University of Reims, France) using a high-resolution FT spectrometer.

Line positions were modeled using an effective Hamiltonian, allowing accurate assignments up to $J = 45$ and $K = 15$. Line intensities were determined for both the $2\nu_3$ and $\nu_3 + \nu_6$ bands, enabling the derivation of vibrational transition moments. *Self-broadening coefficients* were analyzed for the $\nu_3 + \nu_6$ band, and *air-broadening coefficients* were obtained for both $2\nu_3$ and $\nu_3 + \nu_6$, providing essential spectroscopic parameters for atmospheric applications.

This work significantly expands the spectroscopic database of CH_3F by providing high-precision data on *line positions, intensities, self-broadening, and air-broadening coefficients* across key spectral regions. These results are valuable for *remote sensing*, *atmospheric monitoring*, and *industrial detection* of CH_3F, and contribute to a deeper understanding of its rotational-vibrational structure.

COMPETITION BETWEEN PRODUCT CHANNELS IN ION-MOLECULE REACTIONS NEAR 0 K: $H_2{}^+$, HD^+ AND $D_2{}^+$ + CH_3F

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Ion-molecule reactions are essential steps of astrophysical and atmospheric chemical networks but are difficult to study in the laboratory at low energies ($< k_B \times 50\,\mathrm{K}$) because stray fields heat the ions up. We circumvent this difficulty by replacing the ion (here $H_2{}^+$, HD^+ and $D_2{}^+$) with a highly excited Rydberg state of these molecules.[1,2] The distant Rydberg electron shields the ion core from external fields without influencing the ion-molecule reaction taking place within its orbit. We use a Rydberg-Stark deflector[3] to merge a supersonic beam of hydrogen molecules in high Rydberg states with a supersonic beam of ground-state neutral CH_3F.

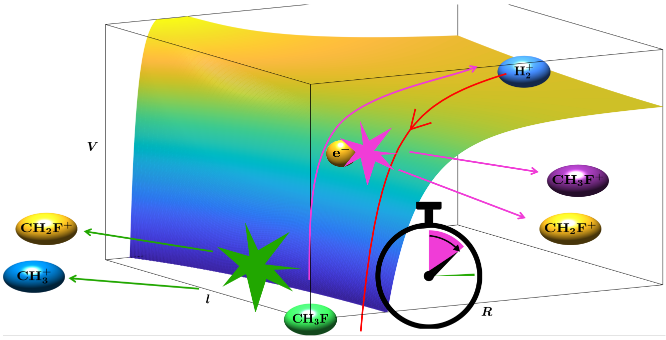

Figure 1: Competition between intermediate-range electron-transfer (pink) and short-range atom-transfer (green).

This deflector is also used to set the velocity of the Rydberg molecules (v_{Ryd}). By tuning v_{Ryd} relative to the velocity of the ground-state molecules, we can scan the collision energy E_{coll} from $\sim k_B \times 500\,\mathrm{mK}$ to $\sim k_B \times 50\,\mathrm{K}$. The product ions, the energy dependence of the reaction rates and the branching ratios for the formation of CH_3F^+, CH_2F^+ and $CH_3{}^+$ product ions are measured as a function of E_{coll}. Short ($\sim 20\,\mu\mathrm{s}$) gas pulses ensure a high collision-energy resolution.

We report here on a study of the reactions of $H_2{}^+$, HD^+ and $D_2{}^+$ with CH_3F. The energy dependence of the rate coefficients of these reactions deviate strongly from Langevin capture behaviour and exhibit a sharp increase below 2 K, as expected for reactions between ions and dipolar molecules. These observations are analysed using (I) a rotationally adiabatic capture model including the Stark effect of the rotational states of the symmetric-top CH_3F in the electric field of the ion[4,5,6] and (II) classical trajectory calculations of a dipolar molecule approaching a point-like ion.

All reactive systems exhibit a competition between electron-transfer with dominant product CH_2F^+ and short-range F^--transfer ($CH_3{}^+$) and H^--transfer (CH_2F^+) processes. We observe that the increasing level of deuteration favours the electron transfer whereas low collision energies favour atom transfer. On the basis of our model calculations, we attribute this behaviour as arising from the fact that electron transfer occurs at larger distances than atom transfer and that the time available for electron transfer increases with increasing reduced mass and decreases with the larger degree of dipole orientation at low collision energies.

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MICROWAVE-CONTROLLED COLD CHEMISTRY

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Ion–molecule reactions proceed with highly rotational-state-specific rate coefficients and are amenable to stereodynamical control at low temperatures. The general theoretical framework to understand the key features of the state specificities and stereodynamics of low-temperature ion–molecule capture reactions, rotationally adiabatic capture theory,[1,2] has been derived more than 30 years ago. It is, however, only recently that experiments have reached the low temperatures and the low collision energies needed to rigorously test the theoretical predictions.[3–6] Based on theory and experiments, it is now established that the inhomogeneous electric field emanating from the ion acts differently on different conformation isomers,[7] different isotopologues,[8] and different nuclear-spin isomers[9] of the neutral molecules, and also on their different rotational levels.[10]

This contribution presents a scheme to control cold ion–molecule chemistry with microwaves based on the coherent transfer of molecular rotational-state populations.[11] To reach collision energies from 10 K down to $\sim$ 200 mK, we use the Rydberg–merged-beam approach and study the ion–molecule reaction taking place within the orbit of a highly excited Rydberg electron, which prevents the heating up of the ions by stray electric fields without influencing the reaction. We investigate the reaction between He^+ and rotationally cold CO and NO molecules ($T_{\mathrm{rot}} \approx 3$ K) and manipulate the molecular rotational-state population using microwave pulses. The relevant rotational-state transitions in CO and hyperfine-state transitions in NO are characterized with microwave spectroscopy. REMPI spectroscopy is employed to assess the rotational-state populations before and after the microwave-driven transitions. A reaction inhibition of up to $\sim$ 40% ($\sim$ 20%) is achieved with microwave pulses resonant with pure-rotational transitions in CO (NO), unambiguously demonstrating a nonthermal mechanism for microwave-assisted chemistry.

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THE STRUCTURE OF *GAUCHE*-1,3-BUTADIENE: FURTHER INSIGHTS FROM THE CENTIMETER-WAVE, MILLIMETER-WAVE, AND FAR-INFRARED HIGH RESOLUTION SPECTRA

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The high-energy conformer of 1,3-butadiene (lying approximately 12 kJ mol^{-1} above the *s-trans* form) has been proven to adopt a non-planar *s-gauche* configuration, characterized by a significant dihedral angle[1]. A key piece of evidence supporting this conclusion was the observation of doublets for each rotational transition, attributed to quantum tunneling between the two equivalent *s-gauche* enantiomeric forms. Additionally, a partial semi-experimental equilibrium structure was derived by analyzing five isotopologues of the molecule (the two singly-substituted ^{13}C species, and three multi-deuterated forms), allowing for the determination of 11 structural parameters, out of the 13 total, including the dihedral angle of $33.8 \pm 1.3\,^\circ$.

Yet, much remains to be learned about *s-gauche*-butadiene. Firstly, the limited dataset prevented an experimental determination of the tunneling splitting, which was only estimated through calculations at approximately 55 GHz, with a margin of error of about 20 %. Secondly, a full semi-experimental structure determination is still lacking, which can only be achieved through isotopic substitution. Consequently, further insights into *s-gauche*-butadiene require an extensive spectroscopic campaign.

We will present a follow-up study on *s-gauche*-1,3-butadiene:

- The pure rotational spectrum of the main isotopic species has been recorded at millimeter wavelengths, allowing for an indirect determination (through Coriolis de-perturbation treatment) of the tunneling splitting;
- The pure rotational spectrum of three singly-deuterated isotopic variant has been observed at centimeter wavelengths, allowing for a refinement of the semi-experimental equilibrium structure;
- The ro-vibrational spectrum was investigated at high resolution in the far-infrared domain, at two synchrotron facilities, to investigate the lowest energy vibrational band, in an attempt to detect direct transitions between tunneling states.

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MILLIMETER-WAVE MEASUREMENTS IN HIGH-FINESSE CAVITY OF NITRO-DERIVATIVES TRACES: A NEW INSIGHT IN THE EXPLOSIVE VAPOR SENSING

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Detecting explosive vapors under realistic conditions remains a challenge. Canine detection provides excellent sensitivity and selectivity, but it is not compatible for continuous monitoring. Ion Mobility Spectrometry (IMS) techniques, on the other hand, allow for continuous operation but may lack molecular selectivity. In this context, millimeter-wave rotational spectroscopy provides a promising alternative, provided reliable spectral data are available.

Several nitroaromatic compounds were studied using high-resolution spectroscopy, including nitromethane (NM)[1], 2-nitrotoluene (2-NT) and 4-nitrotoluene (4-NT)[2]. Their strong dipole moments and moderate vapor pressures, combined with internal methyl rotation coupling, give rise to rich but distinctive spectral features for their identification. In this study, we present recent results on near-realistic detection of nitroaromatic compounds using a high-finesse cavity (>3000) with a 2 km effective path length in the 150–215 GHz range.

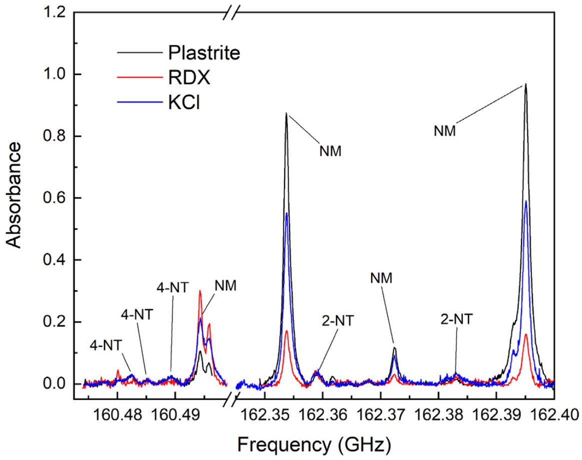

Figure 1: Millimeter-wave CEAS spectrum of solid explosive matrices (KCl, RDX, plastrite) spiked with NM, 2-NT, and 4-NT and vaporized under controlled thermal and vacuum conditions.

In laboratory conditions, gas-phase mixtures of NM, 2-NT, and 4-NT were firstly analyzed using Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring-Down Spectroscopy (CRDS), achieving selective detection and detection limits down to 2 ppmv for NM. The spectrometer was then used on explosive matrices (KCl, RDX) and commercial plastic explosives (Plastrite), spiked with NM, 2-NT, and 4-NT, which were vaporized under controlled thermal and vacuum conditions. As shown in Fig. 1, all taggants were clearly identified using CEAS. Additional CRDS measurements confirmed that the concentrations estimated from the spectral signatures were consistent with the known matrix compositions[3]

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ADVANCEMENTS IN HOME-BUILT CHIRPED-PULSE SPECTROMETERS AT KÖLN

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Rotational spectroscopy plays a prominent role in astrochemistry, enabling the identification of most of the 330 molecules[1] in interstellar and circumstellar environments through their unique rotational fingerprints. These molecular detections offer key insights into the chemical diversity, physical conditions, and evolutionary processes of various astrophysical regions, particularly those involved in star and planet formation.

At the Laboratory Astrophysics Group in Köln, we measure high-resolution broadband rotational spectra of astrophysically relevant molecules using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. Our home-built spectrometers cover the microwave (12–26 GHz) and millimeter-wave (75–110 GHz)GHz[2] ranges, aligning with the observation bands of the Green Bank Telescope and ALMA Band 3.

Our microwave spectrometer utilizes state-of-the-art RF modulation and detection technology, eliminating the need for frequency mixing by directly generating and receiving signals. Motivated by the recent detection of 1- and 2-cyanonaphthalene ($C_{10}H_7CN$) in the TMC-1 cloud[3], which highlights the astrophysical importance of polycyclic aromatic hydrocarbons (PAHs), we plan to extend the frequency range of the spectrometer down to include 2-12 GHz. This extension will provide crucial laboratory data on heavier PAHs and other complex organic molecules, supporting their future identification in the interstellar medium. We will present the design and plans for the new spectrometer.

The millimeter-wave spectrometer employs a heterodyne receiver built for emission spectroscopy[4], which, as a result of up- and down-conversion of the intermediate frequency (IF), produces mirror lines or sidebands. To overcome this, we upgraded it with a new DAC/ADC board (U-SAGE) for phase-coherent signal generation and acquisition, as well as rapid integration in the time domain. This upgrade facilitates sideband separation and is useful for other applications, including study of time-evolution of processes and double-resonance spectroscopy. We present results from the U-SAGE that demonstrate these enhanced capabilities.

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DISENTANGLING THE SPECTRA OF COMPLEX ORGANIC RADICALS USING FARADAY-ROTATION-BASED MILLIMETER-WAVE INSTRUMENTATION

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Complex organic radicals play a crucial role in both the formation and destruction pathways that give rise to complex organic molecules (COMs) observed in the interstellar medium [1]. These species are also key intermediates in atmospheric and combustion chemistry [2], and represent valuable systems for advancing our understanding of molecular physics, as large radicals often exhibit a complex internal dynamics [3].

This poster presents the methodology that we developed in the last couple of years for investigating specific dehydrogenated COMs in the gas phase, illustrated through our recent studies on the acetonyl (CH_3COCH_2) [4], the vinyloxy (CH_2OCHO), and the hydroxy vinoxy (CHOCHOH) radicals at millimeter and sub-millimeter wavelengths (160–450 GHz). Spectra of these radical species were acquired using Faraday rotation modulation spectroscopy, a technique enabling selective detection of paramagnetic species and discrimination of spin-rotation components originating from a single rotational level [5]. The wide spectral coverage of our recordings allowed for rapid identification of line series using Loomis-Wood diagrams [6], significantly facilitating the laboratory detection of these novel species, for which no prior rotational data existed in the literature. We will detail the instrumental developments and the methodology employed for the study of the rotational spectrum of these relatively large and heavy radicals.

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MILLIMETERWAVE CHIRPED-PULSE FOURIER TRANSFORM SPECTROSCOPY OF $BiBr_3$ BY LASER ABLATION IN A MULTIPASS CELL

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Millimeter-wave chirped-pulse Fourier transform spectroscopy (mmw CP-FT), laser ablation and multipass optics (MPO) are each well-established techniques in their own right and have already been used in various combinations, e.g. mmw CP-FT spectroscopy with laser ablation[1] or mmw CP-FT spectroscopy with MPO[2].

Here, we present a new approach using a combination of all three techniques to investigate heavy element containing chiral molecular species. For this kind of species, a small difference in the potential minimum between the left- and right-handed enantiomer can be expected due to parity violation effects. Phenyl bismuth dibromide would be a candidate molecule for this kind of study. However, as a preparatory work we investigate the achiral $BiBr_3$ which is easier to produce and has a less complex spectrum in the mmw region than the aforementioned chiral species.

With the combination of the three experimental methods, mmw CP-FT, laser ablation and MPO, we expect an increased sensitivity with respect to other experimental methods. The mmw CP-FT spectrometer is home build with a bandwidth of 100-112 GHz. The mmw radiation coherently excites the sample with a total of 10-26 passes in an area of 68.42 cm^2 -183.78 cm^2 dependant on the MPO configuration. The result of our experiments will be presented and discussed. In addition to the application presented here, the experimental setup can also be used for other purposes, e.g. to study other species formed by laser ablation. Furthermore, the molecule production scheme can be changed, and an electrical discharge source can be used instead of the laser ablation technique.

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A HIGH-PURITY PARA-H_2 SOURCE FOR THE STUDY OF COLD ION-MOLECULE CHEMISTRY

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The ability to control the translational motion of Rydberg atoms and molecules by Rydberg-Stark deceleration has enabled the study of several ion-molecule reactions at a broad range of low collision energies between $k_\mathrm{B} \cdot 0\,\mathrm{K}$ and $k_\mathrm{B} \cdot 50\,\mathrm{K}$.[1] In these studies, a molecule or atom in a Rydberg state of large principal quantum number, that is $n \approx 30$, is employed in place of the ion. The Rydberg electron takes a "spectator role"[2] and at the same time shields the ion from stray electric fields, which allows one to precisely control the collision energies. An ion-molecule reaction of special interest is the para-$\mathrm{H}_2^+(v^+ = 0, N^+ = 0) + \text{para-}\mathrm{H}_2(v = 0, N = 0) \rightarrow \mathrm{H}_3^+ + \mathrm{H}$ reaction because it is a good candidate to study quantum effects caused by the wave character of the collision system at low temperatures. In particular, owing to its low reduced mass and strong exothermicity, it is an ideal reaction to verify the theoretical prediction of a twofold reaction-rate enhancement over the classical Langevin rate, arising from s-wave scattering in the pure charge–induced-dipole interaction potential of the collision partners.[3] For the effects of quantum capture to become apparent in the $\mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H}$ reaction, the (para-)H_2 molecules need to be prepared in their rotational ground states where $N = 0$ because all states where $N \geq 1$ give rise to additional charge-quadrupole interactions.[4]

The observation of quantum capture in an ion-molecule reaction was the main objective of a recent experimental study of the $\mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H}$ reaction by Höveler *et al.*[5] However, an observation of the full twofold rate enhancement was hampered by the collision-energy resolution of their experiment and by the para:ortho ratio of about 80 %:20 % of their para-H_2 source. Here, we present a high-purity and continuous-flow para-H_2 source and its spectroscopic characterisation by laser-induced-fluorescence spectroscopy of B ← X transitions in H_2 using a vacuum-ultraviolet laser system. Our characterisation demonstrates that we can realise a molecular beam of H_2 in which the para-H_2 population fraction is larger than 99 %. Moreover, by cooling the reservoir of the H_2 valve to about 55 K, the population fractions in $N \geq 2$ rotational levels are suppressed to less than 1 %. This paves the way for a quantitative study of quantum capture in an ion-molecule reaction.

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[1] P. Allmendinger, J. Deiglmayr, O. Schullian, K. Höveler, J. A. Agner, H. Schmutz, and F. Merkt, "New method to study ion-molecule reactions at low temperatures and application to the $\mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H}$ reaction", *ChemPhysChem* **17,** 3596 (2016).

[2] F. B. V. Martins, V. Zhelyazkova, C. Seiler, and F. Merkt, "Cold ion chemistry within a Rydberg-electron orbit: test of the spectator role of the Rydberg electron in the $\mathrm{He}(n) + \mathrm{CO} \rightarrow \mathrm{C}(n') + \mathrm{O} + \mathrm{He}$ reaction", *New J. Phys.* **23,** 095011 (2021).

[3] E. Vogt and G. H. Wannier, "Scattering of ions by polarization forces", *Phys. Rev.* **95,** 1190 (1954).

[4] E. I. Dashevskaya, I. Litvin, E. E. Nikitin, and J. Troe, "Relocking of intrinsic angular momenta in collisions of diatoms with ions: capture of $\mathrm{H}_2(j = 0, 1)$ by H_2^+", *J. Chem. Phys.* **145,** 244315 (2016).

[5] K. Köveler, J. Deiglmayr, J. A. Agner, R. Hahn, V. Zhelyazkova, and F. Merkt, "Observation of quantum capture in an ion-molecule reaction", *Phys. Rev. A* **106,** 052806 (2022).

IMPROVING SPECTRAL ASSIGNMENT WITH NORMALIZING-FLOW COORDINATES

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Andrey Yachmenev[a]

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[b] Center for Ultrafast Imaging, Universität Hamburg
[c] Department of Physics, Universität Hamburg

Spectral assignment of rovibrational spectra links observed features to energy levels labeled by approximate quantum numbers. The approximate quantum numbers are the indexes of eigenfunctions and eigenvalues of a constructed effective Hamiltonian. This labeling relies on identifying coordinates that approximately separate the Hamiltonian into subsystems. For example, in the harmonic approximation, normal coordinates decouple the vibrational Hamiltonian into $3N-6$ independent modes. However, when anharmonicity is included the assignment becomes less direct, as energy levels no longer correspond directly to individual mode excitations. In general, assigning quantum numbers becomes increasingly difficult as the complexity of the computational model grows. This challenge is especially pronounced for delocalized vibrational states, such as those found in highly excited molecules, where calculating accurate spectra requires advanced models. In such cases, the wavefunctions show strong mode coupling, reflecting a suboptimal choice of coordinates that do not decouple the vibrational motions.

We introduce normalizing-flow vibrational coordinates[1,2], a new class of coordinates that can be tailored to a specific system and basis set. Similar to how spherical coordinates naturally simplify the hydrogen atom problem by embedding physical insight into the coordinate system, normalizing-flow coordinates offload complexity from the basis functions into the coordinates (See Figure). This shift improves basis set convergence, interpretability, and spectral assignment.

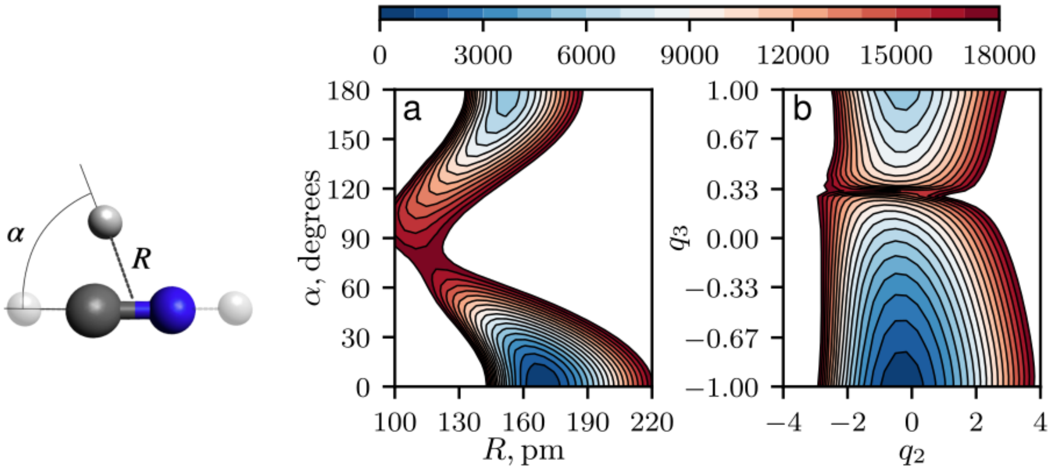

Figure 1: Potential energy surface cut of HCN/HCN in Jacobi (a) and normalizing-flows (b) coordinates. The color scale represents potential energy in cm^{-1}. The reduced anisotropy of the surface in the normalizing-flow coordinates leads to decoupled vibrations.

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[1] Y. Saleh, Á. Fernández Corral, E. Vogt, A. Iske, J. Küpper, A. Yachmenev, **2025**, *JCTC*, 21, 5221

[2] E. Vogt, Á. Fernández Corral, Y. Saleh, A. Yachmenev, **2025**, *arXiv:2502.15750*

CRAZY ACCURACIES FROM THE FIRST PRINCIPLE. LINE INTENSITIES AND LINE CENTERS

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The requirement to the accuracy of the line intensity by the users in astrophysics and planetary sciences increased recently from 1 % to 0.1 %. However, the requirements of the use in metrology, such as pressure measurements, temperature measurements or isotopologue abundance determination goes up to overwhelming 10^{-3} %.

In this talk we describe how we meet these unbelievable requirements. We demonstrate how we reached 0.009 % accuracy in CO 0-3 band line intensities calculations, order of magnitude better, than very high sub-promille accuracy of the recently published paper [1] . We show our progress in *ab initio* sub-percent accuracy of all CO bands. The mean accuracy of 0.3x10^{-3} % was achieved for the CO line intensities ratios of the 0-3 band. The details of the reaching such incredible accuracy experimentally are given in the abstract [2]. Here we give the details of the calculations.

We show, that the accuracy of the energy levels and corresponding wavefunctions far better than 10^{-3} cm^{-1} is necessary in order to achieve the needed line intensity accuracy. We prove, that our DVR3D code [3] solves the Schrödinger equation for the rovibrational energy levels of CO_2 molecule with the accuracy of up to 10 KHz (parts of 10^{-6} cm^{-1}). Using this program we fitted the potential energy surface (PES) of N_2O molecule with the standard deviation of the fit about 3x10^{-3} cm^{-1} which improves by several times the previously achieved accuracy of the PES. It allows us to reach the sub-percent accuracy of the line intensity calculations.

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[1] K. Bielska et.al, *Physical Review Letters*, **129**,043002,**(2022)**

[2] Jin-Ke Li, Jin Wang, Rui-Heng Yin, Qi Huang, Yan Tan, Chang-Le Hu, Yu R. Sun, Oleg L. Polyansky, Nikolai F. Zobov, Evgenii I. Lebedev, Rainer Stosch, Jonathan Tennyson, Gang Li, Shui-Ming Hu, this Conference

[3] J.Tennyson et al., *Computer Physics Communications*, **163**,p.85-116,**2004**

CALCULATIONS OF COLLISION-INDUCED LINE-SHAPE PARAMETERS FOR N_2-PERTURBED LINES IN HF

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

We report the results of the first fully quantum scattering calculations for the electric dipole R(0) 0-0 transition in HF perturbed by N_2. For our quantum scattering calculations we use the six-dimensional *ab initio* potential energy surface [1]. Close-coupling equations are solved using BIGOS - a computational package developed in our group [2,3], scattering S-matrices are used to calculate the generalized spectroscopic cross sections, which determine the speed-dependent collisional broadening and shift, and the Dicke effect parameters. We perform a detailed study of convergence of the obtained cross sections with respect to the size of the rotational basis set. Such investigations are important for populating spectroscopic databases.

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[1] Liu, Q., et al. **2020** *J. Chem. Phys.*, 152, 8

[2] Jóźwiak, H., et al. **2024** *A&A*, 685, A113

[3] Olejnik, A., et al. **2023** *J. Chem. Phys.*, 159, 134301

HYPERFINE ROVIBRATIONAL STATES OF H_3^+ IN A WEAK EXTERNAL MAGNETIC FIELD

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[b] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, 84536 Bratislava, Slovakia

Rovibrational energies, wave functions, and Raman transition moments are computed for the lowest-energy states of the H_3^+ molecular ion, including the proton spins' magnetic couplings and molecular rotation in the presence of a weak external magnetic field (Figure 1).[1] The rovibrational-hyperfine-Zeeman Hamiltonian matrix is constructed and diagonalised using the rovibrational eigenstates and the proton spin functions. The developed methodology can be used to compute hyperfine-Zeeman effects and higher-energy rovibrational excitations of H_3^+ (Figure 2).[2] These developments and computations have been carried out to guide future experiments extending quantum logic spectroscopy to polyatomic systems.

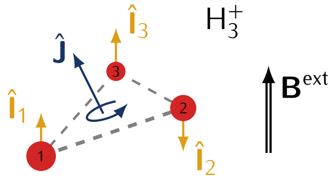

Figure 1: Proton spin and rotational angular momenta considered in this work for H_3^+.

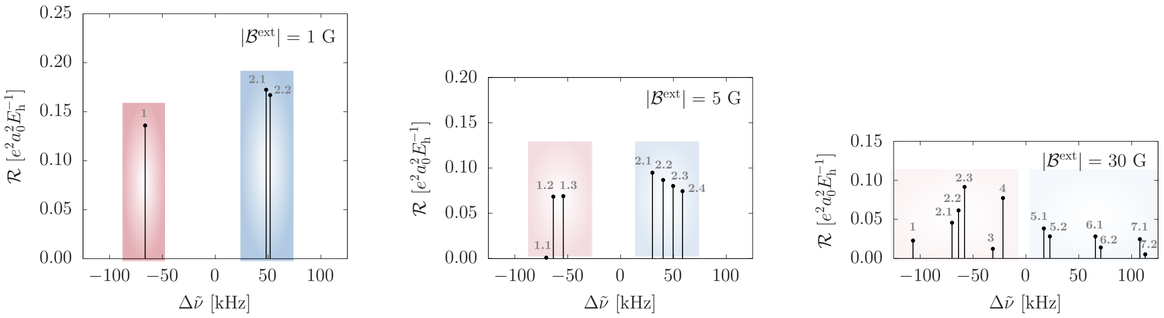

Figure 2: Computed Raman transition moments within the hyperfine-Zeeman manifold of the rovibrational ground state of H_3^+, $|1,1\rangle$ E'' (64.128 cm^{-1}).

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[1] G. Avila, A. Sunaga, S. Komorovsky, E. Mátyus **2025** *Phys. Rev. Lett.* (in press) doi:10.1103/lclp-852d
[2] G. Avila, E. Mátyus **2025** *Mol. Phys.* (Bačić Festschrift) arXiv:2504.21825

HIGH RESOLUTION X-RAY SPECTRA OF CH_2Cl_2 - A QUANTUM CHEMICAL SIMULATION

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Technická 6, 16200 Prague (Czech Republic)
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Technická 6, 16200 Prague (Czech Republic)

High-energy photons can induce several fundamental electronic processes, such as excitation of core electrons to unoccupied orbitals (X-ray absorption spectroscopy), ejection of core electrons (photoelectron spectroscopy), and various relaxation mechanisms including Auger decay (Auger electron spectroscopy)—where a valence electron fills a core hole and a second electron is emitted—as well as resonant Auger decay (RAES), in which AES can be performed also resonantly. By tuning the incident X-ray photon energy, specific transitions within the inner atomic shells of the observed molecule can be selectively probed. This enables detailed insights into the complete electronic structure of the species.

This study aims to provide *ab initio* simulated X-ray spectra across a wide range of excitation energies. Since this study concerns CH_2Cl_2, which contains heavy chlorine atoms, it is necessary to consider spin-orbit coupling and relativistic corrections. Special attention is devoted to reproducing experimental REAS spectra reported by A.C.F. Santos *et al.*[1,2], focusing not only on the position of spectral features but also on their relative intensities, with explicit consideration of spin-orbit coupling effects.

[1] Antonio C. F. Santos *et. al.*, Eur. Phys. J. D (2019) 73: 81; DOI: 10.1140/epjd/e2019-90625-y [2] Antonio C. F. Santos *et. al.*, Chem. Phys. 149, 054303 (2018); DOI: 10.1063/1.5030644

AN EXACT OMEGA REPRESENTATION AS AN ADIABATIC TRANSFORMATION OF SPIN-ORBIT INTERACTIONS AND THEIR ASSOCIATED NON-ADIABATIC COUPLINGS: COMMON MISCONCEPTIONS

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Removal of Spin-Orbit couplings (SO) for diatomic systems is a well established method which is thought to reduce the complexity of the system of study. This is done via diagonalisation of the associated Hamiltonian matrix with potential energy curves (PECs), transforming from the coupled $\Lambda - \Sigma$ (diabatic) basis to the Ω (adiabatic) representation where SO couplings vanish. This Ω–representation is thought to reduce the diatomic system to a desirable single state problem, which is simpler to treat and allows effective dipole moments to be computed for dipole-forbidden transitions. This method is widely used with the Level program[1]. However, transforming to the Ω–representation does not completely decouple the system, in fact, strong non-adiabatic couplings (NACs) are introduced upon transformation of the kinetic energy, often ignored, and bond-length dependence into the rotational kinetic energy, such as spin-uncoupling terms, which should be included. We show using our rovibronic code Duo[2] on selected diatomic systems that removal of SOC is not free, and omission of these "spin-orbit induced" NACs and bond-length dependent spin terms leads to gross errors into the rovibronic energies and intensities, unsuitable for high resolution spectroscopy. With the new Ω representation implemented in Duo, we demonstrate numerical equivalence between the $\Lambda - \Sigma$ 'diabatic' representation and Ω 'adiabatic' representation is achieved when all associated coupling terms are included. This is true for any unitary transformation on the diatomic Hamiltonian, *nothing is achieved for free and simplification of one part leads to the complication of another.*

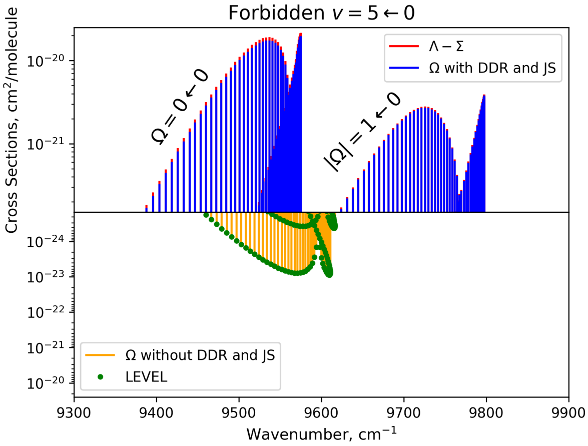

Figure 1: Comparison of computed spin-forbidden vibronic band intensities using the Λ–Σ (with spin-orbit coupling) and Ω (without spin-orbit coupling) representations in our rovibronic code Duo[2]. The top panel shows results from the Λ–Σ (blue) and Ω (red) representations, both including all coupling effects (e.g., nonadiabatic and spin-uncoupling terms), demonstrating excellent agreement between the two. The bottom panel compares single-state approximated band intensities calculated using the Level program[1] (green) and the Ω representation in Duo[2] (orange), with nonadiabatic and spin-uncoupling terms removed. Their remarkable agreement highlights that the common usage of the Ω representation (as implemented in Level[1]) can yield significantly shifted line positions and severely underestimated line intensities, potentially by several orders of magnitude.

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[1] R. J. Le Roy, LEVEL: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasi-bound Levels, 186, 167 (2017)

[2] S. N. Yurchenko, L. Lodi, J. Tennyson, and A. V. Stolyarov, Duo: A general program for calculating spectra of diatomic molecules, Comp. Phys. Comm. 202, 262 (2016).

AB INITIO LINE INTENSITIES OF ROVIBRATIONAL TRANSITIONS IN $O_2(X^3\Sigma_g^-)$

M. Gancewski[a], H. Jóźwiak[a], H. Cybulski[b], and P. Wcisło[a]

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[b] Faculty of Physics, Kazimierz Wielki University, al. Powstańców Wielkopolskich 2, Bydgoszcz, 85-090, Poland

As a homonuclear diatomic, $^{16}O_2$ does not posses a permanent electric dipole moment whence its microwave spectrum is due to magnetic dipole (*M1*) and electric quadrupole (*E2*) transitions. In the particular case of the ground electronic $X^3\Sigma_g^-$ term of O_2, the *M1* and *E2* transitions may occur both within the triplet fine structure of a given rotational energy level as well as between different rotational levels, in which case it is necessary to go beyond the common Hund's case (*b*) description and explicitly include the effect of rotational state-mixing by the electronic spin-spin interaction of the two valence electrons in O_2. Due to scarcity of accurate contemporary experimental data, *ab initio* calculations of *M1* and *E2* line intensities of $O_2(X^3\Sigma_g^-)$ [1,2] may serve not only as an aid in the interpretation of the new intensity measurements but also as a means towards populating the spectroscopic databases (such as HITRAN or EXOMOL) with reference results spanning many rotation-vibration transitions which may not be easily scrutinized by experiments. We discuss the non-adiabatic [3] and spin-induced [2] effects responsible for the *M1* and *E2* intensities of the rovibrational lines in $O_2(X^3\Sigma_g^-)$ and present the results of *ab initio* calculations concerning these lines. In particular, we report the new pure-rotational, overtone and hot-band *E2* intensities which will be incorporated in the new 2024 edition of the HITRAN database for O_2.

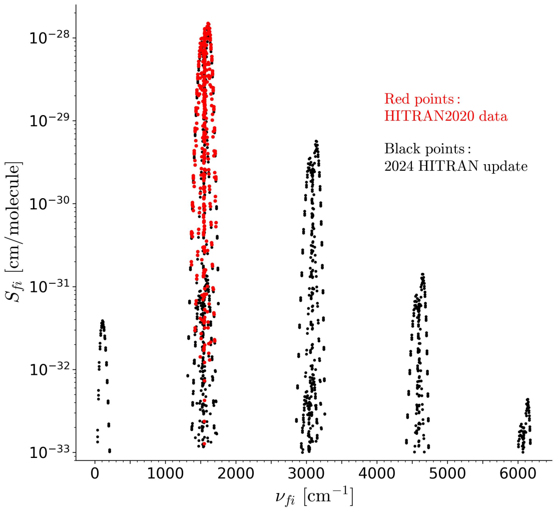

Figure 1: Example of the *ab initio* rovibrational electric quadrupole line intensities in $O_2(X^3\Sigma_g^-)$ included in the new 2024 edition of the HITRAN database.

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[1] W. Somogyi, S. N. Yurchenko and G-S. Kim, *Phys. Chem. Chem. Phys.* **26**, 27419 (2024)

[2] M. Gancewski, H. Jóźwiak, H. Cybulski and P. Wcisło, *J. Quant. Spectrosc. Radiat. Transf.* **337**, 109395 (2025)

[3] T. K. Balasubramanian, V. P. Bellary and K. N. Rao *Can. J. Phys.* **72**, 971 (1994)

VIBRATIONAL SPECTRA OF 3,4-DIMETHYLMETHCATHINONE (3,4-DMMC)

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In response to the growing number of new psychoactive substances (NPS), there is an urgent need for reliable methods of their detection and identification. In 2023 alone, 41 tonnes of NPS were seized under the European Warning System (EWS), 85 % of which were synthetic cathinones[1]. These compounds now represent the second most frequently seized class of drugs in the EU, following synthetic cannabinoids.

High-resolution spectroscopy occupies a unique position among analytical techniques due to its precision, making it invaluable both for detection and for understanding the internal structure of molecules. Structural differentiation between individual derivatives is essential, not only for their successful identification in forensic samples but also for the evaluation of their biological effects and regulatory classification.

In this study, high-resolution vibrational spectra of 3,4-DMMC hydrochloride crystals were measured and analyzed using both FTIR and Raman spectroscopy (200-3500 cm^{-1}). The experimental data were further supported by quantum chemical calculations, primarily using DFT-D3 methods. The resulting experimental and theoretical IR spectra are valuable additions to detection databases and enable spectral prediction of conformers of emerging synthetic drugs, particularly those not yet present in forensic libraries.

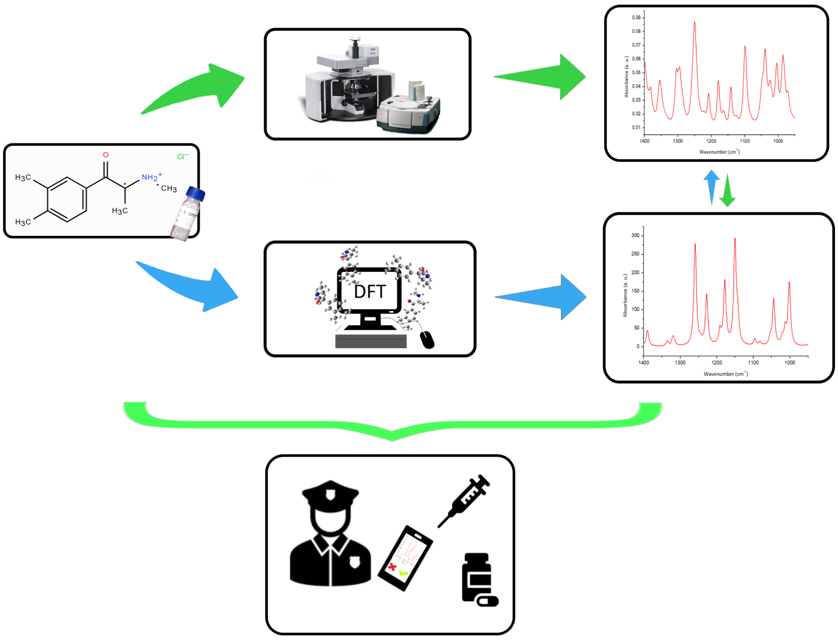

Figure 1: Workflow diagram

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[1] EUDA. **2024** *The EU Early Warning System monitors 1000 NPS*

ELECTRON SPIN-TORSION COUPLING IN THE OBLATE-TOP ACETONYL RADICAL

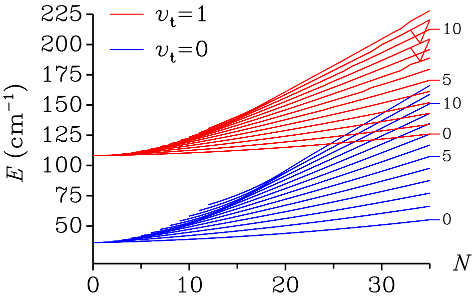
O. Pirali, R. Chahbazian, and L. H. Coudert

Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France

A recent spectroscopic investigation[1] of the (sub-)millimeter wave spectrum of the acetyl radical (CH_3CO), a benchmark system for non-rigid open-shell molecules displaying internal rotation, allowed us to evidence a new coupling referred to as the electron spin-torsion coupling. The present investigation deals with the analogous open-shell acetonyl radical ($CH_2C(O)CH_3$) which also displays a large amplitude torsional motion of its methyl group and which is a likely candidate for this new coupling. The acetonyl radical is however quantitatively different from the acetyl radical.

The (sub-)millimeter spectrum used in the present investigation has already been reported.[2] It was recorded in the 140 to 660 GHz range using a detection scheme based on Faraday rotation modulation which warrants an increased sensitivity for open shell species. In the ground $v_t = 0$ torsional state, more than 2000 transitions with $16 \leq N \leq 42$ have been assigned. In the $v_t = 1$ state, about 430 transitions have been tentatively assigned. In both torsional states, these transitions result from the combined effects of the torsional motion and of the fine interaction which lead to a splitting into four components. The fine interaction and torsional line splittings, on the order of 10 and 100 MHz, respectively, are well resolved in the experimental spectrum and are strongly dependent on the rotational quantum numbers.

The theoretical modeling of the spectrum makes use of the approach introduced for the acetyl radical.[1] However, the fact that the latter is a prolate-top species with $\kappa = -0.98$ while the acetonyl radical is an oblate-top with $\kappa = +0.21$ leads to qualitative differences. In the acetyl radical, a small asymmetry and an axis of internal rotation nearly parallel to the a-axis lead to well separated electron spin-rotation-torsion energy levels that can easily be assigned in terms of rotational, torsional, and spin quantum numbers. In the acetonyl radical, the large asymmetry leads to large matrix elements between torsional levels characterized by different values of k and v_t, and to a slow convergence of the energies when the size of the Hamiltonian matrix is increased. As evidenced by the figure on the right, showing the variations of the energy with the rotational quantum number N for different values of K_a, these couplings are expected to be dominant for $N \geq 25$. A straightforward level assignment will also no longer be possible.



In the poster the effects of the electron spin-torsion coupling[1] will be investigated. The results of line frequency analyses for transitions belonging to the ground $v_t = 0$ torsional state only and to both $v_t = 0$ and 1 will be presented. Work is still in progress and we are hoping to be able to assign and fit new transitions within the first excited $v_t = 1$ torsional state.

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[1] Coudert, Pirali, Martin-Drumel, Chahbazian, Zou, Motiyenko, and Margulès, *Phys. Rev. Letters* **134** (2025) 173001

[2] Chahbazian *et al.,* 77th ISMS conference, paper FB06; and *ibid., J. Phys. Chem. Lett.* **15** (2024) 9803

I: Plenary

Wednesday, August 27, 9:00
Hörsaal I

Chair: Thérèse Huet

HIGH RESOLUTION INFRARED SPECTROSCOPIES OF JET-COOLED LARGE MOLECULES RELEVANT FOR ASTRONOMICAL AND ATMOSPHERIC ISSUES

P. Asselin[a], S. Chawananon[a], O. Pirali[b], M. Goubet[c] and A. Cuisset[d]

[a]Sorbonne Université, MONARIS, CNRS, UMR 8233, 4 Pl Jussieu, F-75005 Paris, France. [b]Université de Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay, France. [c]Univ. Lille, CNRS, UMR8523 - PhLAM - Physique des Lasers Atomes et Molecules, F-59000 Lille, France. [d]Université du Littoral Côte d'Opale, UR4493, LPCA, Laboratoire de Physico-Chimie de l'Atmosphére, F-59140 Dunkerque, France.

High resolution (HR) infrared (IR) spectroscopy is essential to characterize the detailed energy level structures of molecules. Rotationally resolved spectra of larger molecular systems are more challenging to obtain, which require high intensity and tunable light sources to build high resolution and sensitive spectrometers to be coupled with cold and dense molecular gaseous environments. In the context of both increasing astronomical observations for the hunting of molecular organic complexes, and the urgent need to characterize biogenic volatile compounds as precursors of secondary organic aerosols (SOA) in our atmosphere, several low temperature HR IR studies of large molecules relevant for astrophysics and atmospheric chemistry are presented. Two complementary set-ups, a sensitive mid-IR QCL spectrometer coupled to a pulsed supersonic jet (SPIRALES) and a widely tunable HR Fourier transform IR spectrometer coupled to a continuous supersonic jet (Jet-AILES), have been exploited. About SOA precursors, an extended vibrational and conformational analysis of the different methoxyphenol isomers in both millimeter-wave, far- and mid-IR ranges as well as the first rovibrational study of the conformational landscape in the fingerprint region have been realized.[1] The extensive jet-cooled rovibrational study of *trans* and *cis* conformers of furfural produced a wealth of precise excited-state rotational parameters in the mid-IR range. The reconstruction of HITRAN vibrational cross-sections of fundamental bands by extrapolating the rovibrational data from low temperature HR analyses has enabled to quantify the dominant contribution of hot bands in the room temperature spectra.[2] Last, comprehensive rovibrational measurements of two-ring centrosymmetric Polycyclic Aromatic Hydrocarbons (PAH) have provided ground and excited states molecular parameters with an improved precision[3] while different levels of vibrational perturbations have been evidenced in high energy states of N-bearing PAHs (Fig.1).[4]

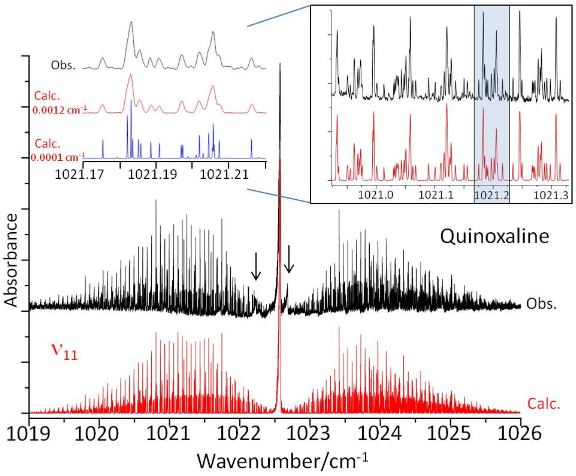

Figure 1: *Overall view of the ν_{11} band of quinoxaline : the SPIRALES spectrum in black ; the ν_{11} band simulated at a rotational temperature of 25 K using a Gaussian line shape of 0.0012 cm^{-1} FWHM in red.*

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[1] Asselin, P., Bruckhuisen, J., Roucou, A., Goubet, M., Martin-Drumel, M-A., Jabri, A., Belkhodja, Y., Soulard, P., Georges, R. and Cuisset, A., **2019** *J. Chem. Phys.*, 151, 194302.

[2] Chawananon, S., Goubet, M., Pirali, O., Georges, R., Roucou, A., Hadj Said, I., Senent, M-L., Cuisset, A. and Asselin, P., **2024** *J. Chem. Phys.*, 161, 014308.

[3] Chawananon, S., Pirali, O., Goubet, M., and Asselin, P., **2022** *J. Chem. Phys.*, 157, 064301.

[4] Chawananon, S., Pirali, O., Goubet, M., and Asselin, P., **2025** *Phys. Chem. Chem. Phys.*, 27, 5531.

MOLECULAR SPECTROSCOPY IN HELIUM NANODROPLETS NEW INSIGHTS AND OPPORTUNITIES

Wofgang E. Ernst[a]

[a] Institute of Experimental Physics, Graz University of Technology

Initially, it was the low temperature physics community that was fascinated by the helium clustering process and by fundamental questions about finite size superfluidity (for the history, see J. P. Toennies[1]), but soon the application of the 0.4 Kelvin cold helium droplets as “nanolab” and as low temperature and weakly interacting confinement for atoms and molecules started to gain interest[2]. Helium droplets were doped with foreign atoms and molecules that cooled down to the droplet temperature, thus allowing for a special matrix spectroscopy. Rotational and vibrational motion of dopants inside the droplets were almost unhindered. Evidence of the anticipated finite size superfluidity in helium droplets showed up as rather sharp rotational lines after molecular IR excitation, as collective helium roton modes in the phonon wings of spectral lines, and as vortices in diffraction, all detected via measurements on doped droplets.

Due to the low temperature and small helium interaction, weak van der Waals bonds can be formed among dopants and otherwise unstable molecular conformations are observed and spectroscopically investigated[3]. Numerous nanolab applications in a widening helium community have allowed new spectroscopy in the frequency and time domains, aggregation of weakly bound clusters, creation of tailored nanoparticles[4,5], cold reaction dynamics, and more. While electronic excitation spectra of atoms and molecules show strong broadening because of the Pauly repulsion between the dopant electron orbitals and the helium closed shell environment, some of the resulting interpretation problems can be overcome by multiple resonance and by accompanying model calculations.

In this lecture, I will present examples of electron spin transitions in alkali atoms on helium droplets at high resolution, Rydberg state excitation of alkali electrons into orbitals surrounding the helium droplet, and spin relaxation of excited transition metals. In spectra of high spin dimers and trimers effects of spin-orbit coupling and vibronic interaction could be separated by additional application of external magnetic fields, and the electronic spectra of alkali – alkaline earth diatomics were successfully analyzed with the help of high-level quantum chemistry calculations. Femtosecond pump-probe measurements allowed to follow the collective oscillations of the helium density around a laser excited dopant atom. An outline of future opportunities will be given.

Acknowledgement: Special thanks go to Markus Koch and Andreas W. Hauser for many years of excellent collaboration.

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[1] J. Peter Toennies, "Helium Nanodroplets: Formation, Physical Properties and Superfluidity", chapter 1 in: Molecules in Superfluid Helium Nanodroplets (eds. Alkwin Slenczka and Jan Peter Toennies), Springer Topics in Applied Physics Vol. 145 **2022**.

[2] K. K. Lehmann and G. Scoles, "The Ultimate Spectroscopic Matrix?" **1998** Research Commentary in *Science* 279, 2065-2066.

[3] C. Callegari and W. E. Ernst, “Helium Droplets as Nanocryostats for Molecular Spectroscopy—from the Vacuum Ultraviolet to the Microwave Regime” in: Handbook of High-Resolution Spectroscopy, Eds. F. Merkt and M. Quack, 1st Edition, Vol. 3, p. 1551-1594, John Wiley & Sons, Chichester **2011**.

[4] W. E. Ernst and A. W. Hauser, Metal Clusters Synthesized in Helium Droplets: Structure and Dynamics from Experiment and Theory, Perspective Article, **2021** *PCCP*, 23, 7553-7574.

[5] M. Alešković, J. Alić, W. E. Ernst, and Marina Šekutor, Self-Assembly of Diamondoid Clusters in Helium Nanodroplets Driven by Non-Covalent Interactions **2025** short review submitted to *Journal of Organic Chemistry.*

J-I: Contributed Talks

Wednesday, August 27, 11:00
Hörsaal I

Chair: Silvia Spezzano

INVESTIGATING ENOLS CHEMISTRY IN THE INTERSTELLAR MEDIUM: ROTATIONAL SPECTROSCOPY AND INTERSTELLAR SEARCH OF (*E*)-1-PROPENOL

M. Nonne[a,b], M. Melosso[b], F. Tonolo[b,c], L. Bizzocchi[b], S. Alessandrini[b], J.-C. Guillemin[d], V. M. Rivilla[e] and C. Puzzarini[b]

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[b] Dipartimento di Chimica “Giacomo Ciamician”, Università di Bologna, via F. Selmi 2, 40126 Bologna, Italy
[c] Université de Rennes, CNRS, IPR (Institut de Physique de Rennes) – UMR 6251, 35000 Rennes, France
[d] Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR–UMR6226, 35000 Rennes, France
[e] Centro de Astrobiología (CSIC-INTA), Ctra. de Ajalvir Km. 4, Torrejón de Ardoz, 28850 Madrid, Spain

Enols represent a significant class of Complex Organic Molecules[1] as they are highly reactive intermediates potentially involved in the formation of interstellar bio-molecules and in the non-equilibrium chemistry occurring on the interstellar icy grains under the influence of Galactic Cosmic Rays[2]. Propenol belongs to this class and is considered a promising candidate for a future astronomical detection. In this context, we report the spectroscopic characterization and astronomical search of (*E*)-1-propenol ($CH_3CH{=}CHOH$). The pure rotational spectrum was recorded across several frequency ranges, namely between 80-115 GHz, 170-230 GHz, 240-345 GHz and 330-500 GHz, using a millimeter/submillimeter-wave frequency-modulation spectrometer. Accurate quantum chemical calculations enabled a reliable estimation of the spectroscopic parameters, including the torsional potential relative to the internal rotation motion of the methyl group, which causes the splitting of transitions into a non-degenerate (A) component and a doubly-degenerate (E) component. This allowed the correct identification and assignment of the experimental transitions as shown in Figure 1. The overall analysis led to an accurate spectroscopic characterization and an astronomical search towards the Galactic Center molecular cloud G+0.693-0.027. No unambiguous transitions attributable to (*E*)-1-propenol were identified. The derived column density upper limit ($N < 2.2 \times 10^{13}\,\mathrm{cm}^{-2}$) is fully consistent with the expected abundance ($N = (6.4-8) \times 10^{12}\,\mathrm{cm}^{-2}$) estimated by taking into account other aldehyde/enol ratios in the same source, suggesting that a higher sensitivity of the observations is required to detect this species.

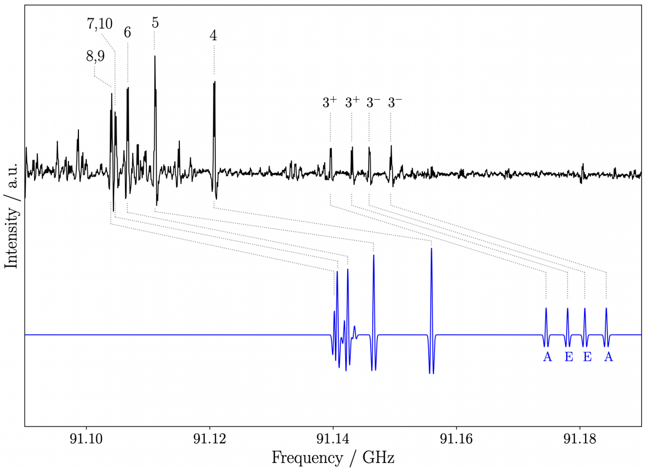

Figure 1: Portion of experimental millimeter-wave spectrum (black trace) compared with the simulated one (blue trace) based on quantum chemical calculations in the frequency range between 91.09 and 91.19 GHz.

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[1] E. Herbst and E. F. Van Dishoeck, **2009** *Annu. Rev. Astron. Astr.*, 47, 427-480.

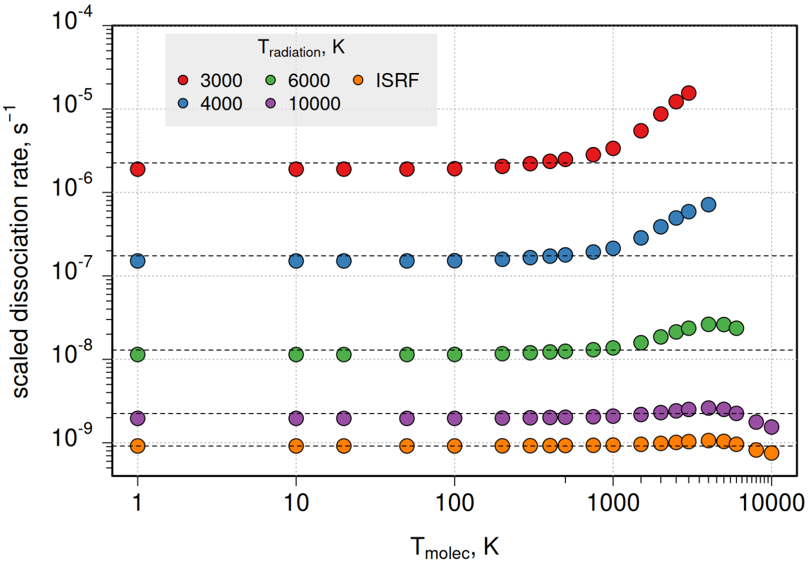
[2] Abplanalp M.J. et al., **2016** *Procl. Natl. Acad. Sci U S A*, 113, 28, 7727-7732.

TEMPERATURE-DEPENDENT PHOTODISSOCIATION RATES OF THE CH RADICAL

A. Sokolov, R. P. Brady, S. N. Yurchenko, and J. Tennyson

Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT
London, United Kingdom

Understanding of photodissociation rates is essential for chemical modeling in various astrophysical environments, particularly in UV-rich regions such as the interstellar medium and exoplanetary atmospheres[1]. Conventional models often assume 0 K conditions for the molecules, which may be insufficient for high-temperature systems and non-LTE environments. To address this, novel temperature-dependent approaches have been proposed for the calculation of dissociation rates and photoabsorption spectra[2]. In this work, we are using new electronic structure data for CH[3] combined with experimental lifetimes measurements and computational tools like Duo[4] and Exocross[5] to generate updated, temperature-dependent photodissociation rates and photoabsorption spectra. Our results are compared with the Leiden database data for CH[6,7] and can be used in astrophysical models, particularly those targeting hot carbon-rich environments.



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[1] Heays et al., 2017, 10.1051/0004-6361/201628742
[2] Pezzella et al., 2021, 10.1039/D1CP02162A
[3] Hou and Liu, 2024, 10.1039/D4CP03298E
[4] Yurchenko et al., 2016, 10.1016/j.cpc.2015.12.021
[5] Yurchenko et al., 2018, 10.1051/0004-6361/201732531
[6] Van Dishoeck, 1987, 10.1063/1.452610
[7] Hrodmarsson and Van Dishoeck, 2023, 10.1051/0004-6361/202346645

ROTATIONAL SPECTROSCOPY OF NAPHTHYLAMINES

Gayatri Batra[a,b], Colin Sueyoshi[c], Wenhao Sun[a], Mark D. Marshall[c], Helen O. Leung[c], Marie-Aline Martin-Drumel[d], Melanie Schnell[a,b]

[a] Deutsches Elektronen-Synchrotron DESY
[b] Christian-Albrechts-Universität zu Kiel
[c] Amherst College, Massachusetts
[d] Université Paris-Saclay, CNRS

Polycyclic aromatic hydrocarbons (PAHs) are widespread throughout the interstellar medium (ISM), where they serve as major carriers of aromatic infrared bands and represent a significant reservoir of cosmic carbon. Recent advances in radio astronomy have enabled the detection of various PAHs, such as cyano-substituted naphthalene[1] and indene[2], and many more are underway. Furthermore, PAHs are often embedded in ice[3], where they potentially undergo UV-catalyzed reactions with water and ammonia, *etc.* potentially leading to the formation of more complex organic species.

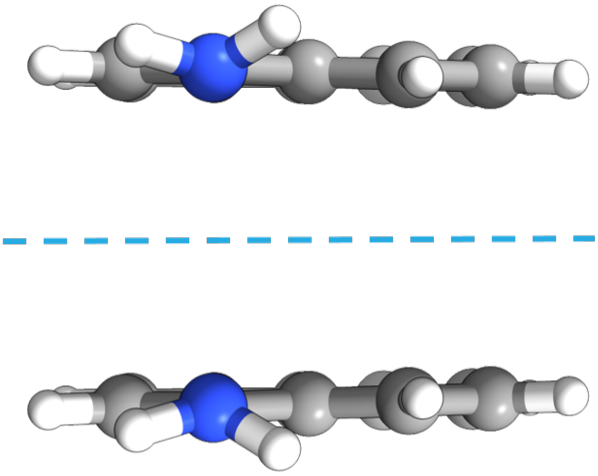

Figure 1: Depiction of the inversion motion of amino hydrogen atoms

In this study, we present a comprehensive rotational spectroscopic analysis of the two isomers of naphthylamine, 1- and 2-naphthylamine, with particular attention to their molecular structures. The rotational spectra were recorded using the COMPACT spectrometer in the 2–18 GHz range. Quantum chemical calculations at the B3LYP-D3/def2-QZVP level predict both isomers to adopt non-planar geometries, with a calculated dipole moment component μ_c of 0.85 D; however, no *c*-type transitions were observed experimentally. Our findings are compared with the microwave study of aniline by Lister and Tyler (1974)[4], where they attributed the non-planar structure of the naphthylamine to the inversion motion of the amino hydrogens. Using a Nudged Elastic Band (NEB) approach, we estimate the barrier to this inversion motion in naphthylamines to be approximately 4 kJ/mol. Upon analysis of the high-frequency rotational spectra at room temperature, we were able to assign the split transitions (0^+ and 0^-) caused by the inversion motion of the amino hydrogens.

The rotational constants, along with resolved nuclear quadrupole coupling constants determined for both naphthylamine isomers, along with the generated spectral line lists, provide valuable data for future astronomical searches and may facilitate the identification of these nitrogen-containing PAHs in the ISM.

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[1] B. A. McGuire, et al., *Science*, **2021**, 371, 1265–1269

[2] M. L. Sita, et al., *The Astrophysical Journal Letters*, **2022**, 938, L12

[3] Burke and Brown et. al., *Physical Chemistry Chemical Physics*, **2010**, 12, 5947–5969

[4] DG Lister et al. *Journal of Molecular Structure*, **1974**, 23, pp. 253–264.

A MULTI-LEVEL EXCITATION DIAGRAM ANALYSIS OF VIBRATIONALLY EXCITED TiO IN THE ENVELOPE OF THE VARIABLE STAR χ CYG AT HIGH SPECTRAL RESOLUTION

E. Döring[a], J. H. Lacy[b], R. S. Giles[c], T. K. Greathouse[c], T.F. Giesen[a] and G. W. Fuchs[a]

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[b] The University of Texas at Austin, 2515 Speedway Stop C1400 Austin, Texas 78712-1205, USA
[c] Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78238, USA

Mira-type variables are intermediate mass late-type stars with a significant mass loss resulting in the formation of small molecules and dust outside the stellar atmosphere. The TiO molecule is thought to play an important role in the dust formation and contributes to the opacity of χ Cyg[1]. We have observed the TiO (titanium monoxide) molecule in the vicinity of the S-type AGB (asymptotic giant branch) star χ Cyg using the high-resolution spectrograph TEXES (Texas Echelon Cross Echelle Spectrograph) [R =100,000] at the IRTF (Infrared Telescope Fascility) on Mauna Kea, Hawai'i. Our aim was to observe the star at several stellar phases in order to study the dynamics of the inner molecular shell and to determine the excitation temperatures and abundances of the TiO molecule. Combined with our analysis of the TiO molecule around 10 µm[2], and the development of the new Multi-Level Excitation Diagram method, this enabled a detailed study of the abundances and excitation states of TiO in the molecular envelope surrounding the star. Over a period of three years, TiO spectra around 970 cm^{-1} were analyzed across various stellar phases, revealing a clear phase dependence of the observed TiO lines.

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[1] Reid,M.J & Peek, J.E.G. **2002** *Astrophys. J.*,568, 931

[2] Witsch, D., Döring, E., Breier, A. A., *et.al.* **2021** *J. Mol. Spectros.*, 377, 111439.

SIMULATING SOLAR WIND–PAH COLLISIONS: A NEW PERSPECTIVE ON SMALL HYDROCARBON CATION FORMATION IN ASTROPHYSICAL ENVIRONMENTS

E. Dudás[a], P. Moretto-Capelle[a], M. Rapacioli[b] and J-P. Champeaux[a]

[a] Laboratoire Collisions Agrégats Réactivité
[b] Laboratoire de Chimie et Physique Quantiques

Recent observations by the James Webb Space Telescope using its high-resolution and high-sensitivity instruments have revealed the presence of small hydrocarbon cations, such as $CH_3{}^+$ in a proto-planetary disk within the Orion star-forming region[1]. While this small hydrocarbon cation has been detected with confidence, explanations of its origins under interstellar conditions are currently insufficient.[2] Concurrently, the presence of cationic polycyclic aromatic hydrocarbons (PAHs) has been reported as well.[3]

In this study, we explore an alternative formation pathway of $CH_3{}^+$ by experimentally imitating the interaction between solar wind particles and a representative PAH, namely methylpyrene ($C_{17}H_{12}$). The investigation is conducted using the SWEET experimental platform[4], which combines a custom-built, pulsed time-of-flight mass spectrometer with a velocity map imaging (TOF-VMI) system. By employing electron and proton beams as controlled proxies for solar wind particles, we probe the collision-induced dissociation dynamics of methylpyrene using single collision event-by-event multiple correlation spectroscopy.
This technique allows for precise, energy-resolved detection of charged fragments, providing both qualitative and quantitative insights into the dissociation process. In addition, our experimental results are compared to molecular dynamics simulations using Density Functional based Tight Binding (DFTB) potential. Our approach directly addresses key challenges—including unknown fragmentation pathways, the energy resolution of the interactions, and the correlation of products on an event basis—and contributes to a more comprehensive understanding of ion formation mechanisms relevant to astrophysical environments.

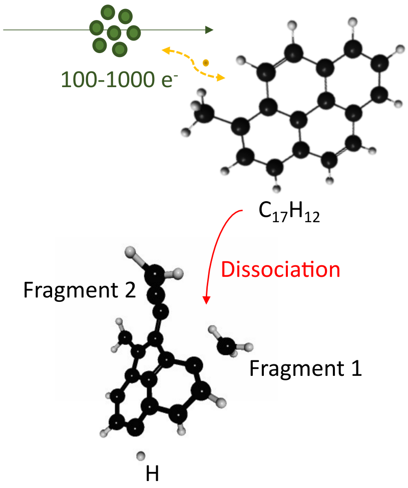

Figure 1: Collision induced dissociation

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[1] Berné, O., Martin-Drumel, MA., Schroetter, I. et al. **2023** *Nature*, 621, 56-59.

[2] Herbst E. **2021** *Frontiers in Astronomy and Space Sciences*, 8, 776942.

[3] Knight C. et al. **2021** *Monthly Notices of the Royal Astronomical Society*, 509, 3523–3546.

[4] J. P. Champeaux, P. Moretto-Capelle, J. Renoud et al. **2023** *Physical Chemistry Chemical Physics*, 25, 15497-15507.

VIBRONIC AND OVERTONE BANDS OF HNC$^+$ AND HCN$^+$

M. Jiménez-Redondo[a], J. Palotás[b], H. A. Bunn[a], C. Schleif[a], P. Dohnal[c], O. Roncero[d], P. Caselli[a], and P. Jusko[a]

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[b] School of Chemistry, University of Edinburgh, Joseph Black Building, Kings Buildings, David Brewster Road, Edinburgh, EH9 3FJ, UK
[c] Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, Prague 18000, Czech Republic
[d] Instituto de Física Fundamental, CSIC, C/ Serrano 123, 28006 Madrid, Spain

HCN and HNC, one of the simplest pairs of molecular isomers, are ubiquitous in the interstellar medium[1]. They play an important role in astrochemistry along with their corresponding ions, HCN$^+$ and HNC$^+$. The low energy ionic isomer is HNC$^+$, unlike in the case of the neutral species, with HCN$^+$ lying 0.98 eV higher in energy, and an estimated isomerization barrier of 2.1 eV between them. The two isomers present significant differences in their electronic structure, with a low-lying first excited electronic state $A^2\Sigma^+$ in HCN$^+$ (3260 cm^{-1}) compared to the $A^2\Pi$ state in HNC$^+$ (14300 cm^{-1}).

In this work, we use a cryogenic ion trap to study the electronic and vibrational transitions of HNC$^+$ and HCN$^+$. HCN$^+$ ions are produced in a storage ion source from a mixture of HCN and He and then trapped and correspondingly isomerized to HNC$^+$ by collisions with CO$_2$ molecules. For HNC$^+$, 18 lines from the P and R branches of the $2\nu_1$ overtone band (NH stretch) were observed using a laser-induced reaction action scheme in the infrared (IR) around $\sim$ 6700 cm^{-1}. The same technique was used in the visible region to observe the $X^2\Sigma^+ \rightarrow A^2\Pi$ electronic transition of this ion, and the results have been interpreted with the help of wave-packet calculations. For HCN$^+$, the IR region between $\sim$ 6290 and 6370 cm^{-1} was scanned to observe the $X^2\Pi$, $\nu = 0 \rightarrow A^2\Sigma^+$, $\nu_1 = 1$ vibronic transition (CH stretch), sampling a total of 109 lines using the recently developed leak-out spectroscopy technique[2].

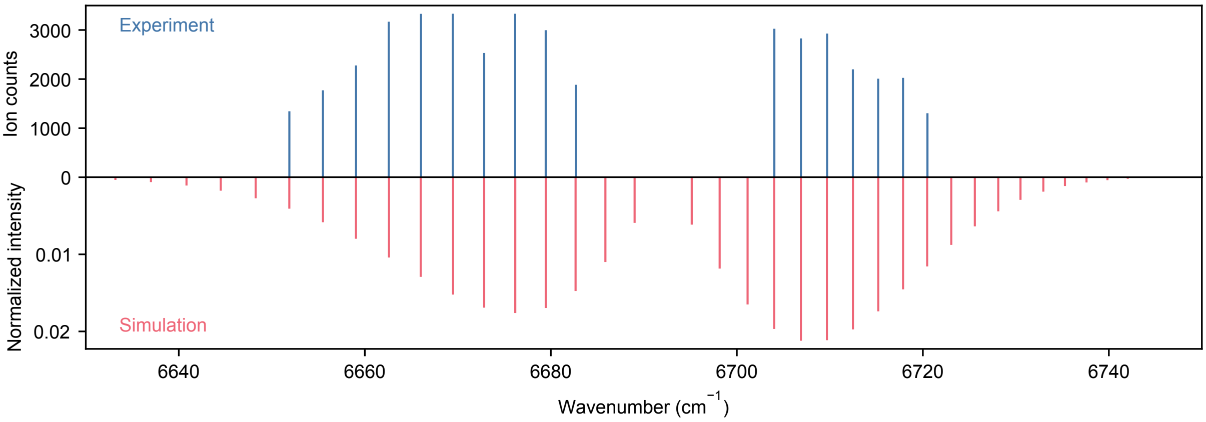

Figure 1: Experimental and simulated absorption spectra of the $2\nu_1$ overtone band of HNC$^+$.

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[1] Loison, J.-C., Wakelam, V. and Hickson, K.M. **2014** *MNRAS*, 443, 398

[2] Schmid, P.C., Asvany, O., Salomon, T., Thorwirth, S. and Schlemmer, S. **2022** *J. Phys. Chem. A*, 126, 8111

J-II: Contributed Talks

Wednesday, August 27, 11:00
Hörsaal II

Chair: Wim Ubachs

CRYOGENIC OPTICAL CAVITY FOR HIGH-ACCURACY DOPPLER-LIMITED SPECTROSCOPY OF HYDROGEN

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

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

We demonstrate the first cavity-enhanced spectrometer fully operating in a deep cryogenic regime down to 4 K.[1] Not only the sample but the entire cavity, including the mirrors and cavity length actuator, is uniformly cooled down ensuring the thermodynamic equilibrium of the gas sample. The setup is designed in a way that efficiently attenuates both external vibrations and those originating from the cryocooler itself ensuring stable operation of the optical cavity. Thermodynamic equilibrium and high tunability of pressure, temperature as well as high tunability of wavelength by implementation of an optical parametric oscillator, opens the way to a variety of fundamental and practical applications.

We performed accurate Doppler-limited spectroscopy of the S(0) 1-0 line in molecular hydrogen, achieving accuracy at the level of 10^{-6}cm^{-1}. We optically measured a part of the H_2 phase diagram covering over three orders of magnitude in pressure.[2] This considerably improves the accuracy of the previous best p(T) curve. Using optical methods, we also determined the conversion dynamics of the ortho-para H_2 spin isomers with high temporal resolution.

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[1] M. Słowiński, M. Makowski, K. L. Sołtys, K. Stankiewicz, S. Wójtewicz, D. Lisak, M. Piwiński, P. Wcisło, **(2022)** *Rev. Sci. Instrum. 93*, 115003

[2] K. Stankiewicz, M. Makowski, M. Słowiński, K.L. Sołtys, B. Bednarski, H. Jóźwiak, N. Stolarczyk, M. Narożnik, D. Kierski, S. Wójtewicz, A. Cygan, G. Kowzan, P. Masłowski, M. Piwiński, D. Lisak, and P. Wcisło, *Cavity-enhanced spectroscopy in a deep cryogenic regime; new hydrogen technologies for quantum sensing*(manuscript in preparation)

HIGH PRECISION MID-INFRARED VIBRATIONAL SPECTROSCOPY WITH COLD MOLECULES

R. Hahn[a], A. Bonifacio[a], M. Saffre[a], W. Dong[a], Y. Liu[a], S. Viel[a], M. N. Ngo[a], O. Lopez[a], E. Cantin[a], A. Amy-Klein[a], M. Manceau[a], B. Darquié[a]

[a] Laboratoire de Physique des Lasers, CNRS, Université Sorbonne Paris Nord, 93430
Villetaneuse, France

There is an increasing demand for precise molecular spectroscopy, in particular in the mid-infrared (MIR) fingerprint window, to feed atmospheric models, to interpret astrophysical spectra or to test fundamental physics. Our approach to tackle this problem encompasses, amongst other things: the production of gases of polyatomic species cooled to a few kelvins in cryogenic buffer-gas cells[1]; the development of high-quality laser sources that are spectrally narrow, broadly tunable, stabilised and ultimately referenced to some of the world's best frequency standards[2,3]; exploring the opportunities offered by cutting-edge mid-IR photonics technologies: new detectors (see figure 1), modulators, and laser sources.

I will present our efforts towards building new-generation mid-infrared spectrometers for precision vibrational spectroscopy of complex polyatomic molecules in the gas phase around 10 µm, but also extensions to around 6 µm, 8-12 µm, and 17 µm[4,5,6,7,8,9]. These developments have allowed sub-Doppler spectroscopy of a variety of species of atmospheric, astrophysical, metrological or fundamental interest and measurements of absolute frequencies with record 12 digit accuracies[10,11].

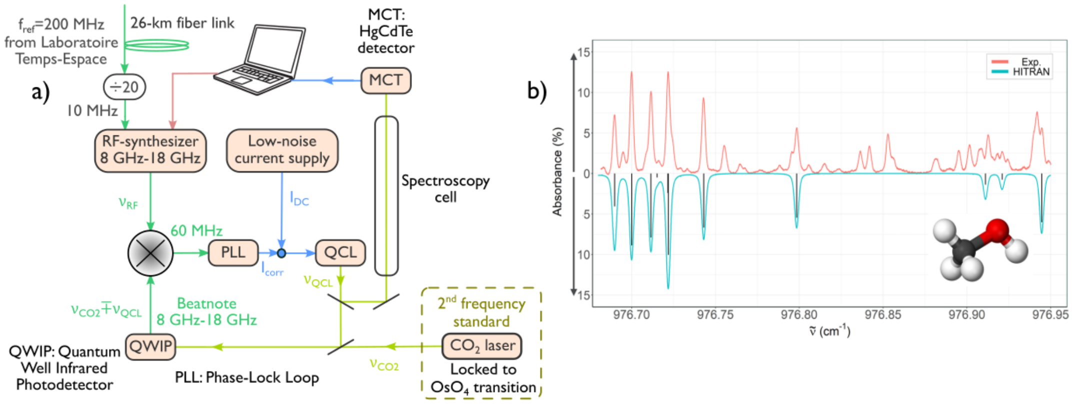

Figure 1: a) Schematic of the setup used to scan a Quantum Cascade Laser (QCL) referenced to a secondary frequency standard continuously over 10 GHz thanks to a novel large-bandwidth Quantum Well Infrared Photodetector (QWIP) b) Example spectrum of methanol (in red) recorded with the setup in a). A simulated spectrum using the HITRAN database is represented in blue.

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[1] Tokunaga *et al.*, *New J Phys* **19**, 053006 (2017)
[2] Argence *et al.*, *Nature Photon* **9**, 456 (2015)
[3] Santagata *et al.*, *Optica* **6**, 411 (2019)
[4] Chomet *et al.*, *Appl Phys Lett* **122**, 231102 (2023)
[5] Dely *et al.*, *Opt Express* **31**, 30876 (2023)
[6] Manceau *et al.*, arXiv:2310.16460 (2023)
[7] Saemian *et al.*, *Nanophotonics* **13**, 10 (2024)
[8] Chomet *et al.*, *Optica* **11**, 1220 (2024)
[9] Wang *et al.*, *New J Phys* **27**, 023038 (2025)
[10] Tran *et al.*, *APL Photonics* **9**, 030801 (2024)
[11] Tran *et al.*, arXiv:250208201 (2025)

INELASTIC RECOIL SPECTROSCOPY: ROTATIONALLY RESOLVED SPECTROSCOPY OF A SINGLE POLYATOMIC MOLECULE

A.Calvin, S. Kresch, M. Brzeczek, L. Satterthwaite, D. Patterson

Department of Physics, University of California, Santa Barbara

Ion traps present a powerful platform for precision spectroscopy of molecular ions. In particular, molecular spectroscopy in mixed-species Coulomb crystals, composed of a molecular ion and laser-cooled atomic ion, affords a level of exceptional molecular control that in turn leads to long interrogation times and unparalleled spectroscopic resolution. These techniques are actively investigated for applications in testing fundamental physics, *ab initio* theory, cold reactions, and chemical dynamics. Within this framework, we demonstrate the method of inelastic recoil spectroscopy (IRS), a technique that offers a complementary approach that combines the generality of leak-out spectroscopy with a resolution approaching that of quantum logic spectroscopy.

Recent demonstrations of IRS include vibrational spectra of polyatomic ions such as tropylium and protonated diacetylene[1], and more recently, the first fully rotationally resolved spectrum of a polyatomic ion (c-$C_3H_3^+$) with a linewidth of 23 MHz, limited only by the first-order Doppler width of the cold (∼15 K) molecular ions[2].

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[1] A. Calvin, S. Eierman, Z. Peng, M. Brzeczek, S. Kresch, E. Lane, L. Satterthwaite, and D. Patterson, *Nondestructive inelastic recoil spectroscopy of a single molecular ion: A versatile tool toward precision action spectroscopy*, Phys. Rev. A **108**, 062819 (2023).

[2] A. Calvin, S. Kresch, M. Brzeczek, E. Lane, L. Satterthwaite, D. Hawkins, and D. Patterson, *Rotationally Resolved Spectroscopy of a Single Polyatomic Molecule*, Phys. Rev. Lett. **134**, 153002 (2025).

DETECTION AND QUANTIFICATION OF HNC AND HCN ISOMERS IN MOLECULAR PLASMAS REVEALED BY FREQUENCY COMB AND QCL SPECTROSCOPY

I. Sadiek[a], Simona Di Bernardo[a,c,d], Uwe Macherius[b], and Jean-Pierre H. van Helden[a]

[a] Faculty of Physics and Astronomy, Ruhr University Bochum, 44780 Bochum, Germany
[b] Leibniz Institute for Plasma Science and Technology (INP), 17489 Greifswald, Germany
[c] Department of Mathematics and Physics, University of Campania “Luigi Vanvitelli”, 81100 Caserta, Italy
[d] Italian Aerospace Research Centre (CIRA), 81043 Capua, Italy

Hydrogen isocyanide (HNC), the high-energy isomer of hydrogen cyanide (HCN), plays a central role in interstellar and reactive plasma environments, yet its presence and significance in low-temperature molecular plasmas remain poorly understood. We report on the first unambiguous detection and quantification of HNC in $N_2/H_2/CH_4$ nitrocarburizing plasmas via its fundamental ν_3 band around 2081 cm^{-1}, using high-resolution quantum cascade laser spectroscopy. Simultaneously, the spectrum of the HCN isomer was recorded on its fundamental ν_1 vibration in the range 3180-3400 cm^{-1}, using broadband mid-infrared frequency comb absorption spectroscopy.[1] Spectral identification of HNC is validated against the ExoMol and GEISA molecular databases. The observed HNC/HCN ratios, in the range $(1.12–2.73) \times 10^{-4}$, are orders of magnitude lower than the near-unity values typical in cold interstellar clouds. This disparity points to fundamentally different formation kinetics in plasma environments, involving vibrationally excited HCN*/HNC* intermediates and fast relaxation or destruction pathways, in contrast to the long-lived cold-ion chemistry dominant in space. Our kinetic modeling further reveals the key processes—formation, relaxation, isomerization, and interconversion—that govern the observed low isomeric ratio. When correlated with experimental parameters such as gas composition, pressure, and pulsed plasma conditions, the resulting HNC/HCN ratio emerges as a sensitive diagnostic tool for optimizing plasma-assisted synthesis and materials processing.

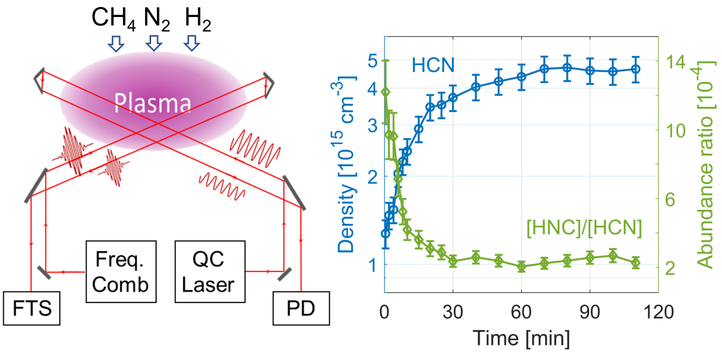

Figure 1: (Left) Simultaneous detection of plasma-generated species using comb and QCL spectroscopy. (Right) Measured accumulated HCN (blue) and determined [HNC]/[HCN] abundance ratio (green) as a function of time.

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[1] Sadiek, I., Puth, A., Kowzan, G., Nishiyama, A., Klose, S.-J., Röpcke, J., Lang, N., Masłowski, P., van Helden, J.-P. H., **2024** *Plasma Sources Sci. Technol.* 33, 075011.

HIGH RESOLUTION SPECTROSCOPY OF $PF^{35}Cl_2$ AND $PF^{35}Cl^{37}Cl$ AND ISOTOPIC CHIRALITY

V. Horká-Zelenková[a], K. Keppler[b], A. Sieben[b], G. Seyfang[b], G. Wichmann[b],
S. Albert[b], J. Stohner[c], and M. Quack[b]

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The concept of isotopic chirality is of fundamental scientific interest, as it introduces a new isotope effect arising from the parity-violating weak nuclear force[1,2,3]. Molecules such as $PF^{35}Cl^{37}Cl$, which are chiral purely due to isotopic substitution, are predicted to exhibit a parity-violating energy difference $\Delta_{\mathrm{pv}}E$ between enantiomers. This is due to the different weak nuclear charges of the isotopes with unequal numbers of neutrons, which affect the parity violating potentials. For $PF^{35}Cl^{37}Cl$, $\Delta_{\mathrm{pv}}E$ is theoretically predicted to be about ≈ 3.5 aeV [3], whereas without parity violation $\Delta_{\mathrm{pv}}E$ would be exactly zero by symmetry. Although very small, this difference is in principle measurable in special experiments[4], although no successful experiment exists until today.

In this study, we take a first step towards such measurements by analyzing rovibrationally resolved high-resolution infrared spectra of $PFCl_2$ isotopomers. Spectra were recorded using two complementary techniques: (i) at room temperature with our Bruker IFS 125HR Zürich Prototype Fourier Transform Infrared (FTIR) spectrometer (650–1000 cm^{-1}, resolution 0.0015 cm^{-1}), and (ii) under supersonic jet expansion conditions (T = 20–30 K) using a tunable diode laser spectrometer in the regions 830–834 cm^{-1} and 838–841 cm^{-1}. The supersonic expansion provided effective vibrational and rotational cooling, leading to considerable spectral simplification and facilitating assignment.

We analyzed the ν_1 (836.6 cm^{-1}) and ν_5 (517.8 cm^{-1}) fundamentals of $PF^{35}Cl_2$, as well as the fundamental ν_1 of the isotopically chiral $PF^{35}Cl^{37}Cl$ (835.5 cm^{-1}). From this work, we also report the first ground-state rotational parameters for $PFCl_2$, determined using combination differences. We have carried out an analysis incorporating the line positions in the ν_1 band (both species, room temperature and cooled-jet spectra) and the ν_5 band ($PF^{35}Cl_2$, room temperature spectrum). The analysis was performed using Watson's A-reduced effective Hamiltonian in the I^r representation to determine effective molecular parameters.[5,6] Simulations performed using the molecular parameters obtained from this study reproduce the observed spectrum well.

Our approach highlights the power of combining room-temperature FTIR spectroscopy with tunable diode laser spectroscopy of cold molecular beams, particularly for studying complex rovibrational structures in isotopically chiral systems. These experimental results are complemented by the *ab initio* quantum chemical calculations. The results are discussed in the broader context of isotopic chirality, molecular parity violation, biomolecular homochirality, and fundamental symmetries of physics and chemistry.

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A DEEP ULTRAVIOLET MAGNETO-OPTICAL TRAP OF ALUMINIUM MONOFLUORIDE

J. E. Padilla-Castillo[1], J. Cai[1,2], P. Agarwal[1], P. Kukreja[1], R. Thomas[1], B. G. Sartakov[1], S. Truppe[2], G. Meijer[1] and S. C. Wright[1]

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[2] Centre for Cold Matter, Blackett Laboratory, Imperial College London, London SW7 2AZ

Despite impressive progress in direct laser cooling of molecules, magneto-optical trapping has thus far been restricted to species with spin-doublet electronic ground states. These molecules are chemically reactive and only support a simple laser cooling scheme when exciting from the first rotationally excited level of the ground state.

In this talk, we will present the first magneto-optical trap (MOT) of the diatomic molecule aluminium monofluoride (AlF)[1]. This $^1\Sigma^+$ ground state molecule is amongst the most deeply bound molecules known, and even survives a collision with vacuum walls of our experiment. Despite the challenging laser wavelengths required for the MOT ($\lambda =$ 227.5 - 232 nm), we take advantage of the intense $A^1\Pi \leftarrow X^1\Sigma^+$ transition in AlF, which allows trapping three different rotationally excited levels of the ground via their respective Q(J) lines, as shown in Figure 1.

Our results set a new record for the shortest wavelength MOT, narrowly surpassing the 18 year old milestone set by atomic Cd ($\lambda =$ 228.9 nm). Similar to Cd, AlF possesses a spin-forbidden transition between its two lowest spin-singlet and triplet states. Magneto-optical trapping is a key step towards precise spectroscopy and control of the molecule via this narrow, ultraviolet transition.

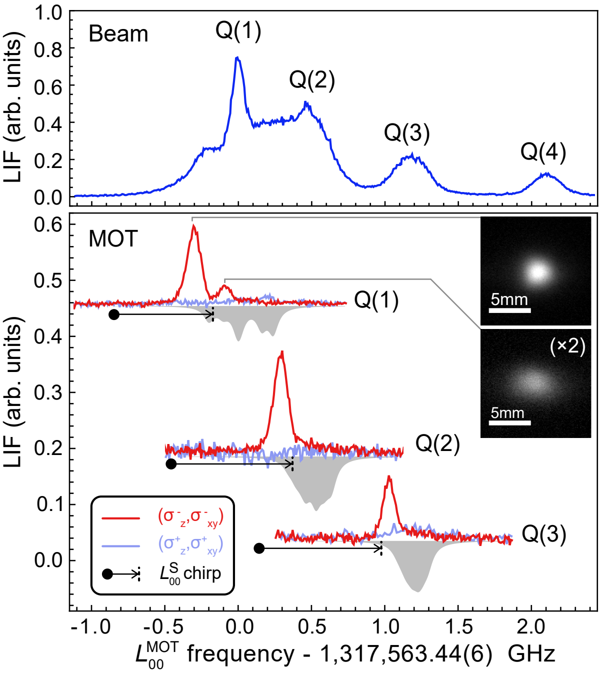

Figure 1: Magneto-optical trapping of AlF. LIF spectra of the molecular beam (upper sub-panel) and each of the three MOTs (lower sub-panel) versus the L^{MOT}_{00} (trap) laser frequency . MOT spectra are vertically offset, and shown for trapping (red) and anti-trapping (blue) polarisation configurations. Black horizontal arrows show the L^S_{00} (slowing) frequency chirp used to load each MOT. Simulations (grey) pointing downwards show the Q(J) lineshapes in zero magnetic field, including hyperfine structure of the $A^1\Pi, v' = 0$ levels. Insets show camera images taken at the indicated laser frequencies.

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[1] Padilla-Castillo, J.E., *et al.* **2025** arXiv:2506.02266

J-III: Contributed Talks

Wednesday, August 27, 11:00
Hörsaal III

Chair: Isabelle Kleiner

COMPLEX TUNNELLING DYNAMICS AND CONFORMATIONS IN 3,3,3-TRIFLUOROPROPANOL$\cdots$WATER$_N$ (N=1-4) CLUSTERS

Alex Mort, Colton D. Carlson, and Yunjie Xu

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

3,3,3-Trifluoropropanol (TFP) is a member of the fluorinated alcohol family, widely used as a co-solvent in studies of protein folding and unfolding, as well as a ‘magic medium’ in organic syntheses.[1] The rich conformational landscapes of the TPF monomer and dimer have previously been investigated using rotational spectroscopy and theoretical calculations.[2] In this presentation, we focus on the complex tunnelling dynamics and conformational landscapes of TFP$\cdots$water$_n$ clusters, with n up to 4, using a similar approach. Compared to trifluoroethanol, TFP has one additional carbon atom in its backbone, making it the smallest trifluoroalcohol to exhibit folded monomer conformations. It therefore serves as a prototype system for examining how folding influences the structural diversity of water-containing aggregates. Extensive conformational searches were carried out using CREST,[3] a conformational search tool, and subsequent DFT optimizations predicted a large number of energetically similar minima, highlighting the flatness of the associated potential energy surfaces with respect to certain structural parameters. We will present the experimentally observed tunnelling splittings, the associated complex tunnelling dynamics, and the challenges involved in identifying the specific structural candidates responsible for the observed sets of rotational transitions.

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[2] K.-M. Marstokk, H. Møllendal, K. D. Klika, F. Fülöp, R. Sillanpää, J. Mattinen, A. Senning, X.-K. Yao, H.-G. Wang, J.-P. Tuchagues, M. Ögren, *Acta Chem. Scand.* **1999**, 53, 202; A. N. Mort, Y. Xu, *J. Mol. Spectrosc.* **2023**, 392, 111745; A. N. Mort, F. Xie, A. S. Hazrah, Y. Xu, P*hys. Chem. Chem. Phys.* **2023**, 25, 16264.

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LIGAND EXCHANGE IN A SUPERSONIC EXPANSION

B. Hartwig[a], J. N. Hasselhorn[a], R. Tovtik[b], N. A. Simeth[b] and D. A. Obenchain[a]

[a] Institut für Physikalische Chemie, Georg-August-August Universität Göttingen
[b] Institut für Organische und Biomolekulare Chemie, Georg-August-August Universität Göttingen

The smallest possible molecule that involves hydrogen atoms forming a van der Waals complex is dihydrogen itself. Complexes of dihydrogen with other binding partners are complicated by the fact that H can exist in two different nuclear spin isomeric forms, one of which must retain its rotation in the complex (*ortho*-H_2, $I = 1$) whereas the other does not (*para*-H_2, $I = 0$). This results in different physical behaviour and can even impact their reactivity in the gas phase.[1] Different gas-phase reactivity has also been observed for *ortho* and *para*-H_2O[2]. Hence, seemingly simple complexes are not necessarily easy to understand and it is commonly observed that *ortho*-H_2 complexes are more stable than *para*-H_2.

Inspired by a rotational study on the OCS-H_2 complex[3], we investigated the formation of the ortho-H_2, *para*-H_2 and He complex with benzonitrile dependent on the H_2 content in the expansion using cavity-resonator rotational jet spectroscopy. Similar to OCS-H_2, an enhancement of the signal intensity of the *ortho*-complex with increasing H_2 content was observed, whereas an inverse behaviour was found for the *para* and He-complex. The assigned global minimum structure of the *para*-H_2-benzonitrile complex is shown in Fig. 1 in the principal axis system of the moment of inertia. To understand this behaviour we kinetically modelled their intensity on the basis of an often proposed ligand exchange mechanism. These results may have implications for the *ortho*/*para*-H_2 ratio observed in the interstellar medium (ISM) for which polycyclic aromatic hydrocarbons (PAHs) have been found to be important.[4,5] Benzonitrile can serve as a small model system for PAHs and has itself been detected in the ISM.[6]

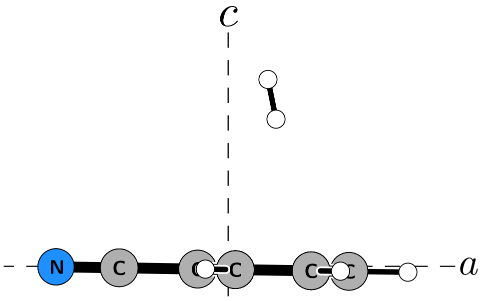

Figure 1: Global minimum of the of the *para*-H_2-benzonitrile complex.

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[6] B. A. McGuire, A. M. Burkhardt, S. Kalenskii, *et al.* **2018** *Science* 359, 202 -– 205.

STUDY OF GEARED MOTION IN WATER-AFFECTED METHYL INTERNAL ROTATION BY MICROWAVE SPECTROSCOPY

Xiaolong Yi[a], Yongtao Wang[a*], and Haoran Li[ab*]

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[b] State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University
* Corresponding Authors: wyongtao@zju.edu.cn, lihr@zju.edu.cn

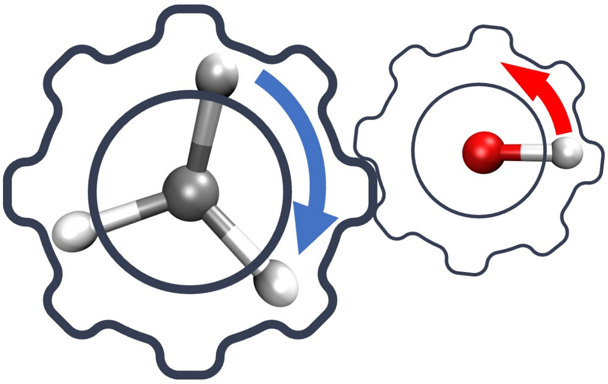

Figure 1: Gear motion accelerated methyl internal rotation.

The methyl internal rotation is a fundamental molecular motion with significant implications for various chemical and physical phenomena, contributing considerable entropy in large molecules.[1] For example, methyl groups are prevalent in proteins but scarce in RNA and DNA, and the distinct behaviors of nucleic acids and proteins under conditions of low temperature and limited hydration could be caused by the influence from methyl internal rotation.[2] However, the precise mechanism by which water affects the internal methyl rotation in protein is poorly understood. In this study, we try to get some clues for water-affected methyl internal rotation with rotational spectroscopy in peptide backbone model molecule, N,N-dimethylformamide (DMF). This study identifies the dynamic nature of gas-phase hydrogen bonding between water molecules and methyl groups as the underlying mechanism, with the specific bonding geometry playing a critical role. In aqueous DMF, methyl group rotation is found to accelerate, an effect opposite to that observed in N-methylformamide.[3] Despite their structural similarity, the contrasting behavior arises from distinct hydrogen-bonding arrangements in their respective monohydrated forms. High resolution microwave spectroscopy enabled precise structural characterization of DMF-water clusters, revealing variations in methyl rotational barriers through line splitting in the spectra. Computational chemistry analysis suggests that different hydrogen bonding types in the two water-interacted molecules totally lead to lower or higher rotational barrier, corresponding to gear-like (shown in Figure 1) or anti-gear-like motion between the methyl group and water. These results enhance our understanding of how subtle changes in structure influence molecular dynamics and may offer insights into protein behavior in aqueous environments.

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ELUCIDATING STRUCTURES AND NONCOVALENT INTERACTIONS IN MICRO-SOLVATED ALLYL PHENYL ETHER VIA ROTATIONAL SPECTROSCOPY

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Christian Albrecht University of Kiel, Institute of Physical Chemistry, 24118 Kiel,Germany

Water is ubiquitous on Earth and plays a vital role in nearly all chemical, biological, and atmospheric processes. In the gas phase, water-solute complexes serve as simple models for probing molecular structure and intermolecular interactions (NCIs) in aqueous environments. However, as the number of water molecules increases, competition among various NCIs gives rise to complex potential energy surfaces with numerous shallow and nearly degenerate minima. Furthermore, zero-point energy can further alter the relative stability of isomers, complicating structural assignments and energy ordering.

Rotational spectroscopy coupled with quantum chemical calculations offers unparalleled precision for elucidating the structures and NCIs of molecular clusters. Particularly, the development of broadband chirp polarization Fourier transform microwave (CP-FTMW) spectroscopy has enabled the detailed investigation of large water clusters and the resolution of multiple conformers.

Ally Phenyl Ether (APE), a classical precursor in the Claisen rearrangement reaction, contains both the allyl (-CH_2-CH=CH_2) and the phenyl ether (Ph-O-) group, resulting in rich conformational landscapes. A previous study has reported two low-energy conformers of APE utilizing CP-FTMW spectroscopy in the 8-12 GHz, providing valuable insight into its internal dynamics and molecular structure [1]. In this work, we employ broadband CP-FTMW spectroscopy [2] in the 2–8 GHz range to investigate the rotational spectra of APE and its hydrated clusters generated in a pulsed supersonic expansion. Aggregation motifs of APE–$(H_2O)_n$ (n = 1–3) were unambiguously identified, providing molecular-level insights into NCIs, conformational preferences and micro-solvation effects during the early-stage hydration interactions.

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STEPWISE MICROSOLVATION STUDY OF PREBIOTIC AMINOACETONITRILE BY ROTATIONAL SPECTROSCOPY: NH_2CH_2CN–$(H_2O)_n$ (n = 1–5, 7)

N. Jiang[a] and M. Schnell[a,b]

[a] Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany
[b] Christian-Albrechts-Universität zu Kiel, Institute of Physical Chemistry, Kiel, Germany

Aminoacetonitrile (NH_2CH_2CN, AAN) is a prebiotically relevant molecule that can hydrolyze to form glycine, the simplest amino acid. It has been detected in interstellar space and in Titan's atmosphere—an analog of early Earth—where gas-phase microsolvation likely played a critical role, as many prebiotic reactions are believed to have occurred in the gas phase. In this study, we investigate the microsolvation of AAN by one to seven water molecules under isolated gas-phase conditions using broadband rotational spectroscopy in the 2–8 GHz and 8–12 GHz frequency ranges. Hydrates of AAN containing one to five and seven water molecules were experimentally identified, while the assignment of the six-water complex was unsuccessful due to its low dipole moment (strongest $\mu_a = 0.5\ D$).

As protonation at either the $-NH_2$ or –CN group is a necessary step in AAN hydrolysis [1], we employed Local Energy Decomposition and N-body analysis [2] to probe site-specific interactions between water molecules and these two functional groups. In parallel, quadrupole coupling constants within the quadrupole principal axes system were employed to semi-experimentally assess the evolving ionic character (i_c) of both functional groups. This combined approach reveals how site-selective ionization tendencies develop during stepwise microsolvation. Our results reveal detailed hydrogen-bonding topologies, cooperative interactions, and the evolution of ionic character at each site, providing deeper insight into the chemical behavior of AAN in gas-phase environments.

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WATER COMPLEXES ON A CYCLIC THIOETHER FROM BROADBAND ROTATIONAL SPECTROSCOPY

Farha Sajeev Hussain[a], Noureddin Osserian[a], Amanda L.Steber[a], and Cristóbal Pérez[a]

[a] Departamento de Química Física y Química Inorgánica, Universidad de Valladolid

Cyclic thioethers, a class of macrocyclic compounds analogous to crown ethers with sulfur replacing oxygen in the ring framework, exhibit unique interaction profiles. Despite the inherently weaker hydrogen bond accepting capabilities of sulfur compared to oxygen, significant interactions with water molecules are observed. In this work, we employed chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 2–8 GHz range to elucidate the gas-phase structures of 1,4,7-trithiacyclononane (TTCN) and its complex with water. This high-resolution spectroscopic technique is highly sensitive to small changes in the mass distribution of the system enabling the determination of experimental molecular structures. While TTCN has been previously investigated,[1] our findings reveal an additional stable conformer. Our presentation will primarily focus on the experimental structure of TTCN and the structural perturbations induced by water binding. We utilized Kraitchman analysis to precisely determine the atomic positions in both the TTCN monomer and the TTCN-water complex. Furthermore, quantum chemical calculations supported our experimental findings, offering deeper insights into the observed structural changes. This work contributes to a better understanding of weak hydrogen bonding involving sulfur and the conformational flexibility of sulfur-containing rings upon interaction with water in the gas phase.

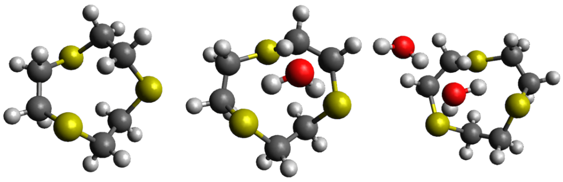

Figure 1: The newly identified conformer of TTCN molecule and the detected isomers water complexes from quantum chemical calculation

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[1] Drouin, Brian J., et al. **2022** *J. Phys. Chem. A.*,101.48 : 9180-9184.

K: Plenary

Thursday, August 28, 9:00
Hörsaal I

Chair: Jonathan Tennyson

PROBING NEW RADICAL SPECIES USING HIGH RESOLUTION THZ SPECTROSCOPY

O. Pirali, R. Chahbazian, L. Juppet, M.-A. Martin-Drumel

Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, France

Neutral radical species play a critical role in photochemical processes across diverse environments, including combustion systems, planetary atmospheres, and the interstellar medium. However, due to their high reactivity, obtaining rotationally resolved spectra—essential for structural characterization, energy level determination, and unambiguous detection—remains experimentally challenging. As a result, a wide range of spectroscopic techniques have been developed in the past by the spectroscopy community to synthesize such radicals and to acquire their high-resolution spectra, often supported by theoretical approaches to account for complex intramolecular interactions.

At ISMO, recent improvements in our experimental setup now allow for the recording of THz spectra of several novel radical species formed via dehydrogenation of complex organic molecules. These radicals often exhibit complex rotational energy level structures due to couplings between the overall molecular rotation, various large-amplitude motions, and the electron spin, requiring the development of adapted theoretical modeling. In parallel to these studies, we have recently initiated the study of sub-Doppler spectra of simpler radical species in the THz range. Applied to the NH_2 radical THz spectrum, both standard saturated absorption and IR-THz double resonance techniques have revealed numerous spectral features previously hidden by Doppler broadening. These results substantially improve the spectroscopic characterization of NH_2 and its fully deuterated isotopologue, opening new avenues for precision studies of reactive species.

USING MOLECULAR SPECTROSCOPY TO INVESTIGATE THE EARTH'S ATMOSPHERE FROM ORBIT

Jeremy J. Harrison[a,b]

[a] National Centre for Earth Observation, Space Park Leicester, Leicester, UK
[b] School of Physics and Astronomy, University of Leicester, Leicester, UK

Spectroscopic remote sensing, particularly by instruments on satellite platforms, is used to acquire information on the distributions of atmospheric trace gases and the physical conditions of the Earth's atmosphere. The derived high quality satellite datasets are then used to inform, for example, international climate action, air quality regulations, and stratospheric ozone recovery. Satellites offer a means of making global measurements, including over remote parts of the world, and provide a snapshot of the Earth's atmosphere from space, providing a continuous record from which we can detect changes, establish trends, and with the aid of models predict future scenarios.

Sophisticated algorithms are used to "retrieve" geophysical information from the measured spectra. These algorithms depend on our ability to model atmospheric radiative transfer accurately, which in turn depends on our knowledge of the underlying spectroscopic properties of molecules in the atmosphere. Spectroscopic databases such as HITRAN contain this information in the form of line parameters for smaller molecules like carbon dioxide and water, or absorption cross sections for larger molecules with congested spectra, such as trichlorofluoromethane (CFC-11).

Molecular spectroscopy, especially in the infrared, underpins a large number of important atmospheric datasets, for example carbon dioxide and methane concentrations, as well as humidity and temperature profiles used for weather forecasting. Increasingly, our use of satellite data is placing more stringent accuracy requirements on the underlying spectroscopic information, necessitating more complex characterisation of spectroscopic lineshape and collisional effects. Current databases generally do not meet these requirements. Hence within the field of quantitative spectroscopy there is a push towards sub-percent accuracy for the most abundant molecules in the atmosphere. This requires the use of more sophisticated non-Voigt lineshape parameters and a proper treatment of line mixing which especially affects the most intense and closely overlapping spectral features for a molecule, e.g. Q branches.

This talk will review the field of infrared quantitative spectroscopy for remote sensing, and discuss recent efforts to improve the quality of spectroscopic data to meet the needs of the atmospheric science community.

L: Posters

Thursday, August 28, 11:00
Foyer

THE ROTATIONAL-TORSIONAL SPECTRUM OF SINGLY DEUTERATED HYDROGEN PEROXIDE HOOD

D. Herberth[a], K.M.T. Yamada[b], and T.F. Giesen[a]

[a] University of Kassel, Laboratory Astrophysics group, Kassel, Germany
[b] Institute for Laser Science (ILS), The University of Electro-communications, Tokyo, Japan

The gas phase rotational-torsional spectrum of singly deuterated hydrogen peroxide HOOD has been extensively investigated using FTIR and high-resolution submillimeter-wave spectroscopic techniques. In the vibrational ground state, over 1500 transitions in the range of 6 to 143 cm^{-1} were assigned, yielding accurate rotational and centrifugal distortion constants. The spectral lines display torsional splitting due to a hindered internal motion, which was determined to be 5.786(13) cm^{-1}, with a clear dependence on the rotational quantum numbers J and K_a. Furthermore, accidental resonances and perturbations affecting the torsional sub-states were identified, enabling the derivation of reliable interaction parameters alongside the standard Watson-type Hamiltonian. These data facilitated the determination of a semi-empirical equilibrium structure for HOOD.

Expanding the investigation to the torsionally excited state, more than 2400 transitions from the ground to the first torsional state were assigned in the range of 118 to 415 cm^{-1}. Owing to the presence of pervasive perturbations between ro-torsional levels in this regime, a hybrid approach combining traditional fitting with an automatic spectral assignment procedure (ASAP) was implemented, allowing the precise localization of 588 ro-torsional energy levels in the first torsional state. Accurate rotational constants and band origins for this state were established. Additionally, the K_a- and J-dependence of the torsional splitting was mapped in both the vibrational ground and first torsional state, providing detailed insight into the dynamics of internal rotation and the underlying potential energy surface.

Overall, this combined analysis delivers a thorough spectroscopic characterization of HOOD, elucidating the rovibrational structure, tunneling dynamics, and molecular parameters in its vibrational ground and first torsionally excited state, and provides reliable experimental benchmarks for future theoretical and astrochemical studies.

HIGH RESOLUTION SPECTROSCOPY OF VIBRATIONAL TUNNELING DOUBLETS AND OVERTONES OF THE INVERSION IN ANILINE

G. Wichmann, S. Albert, P. Lerch, K. Keppler, and M. Quack

Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

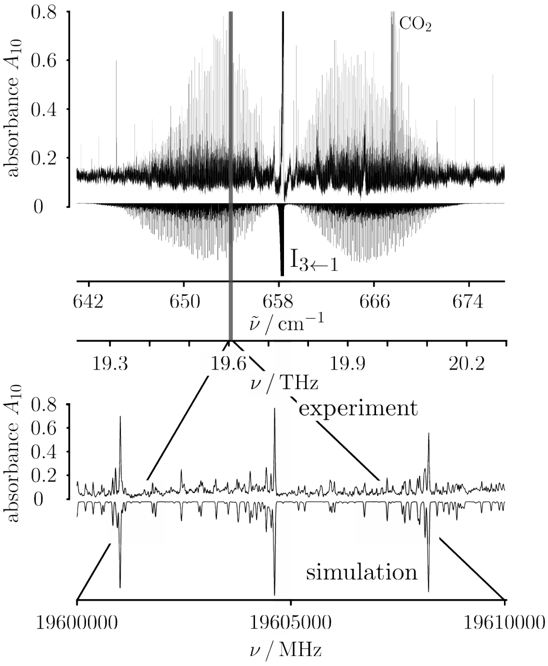

Figure 1: Analysed a-type transition $I_{3\leftarrow 1}$ measured with the 2009 ETH-Bruker prototype spectrometer.

Extending our knowledge about the inversion at the nitrogen atom in aniline ($C_6H_5NH_2$) or in other aromatic amines is of interest because of the widespread occurrence of the -NH_2 substituent in aromatic biomolecular compounds, in particular nucleic acids. The inversion barrier in aniline is about 450+/-80 cm^{-1} [1,2](much lower than for ammonia NH_3 with about 2000 cm^{-1} [3]). Here, we report highest resolution results from our GHz measurement from 75 GHz to 500 GHz and from the THz (FIR) range measured with our 2009 ETH-Bruker prototype spectrometer at the SLS (Swiss Light Source). We observed the rotationally resolved spectrum and analysed the three vibrational-tunneling doublets (I_0, I_1), ($10b_1$, $10b_1I_1$), and (T_1, T_1I_1) and the overtones of the inversion I_2, I_3, and I_4 providing accurate rotational parameters. We firmly assigned the spectra, including also the nuclear spin statistics seen by the intensity patterns in the GHz range and in part also resolved the hyperfine structure. The results are also discussed in relation to transient chirality in aniline -NHD and ammonia NHDT[3] and in relation to our ongoing efforts on precision experiments concerning the electroweak force of the standard model of particle physics (SMPP) by measuring the parity violating energy difference between the two enantiomers of chiral molecules [4,5,6]. We discuss in particular the closely related spectroscopic challenges in the vibrational tunneling dynamics for 1,2-dithiine ($C_4H_4S_2$) as a prototype for measuring parity violation needing the analysis of parity states in the mid-IR range in very dense spectra with multiple overlapping rotation-vibration-tunneling structures (see reviews [5,6]).

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[6] Quack, M., Seyfang, G., Wichmann, G., *Chemical Science*, 2022, **13**, 10598-10643

A THEORETICAL LINE LIST FOR THE HOPO MOLECULE

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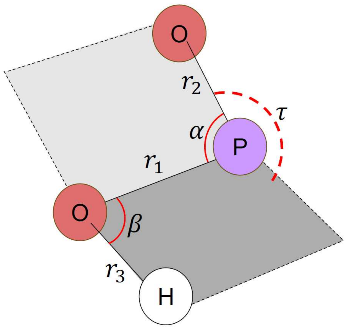

Recent atmospheric photochemical studies show that phosphorus-hydrogen-oxygen (PHO) photochemical network can play a key role in gas giant hydrogen-dominated atmosphere. Among the main phosphorus contained absorbers, HOPO, PO and P_2 are the dominant P carriers for HD 189733 b-like hot Jupiters at pressures important for transit and emission spectra, rather than PH_3.[1] Even for GJ1214 b-like warm Neptune atmospheres at 10 and 100 times Solar metallicity, small oxygenated phosphorus molecules such as HOPO and PO dominate for both thermochemical and photochemical simulations. Here we present a variationally computed *ab inito* line list for HOPO. A new potential energy and dipole moment surfaces of HOPO have been constructed at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory for the *cis*- and *trans*-HOPO conformers, at an energy range up to 20,000 cm^{-1}. Electronic structure calculations are performed with MOLPRO. These surfaces were parameterised using 6D analytic expansions covering both cis- and trans-isomers in single non-rigid representations. A new exact non-rigid kinetic energy operator (KEP) of this system was derived and implemented in the variational program TROVE.[2] The implementation is based on the new KEO constructor TROVE, allowing to treat generic KEOs operators represented as sum-of-products of some basic 1D functions. The *cis*- and *trans*-isomers are connected by low barriers in the torsion mode τ as well as in the bending mode β_{HOP}. The latter leads to a singularity in the KEO at $\beta_{\mathrm{HOP}} = \pi$, which is resolved by using a specially constructed product basis set. The technical details of the variational solution and the results will be presented.

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A CRYOGENIC ION TRAP BEAMLINE AT HFML-FELIX FOR ASTROCHEMICAL STUDIES

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Reactive molecular ions play a central role in the chemistry of planetary atmospheres and the interstellar medium. Laboratory astrophysics studies on the chemical reaction pathways under astronomically relevant conditions are crucial to interpret astronomical observations and as input for simulations in astrochemical networks. Of similar importance are spectroscopic studies of the often elusive, but essential, ionic reaction partners, intermediates and products that yield fundamental insights on their geometric and electronic structure, and provide spectroscopic signatures needed for their identification in space[1].

Cryogenic ion traps have proven to be ideal tools for studying ion-molecule reactions under controlled conditions and allow for sensitive spectroscopic studies of mass-selected, cold, and isolated molecular ions. Here, we will describe the combination of such a cryogenic 22-pole ion trap instrument (FELion)[2] with the widely tunable infrared free-electron lasers at HFML-FELIX[3]. It allows for broadband infrared action spectroscopy of molecular ions such as hydrocarbons and interstellar complex organic molecules (iCOMs) ranging in size from comparatively small systems to polycyclic aromatic hydrocarbon cations (PAHs). We will give a few examples of recent work on i) fundamental molecular physics studies, such as deciphering vibronic coupling effects, ii) in-situ spectroscopic probing of isomer-selective reaction kinetics involving PAHs and prebiotic species, iii) disentangling the isomeric composition of products in dissociative ionization processes.

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DECIPHERING THE COMPLEXITY IN THE ROTATIONAL SPECTRUM OF DEUTERATED ETHYLENE GLYCOL

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Ethylene glycol (CH_2OH-CH_2OH) is an abundant "complex organic molecule" (COM) detected in different astronomical objects, but the steps of its interstellar synthesis are not yet fully understood. In this respect, the observation of deuterated isotopologues could offer insights into its formation mechanism as well as into its chemical evolution in space. Such observations, however, require detailed spectroscopic knowledge of their rotational features. Here, we present an extensive analysis of the rotational spectrum of oxygen-deuterated ethylene glycol, including the singly and doubly deuterated forms. The new measurements, carried out between 75 and 450 GHz, significantly expand the spectroscopic knowledge of the aGg' conformers of the CH_2OH-CH_2OD, CH_2OD-CH_2OH, and CH_2OD-CH_2OD species. We also report, for the first time, the laboratory identification of the gGg' conformers of the two mono-deuterated species. Our results reveal previously unobserved perturbations arising from the interaction between CH_2OH-CH_2OD and CH_2OD-CH_2OH, which has been modeled by including Coriolis coupling and Fermi constants in the Hamiltonian and allowed the accurate determination of the energy difference among them. Additionally, we observed significant anomalies in the spectrum of the doubly deuterated species, which seem to be caused by accidental degeneracies between the levels of the two tunneling substates. Despite the complexity and difficulties, the improved spectroscopic parameters derived from our analyses provide a solid base for future interstellar searches of deuterated ethylene glycol, that in turn would enhance our understanding of the evolution of COMs in the interstellar medium.

MILLIMETER-WAVE SPECTRUM OF HYDANTOIN IN ITS VIBRATIONALLY EXCITED STATES

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Hydantoin (imidazolidine-2,4-dione, $C_3H_4N_2O_2$), a five-membered nitrogen-containing compound, plays an important role as a biomaterial. Its ability to hydrolyze and produce the amino acid glycine makes it a subject of significant interest in research related to the origins of life. The detection of hydantoin in meteorites suggests the possibility of its formation during the evolution of organic matter in space.

We reported the results of measurements of pure rotation spectra primarily in the millimeter wave region in an attempt to detect hydantoin in space.[1] In this study, we heated the sample to approximately 150 °C to vaporize hydantoin, which is solid at room temperature, and obtained the vapor pressure required for measurement. About 400 rotational lines in the ground state and two vibrational excited states were assigned, and the rotational constants and centrifugal distortion constants up to sixth order were determined. However, the assigned spectral lines accounted for only a small fraction of the measured spectral lines, and it was necessary to clarify the large number of unassigned spectral lines. Alonso et al. [2]vaporized hydantoin using laser ablation and applied FT-MW spectroscopy to determine the nuclear quadrupole interaction constants of the nitrogen nucleus in the vibrational ground state, while simultaneously assigning the spectra of various decomposition products, including hydantoic acid derivatives, generated during the ablation process.[3]

In the present study, we measured the frequency range from 90 to 180 GHz and attempted to assign a large number of observed spectral lines. In addition to the previously assigned vibrational ground state and two vibrational excited states, we confirmed three new vibrational excited states of hydantoin. The molecular constants of the five identified vibrational excited states were similar to those of the vibrational ground state, indicating that they were not decomposition products caused by heating, but rather spectral lines originating from hydantoin. Approximately 9,900 spectral lines were assigned, and the molecular constants in the ground and the five vibrational excited states were precisely determined up to the sixth-order centrifugal distortion constants. The assigned spectral lines account for more than half of the observed spectral lines, clearly indicating that thermal decomposition products are virtually absent under our experimental conditions. By comparing the results with first-principles calculations, we discussed which vibrational modes correspond to the five vibrational excited states. According to theoretical calculations, hydantoin possesses low-frequency modes with extremely high anharmonicity, and the vibrational frequencies of these modes vary greatly depending on the calculation method and the choice of basis functions. We have not yet been able to establish a clear correspondence between the observed and the calculated modes. Furthermore, two of the five vibrational excited states have very similar rotational constants and nearly identical spectral intensities, suggesting the possibility of inversion splitting due to a low-lying vibrational mode.

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ELUSIVE TAUTOMER OF ACETONE CHARACTERIZED BY ROTATIONAL SPECTROSCOPY

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Enols, tautomers of aldehydes and ketones, are considered intermediates in the synthesis of more complex organic molecules, such as sugars, and have gained significant attention as potential interstellar molecules. Three enols have already been detected in the interstellar medium: vinyl alcohol[1], 1,2-ethenediol[2], and 3-hydroxypropenal.[3] Here, we present the first measurement of the rotational spectrum of the transient species 1-propen-2-ol, a tautomer of acetone, which was identified in laboratory experiments on acetone-containing ices upon exposure to ionizing radiation.[4] Two conformers of 1-propen-2-ol were observed and their ground state rotational transitions were analyzed in the frequency region from 139 to 180 GHz. The results of this work represent a crucial prerequisite for radioastronomical searches of 1-propen-2-ol.

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ROTATIONAL SPECTROSCOPY AS A TOOL TO STUDY VIBRATION-ROTATION INTERACTION: INVESTIGATIONS OF ^{13}CH$_3$CN AND CH$_3^{13}$CN UP TO $v_8 = 2$ AND A SEARCH FOR $v_8 = 2$ TRANSITIONS TOWARD SAGITTARIUS B2(N)

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Methyl cyanide, CH$_3$CN, occurs in space in diverse environments. It is particularly abundant in the warm and dense parts of star-forming regions. Vibrational satellites up to $v_4 = 1$ (920 cm^{-1}) were identified securely toward the giant molecular cloud Sagittarius B2(N) close to the Galactic center while lines of $v_4 = v_8 = 1$ (1290 cm^{-1}) were detected tentatively.[1] With transitions of ^{13}CH$_3$CN and CH$_3^{13}$CN in $v_8 = 1$ also found in this source, transitions in $v_8 = 2$ of these isotopomers are promising targets for searches in space.

We employed samples enriched in ^{13}CH$_3$CN and CH$_3^{13}$CN, respectively, to record spectra between 35 and 1091 GHz and analyzed states up to $v_8 = 2$. Interactions within $v_8 = 2$ yielded accurate information on the energy differences of the $l = 0$ and $l = 2$ components of $v_8 = 2$, 22.93 and 21.79 cm^{-1} for ^{13}CH$_3$CN and CH$_3^{13}$CN, respectively. Fermi resonances between $v_8 = 1^{-1}$ and $v_8 = 2^{+2}$ probe their energy differences (373.84 and 365.99 cm^{-1}) without the use of high-resolution IR data. A resonance between $v = 0$ and $v_8 = 1$ in ^{13}CH$_3$CN gave information on their energy difference (364.75 cm^{-1}). The resulting spectrocopic parameters were used to search for transitions of $v_8 = 2$ pertaining to these ^{13}C isotopomers in Sagittarius B2(N).

We acknowledge support by the Deutsche Forschungsgemeinschaft via the collaborative research center SFB 1601 (project ID 500700252), subprojects A4 and INF, as well as the Gerätezentrum SCHL 341/15-1 ("Cologne Center for Terahertz Spectroscopy").

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^{13}C- AND ^{15}N-MONOSUBSTITUTED ISOTOPOLOGUES OF HC$_3$N: 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 — H^{13}CCCN, HC^{13}CCN, HCC^{13}CN, and HCCC^{15}N — recorded between 75 and 530 GHz using a frequency-modulated millimeter-wave spectrometer. Over 4000 transitions were assigned in the $J = 9$–58 range, covering the ground and the $v_7 = 1-4$, $v_6 = 1-2$, $v_5 = 1$, $v_4 = 1$, $v_6 = 1+v_7 = 1-2$, and $v_7 = v_5 = 1$ 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 HC$_3$N emission is optically thick.

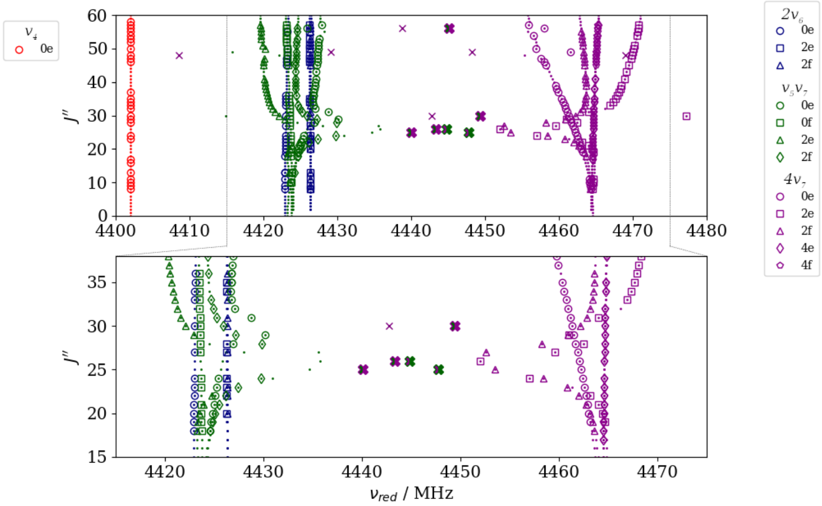

Figure 1: Reduced frequency diagram for the $v_4 = 1 \sim v_5 = v_7 = 1 \sim v_6 = 2 \sim v_7 = 4$ polyad of H^{13}CCCN. Legends report the labeling of l-sublevels of each state. Dots indicate predicted line positions while solid symbols mark the measured lines. Interstate transitions at the avoided crossings are labeled with solid crosses.

Acknowledgments: GASCHEM4air – GAS-phase CHEMistry for AIR quality modeling - PRIN 2022 PNRR

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HIGH-RESOLUTION INFRARED INVESTIGATIONS OF CIRCUMSTELLAR ENVIRONMENTS OF LATE-TYPE STARS USING SMALL MOLECULES AS PROBES

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The immediate surroundings of late-type stars such as the oxygen-rich hyper-giant VY Canis Majoris or the intermediate-mass Mira type stars χ Cyg, IK Tau or others show a rich chemical inventory. These star environments are infrared bright and their spectra show molecular signatures. Although most molecular identifications have been made with radio telescopes many detections can also be found at infrared (IR) wavelengths. When using IR high-resolution spectrographs, also the dynamics of molecular shells close to the star can be observed which opens a new field of investigation. For this, a careful line shape analysis has to be combined with new IR laboratory data and new analytical tools to interpret the excitation level of vibrationally excited states of the observed molecules. In our work we used the TEXES spectrograph on the IRTF telescope on Mauna Kea, Hawai'i and the EXES spectrograph on SOFIA, both with a spectral resolving power of around R=100 000. The investigated molecules include SiO, TiO, VO, NH_3, and H_2O. In the recorded spectra many unidentified lines are found, too. In the case of χ Cyg a dedicated survey of the stellar phases has been performed. Our new multi-level excitation diagram code has been used to determine the column densities and temperatures of the observed molecules. A physical model of the molecular shells around the star has been used to interpret the observed line shapes. First results of this work will be shown.

INVESTIGATION OF WATER-CONTAINING CLUSTERS WITH A 6-18 GHz CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE SPECTROMETER

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Water, CO_2 and O_2 are simple molecules that may form van der Waals and hydrogen-bonded clusters of possible atmospheric relevance. Such aggregates may be implicated as transient species in atmospheric reaction pathways and play a fundamental role in the early stages of homogeneous nucleation and solvation phenomena. Cavity-based, Fourier-transform microwave spectroscopy has long been a powerful tool for unraveling the structures of such weakly bound species. Notable examples include the H_2O–CO_2 aggregate studied by Bauder et al.[1] and the H_2O–O_2 dimer investigated by Endo.[2] More recently, the advent of chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy[3] enabled the structure determination of larger water clusters, as demonstrated by Pérez and co-workers. [4]

Here, we report the development and implementation of a new CP-FTMW spectrometer designed to probe a supersonic jet taking place in the FANTASIO experimental setup.[5] This instrument covers a 6 GHz to 18 GHz frequency range and operates autonomously to acquire a large amount of molecular signals with an effective repetition rate up to 1.6 kHz. The system also features a custom-built piezoelectric valve coupled to original slit and pinhole nozzles, optimized for the generation of large molecular clusters. The sensitivity and broadband capabilities of the instrument have enabled both (i) a re-examination and extension of the aforementioned studies through the acquisition of new spectroscopic data, and (ii) the detection of unobserved clusters for which tentative assignments are discussed.

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CONFORMERS OF THE α-PINENE - WATER COMPLEX: ROTATIONAL SPECTROSCOPY AND ELECTRONIC STRUCTURE CALCULATIONS

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α-Pinene is a biogenic volatile organic compound that is emitted in great quantities into the atmosphere and is a precursor to secondary organic aerosol. α-Pinene can be oxidized in the atmosphere by, for example, ozone or OH radical, to form lower volatility compounds that can aggregate and begin the aerosol particle formation process. Water, being relatively abundant in the atmosphere, is one aggregation partner, but may also affect the oxidation process of α-pinene.

We have studied the α-pinene - water complex using chirped pulse microwave Fourier transform spectroscopy and electronic structure calculations. Several conformers of α-pinene - water were predicted computationally, and two were identified experimentally. In the recorded spectra, narrow splittings of rotational lines with intensity ratio 3:1 are present, which are attributed to a water tunneling motion that exchanges the two protons.

In the two experimentally detected conformers, water O-H$\cdots\pi$-bond interactions exist, which may affect the atmospheric oxidation of α-pinene by ozone. We evaluated the activation energy for the ozonolysis of α-pinene and of the α-pinene - water conformers and found that the presence of water reduces the activation energy. Given the substantial α-pinene emissions, the catalytic effect of hydration on the ozonolysis reaction may affect atmospheric processes.

INVESTIGATION ON NON-COVALENT INTERACTIONS IN 3-FLUOROBENZYLAMINE-WATER COMPLEXES BY MEANS OF MICROWAVE SPECTROSCOPY

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Water plays a fundamental and irreplaceable role in the chemical and biological processes that sustain life on Earth. Beyond its direct participation in chemical reactions, water mediates dynamic processes and stabilizes static conformational structures through non-covalent interactions, most notably the hydrogen bond (HB).

The hydrogen bond network governs water-solute interactions, dictating how water molecules bind to a solute and stabilize its conformations. However, the complexity of non-covalent interactions, both between solute and water and among water molecules themselves, makes it challenging to predict the energetically preferred geometry in growing clusters, with the potential energy surface featuring numerous minima with very similar energies, where zero-point energy contributions may determine the stability ranking.

High-resolution microwave spectroscopy provides an exceptionally precise tool for characterizing intra- and intermolecular interactions, making it ideal for studying gas-phase water-solute clusters. These clusters serve as simplified models for understanding bulk aqueous-phase behavior. By applying Kraitchman’s equations to isotopically substituted species, atomic coordinates can be derived from subtle changes in moments of inertia, enabling detailed structural analysis.

In this work, we characterize water clusters of **3-fluorobenzylamine (3FBA),** a molecule with multiple hydrogen-bonding sites: the nitrogen lone pair, the fluorine atom, and the aromatic pi-system as HB acceptors, as well as the two amino hydrogens as HB donors. Using **chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW)** in the **2–8 GHz range,** we assigned clusters of 3FBA with up to four water molecules. The CP-FTMW technique enables the simultaneous acquisition of 10^6 resolution elements across several GHz in a single measurement, providing high-resolution spectral data for structural analysis.

ROTATIONAL SPECTROSCOPY AND TAUTOMERIC EQUILIBRIA IN COMPLEXES FORMED WITH ISOTHIAZOLINONE

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Solvent properties, such as polarity and proticity, play a significant role in influencing tautomeric equilibria, leading to shifts in preference towards different tautomeric forms[1]. Possessing a tautomeric equilibrium between the NH- and OH-forms, isothiazolinone (IT) is reported to be predominantly in its NH-form in more polar, protic solvents due to its sensitivity to environmental effects, which, however, remains unexplored in the gas phase so far[2, 3]. In our current study, we used a combination of high-resolution rotational spectroscopy and quantum-chemical calculations to investigate the tautomeric conformations of IT complexes with water and formic acid, respectively. In particular, we employed CREST, the conformer-rotamer ensemble sampling tool[4], along with geometry optimization at the B3LYP-D3(BJ)/def2-TZVP level of theory. Rotational spectra of IT-water or formic acid adducts were recorded in the 2-8 GHz range by using a chirped-pulse Fourier transform microwave spectrometer and analyzed. Pure rotational transitions were assigned to several complexes of IT-$(H_2O)_{1,2,3,4}$, IT_2-H_2O and IT-$(HCOOH)_{1,2,3}$, respectively. The relationships between the geometries of the observed structures, the noncovalent interactions, and the tautomeric equilibria of the two mentioned molecular systems will be discussed.

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STRUCTURE AND MICRO-SOLVATION OF A PROTOTYPE PYRANOSE MOLECULE: A ROTATIONAL SPECTROSCOPIC STUDY

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Tetrahydro–2H–pyran–2–ol (THP) is a simple alcohol featuring a pyranose ring without additional substituents. The absence of substituents reduces its conformational flexibility and possible non–covalent intramolecular interactions, distinguishing it from more complex pyranoses like glucose. These characteristics make THP an ideal model system for investigating phenomena in carbohydrate chemistry through rigorous rotational spectroscopic and theoretical studies.[1] We measured and analyzed the rotational spectra of THP and its micro–hydrated complexes in the 2–18 GHz ranges. The gas-phase experimental structures for both the axial and equatorial conformations of THP were determined, providing intrinsic structural insights into the anomeric effect–a preference for the axial conformation despite its higher steric hinderance compared to the equatorial conformation. The open–chain intermediate of THP was also detected in the molecular jet. In comparison, in aqueous solution, the cyclic forms of THP exists in equilibrium with an open–chain intermediate, 5–hydroxypentanal.[2]

Preliminary results on the ring-opening reaction dynamics will be presented. Additionally, we will discuss how micro-hydration affects the conformational preferences of THP which links gas phase and solution phase behavior.

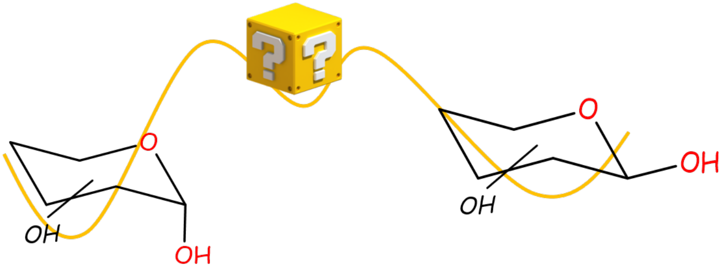

Figure 1: Conformational Preferences of a Prototype Pyranose Molecule Revealed by Spectroscopic Analysis

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MID-INFRARED DETECTION OF MOLECULAR SPECIES IN REACTIVE PLASMAS USING A QUANTUM CASCADE LASER-BASED ABSORPTION SPECTROMETER

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We apply quantum cascade laser absorption spectroscopy in the mid-wave infrared to measure multiple species, specifically CO, HCN and HNC, in a plasma containing N_2, H_2, CH_4 as precursor gases. The key elements of the experimental setup include a continous-wave EC-QCL, with an output power of 150 mW and a wavenumber tunability of $1985 - 2250$ cm^{-1}, two cooled infrared photo detectors for signal and reference arms, and a plasma reactor. The plasma was generated by direct current discharge. For wavenumber calibration, a reference gas cells of CO and CO_2 and a germanium etalon were used in the reference arm. Assignment for HCN and CO lines was performed using HITRAN database[1], while those for HNC were performed with the help of ExoMol database[2].

For HNC, we probed a total of eight rovibrational transitions, which show excellent agreement with those in the ExoMol database.

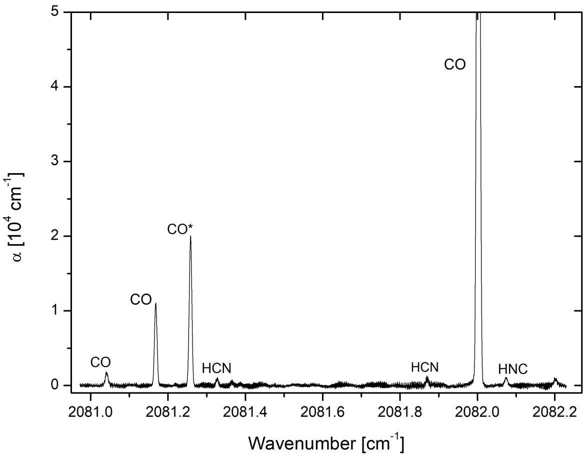

Figure 1: Absorption coefficient, α of plasma-generated species measured using the EC-QCL system in the mid-wave infrared spectral region. The symbol * indicates an overpopulated transition of CO.

Using the measured spectrum, we evaluated the populations of HCN, HNC, and CO. In particular, the CO line at 2081.26 cm^{-1} was found to be strongly overpopulated, reflecting pronounced non-thermal excitation in the plasma. We comprehensively determined the molecular populations as a function of plasma power, pressure, and gas mixture composition, with a particular focus on the HNC/HCN ratio. These results highlight the capability of mid-infrared EC-QCL spectroscopy to provide real-time, species-specific diagnostics of reactive molecular plasmas, revealing non-equilibrium excitation and key chemical pathways.

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PRECISE FREQUENCIES OF $H_2{}^{16}O$ LINES PROTECTED FOR RADIO ASTRONOMY

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Water is a key molecular species throughout the universe, which is why the International Astronomical Union and the Panel on Frequency Allocations of the US National Academy of Sciences have established lists of protected radio lines of water isotopologues. The focus of this talk will be on the improvement of the accuracy of these lines with respect to previous direct radio-frequency measurements for all the protected lines of $H_2{}^{16}O$ between 750 and 3000 GHz.

To achieve this purpose, high-precision Lamb-dip measurements of rovibrational lines of $H_2{}^{16}O$ were performed (see Figure 1 for two examples) using the noise-immune cavity-enhanced optical-heterodyne molecular spectroscopy (NICE-OHMS)[1] method in the wavelength range of 1.2 – 1.4 µm. The accuracy of the transition frequencies measured is estimated to be 2 kHz. These new measurements, combined with a spectroscopic network[2,3,4] built from a large set of previous rovibrational Lamb-dip lines, has lead to a significant improvement of 51 purely rotational microwave lines used for $H_2{}^{16}O$ in radio astronomy. While their accuracy was at the level of 10-200 kHz, it has now been improved to well below 10 kHz for all lines.

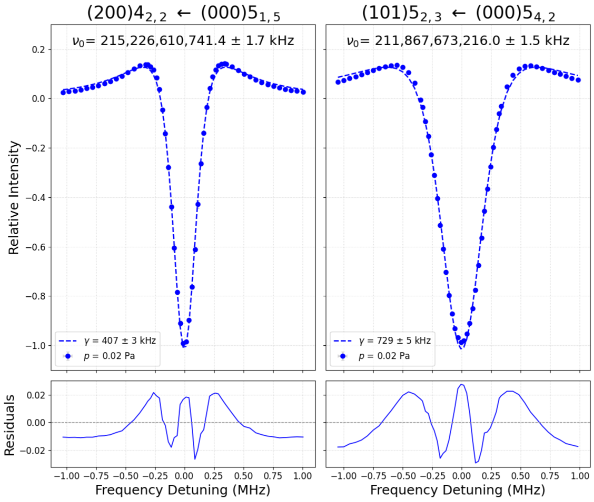

Figure 1: Experimental Lamb-dip spectra of two (ro)vibrational transitions measured *via* our ultrasensitive NICE-OHMS setup for $H_2{}^{16}O$.

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ROVIBRATIONAL ASSIGNMENTS OF HIGHLY CONGESTED SPECTRA BASED ON VARIATIONAL CALCULATIONS: APPLICATION TO ETHYLENE (C_2H_4) AND CH_3D

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The rovibrational assignment of highly congested spectra using traditional methods is very challenging because of the number of interacting bands. In the present work, high level predictions using variational calculations are used to assign the infrared spectra of ethylene and of CH_3D recorded by Fourier spectroscopy at room temperature. Using position and intensity matching with line lists derived from variational calculations [1], approximately 19,000 transitions of CH_3D were assigned to 80 distinct cold bands in the 4000-6600 cm^{-1} region [2]. For C_2H_4, around 10,000 transitions were successfully assigned to 26 distinct cold bands and 4 hot bands in the spectral regions 2900-3300 cm^{-1} [3] and 5800-8050 cm^{-1} [4], based on variational lists [5]. Most of the assignments were validated using Lower State Combination Difference (LSCD) relations i.e., all the upper state energies have several coinciding determinations through several transitions (up to 8). The level of agreement between experiment and theory and comparison with previous literature results will be discussed.

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HIGH-RESOLUTION SPECTROSCOPY OF COMPLEX ORGANIC MOLECULES UNDER UV FIELDS

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One of the fundamental questions regarding astrophysical and exoplanet atmosphere environments is the origin of detected molecular species. Particular interest present complex organic molecules (COMs) that, in many cases, are considered as direct or indirect precursors of prebiotic molecules, thus, linking astrochemistry with the big scientific question - the origin of life on Earth and, potentially, on extrasolar planets. COMs form more efficiently in the solid state (on the surface of dust grains) but are detected more efficiently in the gas phase after their desorption triggered by temperature, energetic fields or excess energy released in molecule formation. However, the destiny of COMs in the gas phase is not clear as they can react with other species or be destroyed by external energetic fields. One of such fields in astrophysical and exoplanet atmosphere environments is UV irradiation.

We've made an attempt to study destruction of COMs in the gas phase by UV light using high resolution spectroscopy. We combined a UV lamp with a long-cell direct absorption spectrometer and measured high-resolution spectra of two COMs abundant in astrophysical environments, methanol and ethanol, before and during UV irradiation. We successfully detected products of dissociation of the COMs, such as formaldehyde and CO for methanol, and methanol, formaldehyde, CO, acetaldehyde, and ketene for ethanol. Estimated product ratios favor conversion of COMs into more simple species. CO is the most abundant product in both cases followed, in the case of ethanol, by formaldehyde, methanol, acetaldehyde, and ketene. The most important outcome of such a study would be experimentally measured UV photodissociation rates of COMs, which are now typically available as a result of quantum-chemical calculations. Our current experimental approach does not allow for direct measurements of photodissociation rates. This is the goal of our future experimental developments and research.

DENSITY DEPENDENCE OF THE MEASURED LINE INTENSITY FOR O_2 TRANSITIONS

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Line intensity is typically obtained as the ratio of the integrated absorption coefficient, retrieved from a fit of laboratory-measured spectra assuming a line-shape model, to the absorber density. In such laboratory determinations, until recently, the integrated absorption coefficient (IAC) was assumed to be independent of the density of the collision partner. This major assumption is now in question: to what extent is the retrieved IAC proportional to the absorber density and independent of the total density of the gas mixture? Here, we refer to any observed density dependence of the IAC as evidence of "intensity depletion". The increasingly demanding performance targets of ground- and satellite-based missions dedicated to the monitoring of greenhouse gases motivate a quantitative understanding of intensity depletion which will be crucially important for many applications.

In this work, depletion of IAC with density is evidenced for O_2 transitions. Specifically, classical molecular dynamics simulations (CMDS) have been performed for O_2 with four different collision partners: O_2, N_2, Ar and He at room temperature and various perturber densities. The theoretical predictions have been validated by comparisons with intensity depletion coefficients, d, derived from high-precision cavity ring down spectroscopy (CRDS) measurements of the 1.27 µm band of O_2 in air, argon and He. These spectra were conducted at NIST (USA) and Grenoble (France). For O_2 in air, a mean depletion of about 0.3 %/amagat is observed, with a weak dependence on the rotational quantum number.

The temperature dependence of the d coefficients for O_2-air has been investigated using both CMDS at 250 K and 296 K, and CRDS measurements at 250, 275 and 296 K. These results lead to a nearly undetectable temperature dependence. Finally, atmospheric spectrum simulations were carried out to quantify the impact of intensity depletion on surface pressure retrievals.

ROTATIONAL SPECTROSCOPY OF EPIIODOHYDRIN AND THE ^{127}I NUCLEAR QUADRUPOLE COUPLING TENSOR

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Nuclear quadrupole coupling (NQC) is a fundamental interaction in atomic and molecular systems, arising from the coupling between a nucleus's quadrupole moment, present in nuclei with spin quantum number $I > 1/2$, and the anisotropic electric field gradient created by surrounding electrons. This interaction serves as a sensitive probe of the local electronic environment, offering valuable information on molecular structure and dynamics. Spectroscopic characterization of NQC is a powerful tool for investigating these interactions and provides essential data for the development and refinement of theoretical models, especially for systems containing heavy nuclei, such as iodine, where relativistic effects cannot be neglected.

In this work, we report a high-resolution investigation of the rotational spectrum of epiiodohydrin, measured using a broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer coupled with a supersonic expansion. This technique enabled the observation of hyperfine-resolved rotational transitions arising from the ^{127}I nuclei. To support spectral interpretation, the ^{127}I NQC constants were computed using density functional theory at the B3LYP-D3(BJ) level, employing the all-electron cc-pVQZ-DK3 basis set for iodine and def2-QZVP for all other atoms. The reliability of the cc-pVQZ-DK3 basis set was established through a benchmark set of known iodine-containing molecules. The accurate NQC predictions, in turn, facilitate the distinction of two conformers of epiiodohydrin in the microwave spectrum.

COMB-ASSISTED CAVITY RING-DOWN SPECTROSCOPY AT 2 μm FOR ACCURATE CO_2 LINE INTENSITY DETERMINATIONS

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Remote sensing of greenhouse-relevant molecules is based on physical models that need accurate knowledge of temperature-dependent molecular parameters, including line intensities, pressure broadening, and shifting coefficients. These data are usually collected in databases such as HITRAN, GEISA, and CDSD-296. Unfortunately, they are provided with a relative accuracy of 1% at best, which is not sufficient for the purpose of modern remote sensing missions dedicated to monitor the concentration of greenhouse gases in the Earth's atmosphere.

Nowadays, the fruitful combination of the optical frequency comb (OFC) technology with cavity-enhanced spectroscopic techniques has led to important contributions in this research field[1]. In fact, the addition of metrological-grade qualities to the recorded molecular spectra represents a crucial ingredient when highly-precise molecular parameters have to be determined. More particularly, comb-assisted Cavity Ring-Down Spectroscopy (CRDS), that allows for sensitive, accurate, and intrinsically absolute measurements of the absorption coefficient of a given gaseous sample, has proven to be a very powerful tool in fundamental studies[2,3], as well as in applied research[4].

Here, we report on recent advances toward the development of a comb-assisted CRDS spectrometer with the aim of recording properly selected CO_2 transitions in the 2-μm spectral region. In the framework of the European project Primary Spectrometric Thermometry for Gases (PriSpecTemp)[5], we present preliminary results of line intensity determinations on carbon dioxide. The spectrometer is based on the use of a external-cavity diode laser (ECDL) which is frequency locked to the signal output of a singly-resonant optical parametric oscillator (OPO)[6]. The OPO signal acts as an intermediate optical link between the ECDL and a self-referenced OFC. In fact, the OPO signal is weakly locked to the nearest tooth of the OFC, which, in turn, is phase-locked to a GPS-disciplined Rb-clock. A precisely controlled tuning of the ECDL offset-frequency, with respect to the OPO signal, allows us to record high-fidelity CO_2 spectra resulting from light-absorption that occurs inside a temperature-stabilized high-finesse optical cavity.

We demonstrate our capability in retrieving highly accurate spectroscopic parameters for several CO_2 transitions in the range 1980-2070 nm. Moreover, we report on preliminary results of stringent tests of *ab-initio* quantum chemistry calculations of the line intensities, with the aim of improving the results obtained by our group in 2017[7].

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NEW LOOK AT PERTURBATIONS IN THE $N_2(C^3\Pi_U, V)$ ELECTRONIC STATE. INDIRECT PREDISSOCIATION THROUGH $C''^5\Pi_U$ AND $1^7\Sigma_U^+$ STATES

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Nitrogen molecule is the most studied diatomic molecule due to its applications in several fields such as spectroscopy [1], Earth and Titan atmospheres [2]. In particular, their spectra still hold several hidden secrets, which are only beginning to be revealed thanks to advances in experimental techniques and theoretical methods, which can provide us spectra with higher resolution and more accurate potential energy curves, respectively. A good example of these hidden secrets can be found in the Second Positive System ($C^3\Pi_u \rightarrow B^3\Pi_g$) of the nitrogen molecule, known as the Second Positive System (SPS) [3] [4] [5]. Although it had been observed and described since 1890, it was only in the 1920's that its rotational structure began to receive more detailed attention. To address a puzzle that has persisted for nearly 90 years, this work presents new evidence on the phenomenon of indirect predissociation in the N_2 molecule, focusing specifically on the $C^3\Pi_u \rightarrow B^3\Pi_g$ electronic transition. A high-resolution experimental analysis of $C^3\Pi_u \rightarrow B^3\Pi_g$ emissions is complemented by high-level *ab initio* calculations of spin-orbit coupling matrix elements as a function of the interatomic distance. Together, these approaches provide comprehensive insights into the predissociation phenomenon observed in the molecular nitrogen spectrum. Figure 1 shows part of the (2-0) band of the transition between the $C^3\Pi_u$ and $B^3\Pi_g$ electronic states. The abnormal distribution of intensities in the R_i branches ($i = 1, 2, 3$) is noticeable. The mixing of the N_2 ($C''^5\Pi_u$) and N_2 ($C^3\Pi_u$) states significantly influences the emission of the second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) and Herman infrared ($C''^5\Pi_u \rightarrow A'^5\Sigma_g$) band systems. Additionally, the $1^7\Sigma_u^+$ state, with a strong spin-orbit coupling with N_2 ($C''^5\Pi u$), plays a crucial role in enabling indirect predissociation, leading to the formation of two $N(^4S)$ atoms. This study provides a crucial step in understanding the indirect predissociation phenomenon in N_2 spectroscopy [6]. Laiz R. Ventura would like to thank the FAPESP for a post-doctoral fellowship (grant number 2023/08074-5). In special, Jayr Amorim thanks the FAPESP (grant number 2023/08074-5) for financial support.

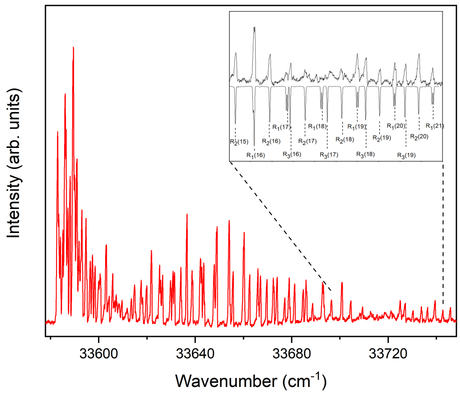

Figure 1: Part of the (2-0) band of $C^3\Pi_u \rightarrow B^3\Pi_g$ electronic state showing in detail the intensity anomaly as a function of the rotational quantum number.

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SYSTEMATIC *AB INITIO* CALCULATION OF ROVIBRATION LINELISTS AND EFFECTIVE HAMILTONIANS USING CANONICAL VAN VLECK OPERATOR PERTURBATION THEORY

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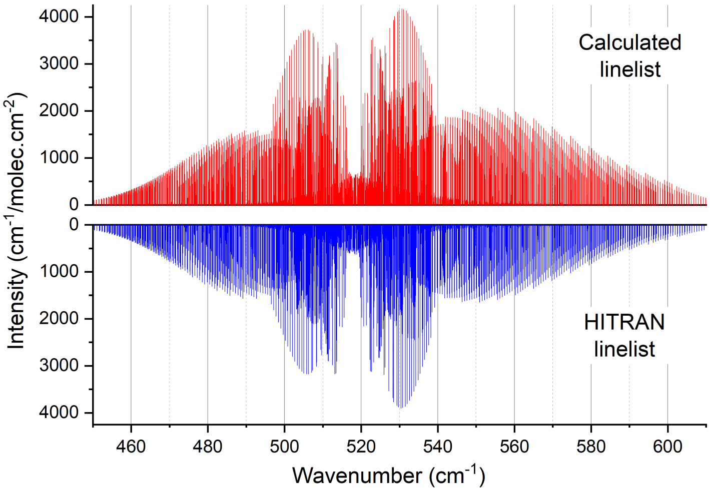

Figure 1: A comparison of calculated and experimental (HITRAN) linelists for ν_2 band of SO_2

A non-empirical prediction of high resolution molecular spectra and effective models provides a crucial supporting information for both deciphering of sophisticated experimental spectra and complementing empirical data missing in spectroscopic databases. While fully *ab-initio* calculation of vibration-rotation spectra involves solving Schrödinger equation with global rovibrational Hamiltonian, a conceptually different inverse problem utilizes effective models with restricted sets of parameters. The bridge between both problems can be built using the operator Van Vleck perturbation theory CVPT(n) that is able to calculate linelists, spectroscopic constants and parameters of effective dipole moment operators. The major computational complication of CVPT(n) arises due to the necessity of evaluation of rotational commutators involving ladder operators of angular momentum (J_z, $J_\pm = J_x \mp iJ_y$). This problem can be efficiently solved using the normal ordering of these operators[1].

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

The obtained effective Hamiltonian and dipole moment operator can be further used for modeling of IR spectra and for iterative solution of inverse spectroscopic problem. A number of numerical examples for 3,4 and 5-atomic molecules is given, demonstrating an efficiency of the developed approach.[2]

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SATURATED ABSORPTION SPECTROSCOPY OF M1 TRANSITIONS OF $^{16}O_2$ IN THE 761-768nm

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Molecular oxygen, an essential atmospheric component, plays critical roles in geochemical and biological processes, motivating its long-term observation across scientific and environmental research. Magnetic dipole transitions of O_2, spanning microwave-to-infrared wavelengths, are vital for remote sensing applications—yet accurate characterization of these weak transitions remains challenging. We report saturated absorption spectroscopy of 38 magnetic transitions in the $^{16}O_2$ A-band ($b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ (0,0)) using a comb-locked cavity ring-down spectrometer[1]. Line positions for 13 ^{P}P, 13 ^{P}Q, 6 ^{R}R and 6 ^{R}Q transitions were determined with <10 kHz uncertainty (zero magnetic field), improving accuracy by two orders of magnitude over prior studies.

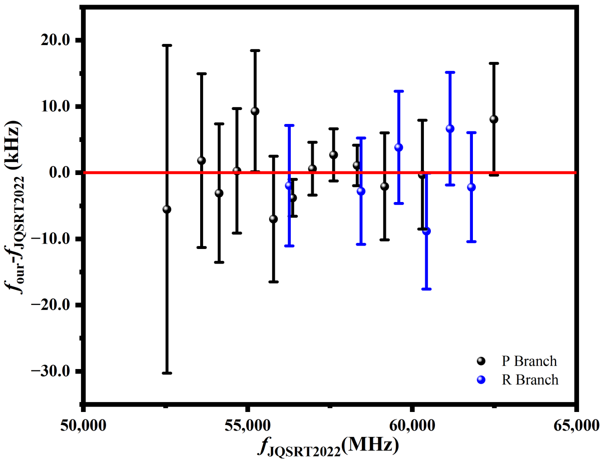

Figure 1: Microwave frequency difference (in kHz) between those determined the vib-rotational energy differences for $\Delta N = 0$ transitions in the $^{16}O_2$ A-band and microwave RAD frequency in [2] with relevant combined 1- σ uncertainties.

The ^{P}P(J)/^{P}Q(J) and ^{R}R(J)/^{R}Q(J) transitions reproduce $\Delta N = 0$ N^-/N^+ transitions (60 GHz region) [2] within 1-σ combination uncertainty, shown in Fig.1. Frequency differences between ^{R}R(J-1)/^{P}Q(J) and ^{R}Q(J)/^{P}Q(J) yield $\Delta N = 2$ THz-region transitions at <10 kHz accuracy—twice as precise as previous measurements. Hamiltonian analysis of $\Delta N = 0$ and $\Delta N = 2$ rotational energy differences enabled determination of new spectroscopic parameters.

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ELECTRONIC SPECTRUM OF JET-COOLED CO_3^-

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The carbonate monoanion, CO_3^-, was generated in supersonic free jet expansions, and measured dispersed fluorescence (DF) spectrum. The anion is isoelectronic with the NO_3 radical. The fluorescence spectrum is in the energy region of the NO_3 $\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$ system. At present, four vibronic bands with interval of $\sim 1100\ \mathrm{cm}^{-1}$ have been identified in the DF spectrum. The interval corresponds to the ν_1 fundamental frequency, $1051\ \mathrm{cm}^{-1}$, of the $\tilde{X}\ ^2A_2'$ state of NO_3 [1,2]. Different from the diffuse rotational structure of the $\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$ transition of NO_3[1,2], the vibronic bands have well-resolved rotational structure. The rotational structures of the vibronic bands are similar among four of them, and they can be roughly simulated assuming the transition as $^2E' - {}^2A_2'$ and adopting rotational constants of NO_3. More precise analyses are now underway.

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A COMPLETE *AB INITIO* SPECTROSCOPIC DATASET OF THE HYDROGEN MOLECULE FOR ASTROPHYSICAL STUDIES

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Diatomic hydrogen is the simplest, yet the most abundant molecule in the Universe. Both H_2 and HD are present in the atmospheres of the giant planets in the Solar System [1], brown dwarfs [2], and interstellar medium [3].

The collisions of the molecules can be directly linked to their spectroscopic properties through the shape of an optical resonance. Our methodology steps beyond the conventional Voigt profile, taking into account the influence of speed-dependent broadening, shift, and velocity-changing collisions on the spectral lines. As will be demonstrated, consideration of such effects allows us to achieve subpercent accuracy when comparing with experiment [4,5].

This presentation encapsulates our recent endeavors aimed at generating a complete spectroscopic dataset for accurate modeling of H_2 and HD interactions within diverse collisional environments. We report over 40 000 unique transitions, providing their positions, frequencies, pressure broadening and shift along with their speed dependencies as well as both the real and imaginary part of the complex Dicke parameter. We report the wide-range temperature dependencies of these parameters in the HITRAN double-power-law (DPL) format at temperatures from 20 to 1000 K [6].

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

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HITRAN2024: MORE MOLECULES/ISOTOPOLOGUES, BROADER SPECTRAL AND DYNAMIC RANGES, MORE PARAMETERS, BETTER QUALITY

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The HITRAN molecular spectroscopic database was established in the 1970s and is used by various computer codes to predict and simulate the transmission and emission of light in gaseous media (with an emphasis on terrestrial and planetary atmospheres). The HITRAN compilation is composed of six major components. The already existing (but updated in this edition) include the line-by-line spectroscopic parameters required for high-resolution radiative-transfer codes, experimental infrared absorption cross-sections (for molecules where it is not yet feasible for representation in a line-by-line form), collision-induced absorption data, aerosol indices of refraction, and general tables (including partition sums) that apply globally to the data. One of the most important achievements of the new edition is that HITRAN2024, the water vapor continuum model, has been added for the first time. The extent of the updates of the line-by-line section in the HITRAN2024 edition ranges from updating a few lines of specific molecules/isotopologues to complete replacements of the lists, and also the introduction of additional isotopologues and new (to HITRAN) molecules. The poster will give a general overview and provide characteristic examples of improvements/enhancements in the database.

The HITRAN2024 edition will be available in September 2025 through `www.hitran.org` and the HITRAN Application Programming Interface (HAPI). The new edition replaces the previous HITRAN edition of 2020 (including its updates during the intervening years).

NEW METROLOGICAL AMMONIA ABSORPTION LINE DATA NEAR 6500 cm^{-1}

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Ammonia (NH_3) is simultaneously an indispensable industrial raw material, a potent atmospheric pollutant, and an emerging hydrogen carrier. In the lower troposphere its emissions drive the formation of fine particulate matter, while in planetary science its rovibrational fingerprints reveal the composition of gas giant and exoplanetary atmospheres. Because NH_3 amount fractions (concentration) span six orders of magnitude - from sub-ppt levels in pristine environments to percent levels in industrial stacks – there has been the need for spectroscopic instruments to accurately retrieve NH_3 concentrations in these applications with high dynamic capabilities. That accuracy of spectroscopic gas concentration results is fundamentally limited by the quality of the underlying absorption line parameters (line centres, intensities, pressure-broadening and -shift coefficients, and their temperature dependences). In the near-infrared window around 6500 cm^{-1} (widely utilized by various analytic instruments) the uncertainties attached to many NH_3 lines in standard databases such as HITRAN still reach several percent. Such deficits propagate e.g. into remote-sensing retrieval errors, bias flux estimates in atmospheric transport models, and constrain the performance of emerging calibration-free instruments known as Optical Gas Standards (OGSs). An OGS is a laser spectrometer that can deliver highly precise and accurate gas concentration results that are directly traceable to the International System of Units (SI) [1, 2]. Precise, SI-traceable line data are therefore a shared requirement for metrology laboratories, environmental networks, and space-borne spectrometers alike.

We present the results of our recent highly accurate measurements of ammonia line data in the spectra around 6500 cm^{-1}. The measurements were performed using a well-established instrument (Bruker 125HR Fourier Transform Spectrometer, resolution of 0.0015 cm^{-1}) equipped with a temperature controlled multi-pass gas cell. Pure ammonia sample pressure and temperature were monitored with calibrated SI-traceable sensors to address the traceability of the line data results. The resulting spectra were processed and analysed with an optimized spectra fitting software to derive the line data. The primary goal of this study was to refine the line parameter values of selected transitions, which will further be used as reference values for an NH_3 Optical Gas Standard (OGS) being developed at PTB. We elaborate on the traceability of the line data to the SI and present a detailed uncertainty budget for the results. Further, we compare our line parameter values (and their uncertainties) to values listed in the HITRAN database.

Acknowledgement: This work was funded by the BMVI-NOW (Bundesministerium für Verkehr und digitale Infrastruktur) RingWaBe (https://www.ringwabe.ptb.de/home) project.

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LINE POSITIONS OF CH_3F IN THE 20 – 100 cm^{-1} AND 1900 – 2400 cm^{-1} SPECTRAL REGIONS

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High-resolution spectra of methyl fluoride (CH_3F) have been analyzed in two key spectral regions: the pure rotational domain (20 – 100 cm^{-1}) and the triad of overlapping rovibrational bands $2\nu_3$, $\nu_3 + \nu_6$, and $2\nu_6$. The rotational spectra were recorded using Fourier Transform (FT) spectroscopy at the **SOLEIL Synchrotron** (AILES beamline, Paris), allowing precise assignments up to $J = 70$. The vibrational spectra were acquired at the **GSMA laboratory** (University of Reims, France) using a high-resolution FT spectrometer.

In this work, measured line positions have been investigated using the MIRS software developed by A.V. Nikitin *et al.*[1] designed for C_{3v} symmetric top molecules, based on a new *ab initio*-based effective Hamiltonian constructed by M. Rey[2] using a potential energy surface built at the CCSD(T)/cc-pVZ level of theory[3]. Transition assignments were performed using **SpectraMatcher**, a dedicated *home-made* code that enables both automatic and manual matching of experimental spectra with theoretical predictions.

The triad formed by the $2\nu_3$, $\nu_3+\nu_6$, and $2\nu_6$ bands was studied in detail. Coriolis interactions between $2\nu_3$ and $\nu_3 + \nu_6$ were found to be significantly stronger than those involving the much weaker $2\nu_6$ band. Assignments were completed up to $J = 45$ for the rovibrational transitions, resulting in nearly 4000 lines successfully identified. These results provide a comprehensive and accurate dataset of line positions that is crucial for atmospheric modeling, spectroscopic databases, and remote sensing applications of CH_3F.

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MARVEL ANALYSIS OF THE MEASURED HIGH-RESOLUTION ROVIBRATIONAL AND ROVIBRONIC SPECTRA OF $^{12}C^{16}O$ MOLECULE

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MARVEL (Measured Active Rotational-Vibrational Energy Levels)[1] is a robust procedure used to derive accurate energy levels of molecules from experimentally measured transition frequencies. In MARVEL, the input consists of experimentally observed transition frequencies, each with an associated uncertainty and quantum state label. These transitions are validated and processed to create a spectroscopic network (SN) where nodes represent energy levels and edges represent transitions. By solving the network using weighted least-squares fitting, MARVEL yields a set of term energies that best reproduce the measured data within their uncertainties.

The electronic structure, and spectral signatures of $^{12}C^{16}O$ molecule have been recently investigated with ab-initio methods[2].As a continuation, this work presents accurate, experimental rovibrational and rovibronic energy levels, with associated uncertainties for the ground[3] and lowest low-lying electronic states. Comparisons of our results with previously published work show remarkable agreement.

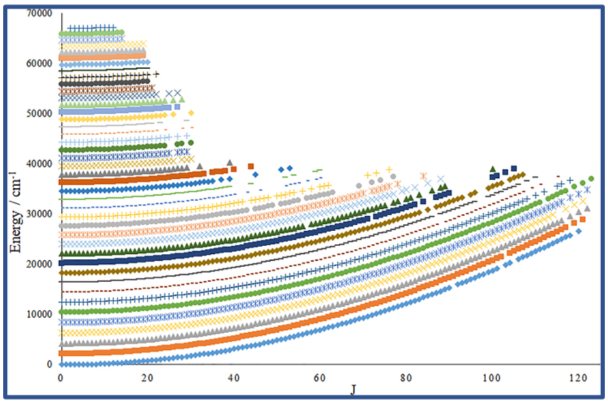

Figure 1: Pictorial representation of the empirical rovibrational energy levels of $^{12}C^{16}O$ as a function of the J rotational quantum number (different colors refer to different vibrational states)

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HIGH RESOLUTION STUDY OF THE ν_{14} BAND OF PYRROLE (C_4H_5N) NEAR 14 μm

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Accurate spectroscopic reference data are crucial for the detection and quantification of trace gases in planetary atmospheres using optical remote sensing techniques. The present study is part of an ongoing effort to supply missing or improved line parameters and absorption cross sections for molecular species of potential interest in planetary environments. The targeted spectral region spans the range 600 to 200 cm^{-1} (16.5 to 5 μm), particularly relevant for current and upcoming space missions.

The present study is a high-resolution investigation of the strong ν_{14} band of pyrrole (C_4H_5N), observed near 14 μm. Building upon the work of Mellouki *et al.*[1], its main objective is to provide for the first time intensity information for this vibrational band.

Ten Fourier transform infrared (FTIR) absorption spectra of pure pyrrole were recorded at pressures between 0.05 and 2.6 hPa, with an absorption path length of 19.7 (2) cm and a spectral resolution of 0.0015 cm^{-1}. Line positions measured therein were analyzed relying on available microwave data for the ground state[2], leading to improved spectroscopic constants characterizing the $v_{14} = 1$ vibrational level of pyrrole. Line intensities and self-broadening coefficients were also retrieved from the recorded FTIR spectra. The line intensities were analyzed using the refined modeling of the rotational structure of the band. The rotational dependence of the measured self-broadening coefficients was studied. As pyrrole exhibits a number of low frequency vibrations, rather prominent hot bands are observed in the FTIR spectra of the ν_{14} band. An analysis of the strongest hot band was undertaken. Results of this ongoing work will be presented and discussed

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EXOMOL LINE LIST FOR THE $A\,^1\Pi$–$X\,^1\Sigma^+$ BAND SYSTEM OF ^{12}C^{16}O AT HIGH TEMPERATURE

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Carbon monoxide (CO) is the second most abundant molecule detected in the universe after H_2, and it plays a crucial role in astrophysics, cosmology, physics, and the chemistry of planetary atmospheres. There is a pressing need for high-quality spectroscopic data on CO to support continued research in these fields.

Regarding current theoretical models of CO, a comprehensive line list for its ground electronic state has already been published[1]. The present work extends this modeling to the fourth-positive band between the excited $A\,^1\Pi$ state and the $X\,^1\Sigma^+$ ground state. The work starts from *ab initio* potential energy curves[2] and uses energy levels determined by a MARVEL (Measured Active Rotational–Vibrational Energy Levels) procedure to improve the representation of the A state. The resulting line list, computed using variation nuclear motion program Duo[3], will be incorporated into the ExoMol database to extend the available CO line list into the ultra-violet.

This new line list will be valuable for spectral characterization and simulation and will serve as input for atmospheric models of exoplanets. To address the specific needs of research on ultra-hot exoplanets, theoretical spectra of CO at 500 K and 3000 K will be provided, in addition to room-temperature spectra for the $A\,^1\Pi$–$X\,^1\Sigma^+$ transition, using the Duo and ExoCross programs. To ensure close agreement between theoretical line positions and experimental measurements, selected hot-band spectra, such as the 10–21 band, will be extracted and compared with experimentally recorded spectra[4].

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CASDA24: LATEST UPDATES TO THE DIJON CALCULATED SPECTROSCOPIC DATABASES

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We introduce `CaSDa24`[1], the latest major update of our high-resolution molecular spectroscopy database cluster developed in Dijon.

This release comprises ten independent databases, each dedicated to a specific molecule (CH_4, CH_3Cl, SF_6, C_2H_4, CF_4, GeH_4, RuO_4, SiF_4, UF_6, SiH_4), integrating significant updates and new molecular data since our 2020 publication. Unlike purely experimental (HITRAN, GEISA) or ab initio databases (ExoMol, TheoReTS), `CaSDa24` adopts the hybrid methodology based on tensorial formalism. Our calculations employ effective Hamiltonian and transition moment operators fitted from line-by-line assigned experimental spectra, ensuring experimental accuracy with comprehensive spectral coverage.

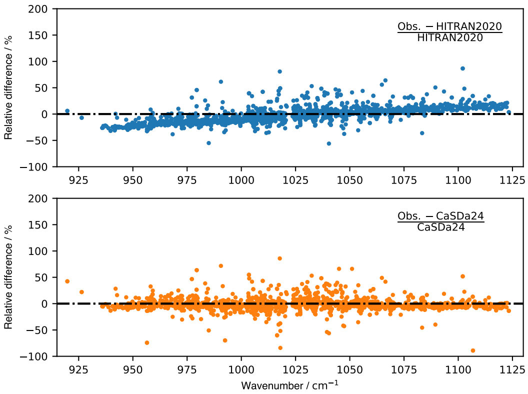

Figure 1: Comparison between HITRAN2020 (blue) and `CaSDa24` (orange) of the ν_6 band of $CH_3{}^{35}Cl$.

This update includes five major revisions: `ECaSDa` (C_2H_4) adds 41,642 transitions in the 2900–3300 cm^{-1} region; `SHeCaSDa` (SF_6) incorporates 31,553 transitions for the $\nu_3 + \nu_5$ combination band; `TFMeCaSDa` (CF_4) adds 284,350 pure rotational transitions via CRDS spectroscopy; `GeCaSDa` (GeH_4) extends to the ν_2/ν_4 dyad with 28,486 new transitions; and `TFSiCaSDa` (SiF_4) receives 677,519 lines including hot bands.

Three new databases are introduced: `UHeCaSDa` (UF_6) with 110,041 transitions for eight isotopologues; `ChMeCaSDa` (CH_3Cl) with 12,152 lines for two isotopologues; and `SiCaSDa` (SiH_4) containing 33,910 transitions including pure rotational lines. All databases maintain identical SQL structure and are freely accessible via `https://vamdc.icb.cnrs.fr` in HITRAN2012 format. Comparative analysis with HITRAN2020 demonstrates superior accuracy for CH_3Cl intensity modeling. These databases serve critical applications in atmospheric remote sensing, exoplanet characterization, and molecular physics research.

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THE ROTATIONAL CONFORMATIONAL BEHAVIORS OF PHENOL – THIOPHENOL HETERODIMER

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Figure 1: The observed conformational structures for the phenol–thiophenol heterodimer (PN–TPN).

Non-covalent interactions (NCIs) play a crucial role across various disciplines, including biology, chemistry, and physical chemistry. In particular, NCIs involving aromatic compounds–which are often key to maintaining balance in certain proteins–have long been a focus of intense study.[1] In previous work, rotational spectroscopic investigations of the phenol dimer[2] and thiophenol dimer[3] have been carried out, revealing notably different interaction preferences between the two. In this study, we investigate the NCIs of the phenol–thiophenol heterodimer (PN–TPN). The experimental approach combines broadband Chirped-Pulsed Fourier Transform Microwave (CP-FTMW) spectroscopy with ab initio and density functional theory (DFT) calculations. The PN–TPN complex was generated in a jet-cooled expansion and analyzed via the rotational spectrum in the 2–8 GHz range. Two distinct dimers were observed, each adopting a so–called "hinged" configuration stabilized primarily by an alcohol-to-alcohol O–H···O hydrogen bond, as well as additional weaker interactions between the aromatic rings. Notably, the structural motifs forming these dimers differ: the trans configuration corresponds to dimer I, while the cis configuration corresponds to dimer II (see Figure 1). Further experimental and computational details related to this system will be presented during the conference.

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THE THRESHOLD PHOTOELECTRON SPECTRUM OF THE THIOFORMYL RADICAL: EXPERIMENT AND MODELING

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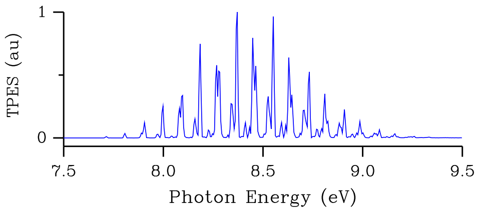
The ground electronic state of the thioformyl radical (HCS) is split into a lower bent $X\,^2A'$ and an upper linear $A\,^2A''$ electronic state by the Renner-Teller coupling. The lower state is characterized by a low barrier to linearity[1–3] calculated to be in the range 2500 to 3330 cm^{-1}. The microwave data available for this lower state are consistent with a slightly asymmetric top molecule characterized by a very large A rotational constant of nearly 1 THz and a small value of $B - C$ equal to 426 MHz.[4,5] The photoionization spectrum of the thioformyl radical was first studied by photoionization mass spectrometry in the pioneering investigation of Ruscic and Berkowitz.[6] They observed a long Franck-Condon progression, starting at 7.51 eV, in the total ion yield and the Franck-Condon active mode was assigned to the bending mode of the cation HCS$^+$. The substantial geometry change undergone by HCS upon ionization was shown to be consistent with the length of the Franck-Condon progression. Ruscic and Berkowitz[6] obtained an upper limit of 7.5 eV for the adiabatic ionization potential but they were unable to unambiguously determine its value.

In the present paper, the photoelectron spectrum of the thioformyl radical has been measured for the first time in the 7 to 10 eV energy range. The radical was formed through the reaction of a mixture of H_2S and C_3H_4 with F atoms in a microwave discharge flow-tube. The resulting products were ionized with synchrotron radiation from the DESIRS beam-line at Synchrotron SOLEIL and the mass-selected threshold photoelectron spectrum (TPES) was recorded with a double-imaging photoelectron photo-ion coincidence spectrometer. The experimental setup allows clear observation of the entirety of the Franck-Condon progression only partially recorded by Ruscic and Berkowitz.[6] This progression spans the region from 7.5 to 9 eV. From 9 to 10 eV, there remain several unassigned features that might be due to the isomeric species HSC.

The photoelectron spectrum will be modeled with a theoretical approach accounting for all three vibrational modes and relying on potential energy surfaces, for the neutral and the cation, already available[2,7] or computed in this work. This approach accounts exactly for the quasi-linearity, due to the low barrier to linearity,[1–3] which is treated using a rovibrational Hamiltonian such that the molecule fixed z axis is parallel to the CS bond. By comparing observed and calculated spectra, we are hoping to retrieve an accurate value of the adiabatic ionization potential. The figure on the right displays a preliminary TPES computed for a rotational temperature of 300 K and a zero vibrational temperature.



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[6] Ruscic and Berkowitz, *J. Chem. Phys.* **98** (1993) 2568

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M: Minisymposium on Clocks and Metrology

Thursday, August 28, 14:00
Hörsaal I

Chair: Paolo De Natale

Molecular Physics Lecture

COHERENCE, CLOCKS, AND FUNDAMENTAL PHYSICS

Jun Ye

JILA, National Institute of Standards and Technology and University of Colorado Boulder,
Colorado 80309-0440, USA

Scaling up quantum systems to long coherence and large system sizes promises to revolutionize the performance of atomic clocks and quantum sensors, giving opportunities for new discoveries. Precise control of optical phase and ultracold matter has brought tens of thousands of atoms to minute-long optical coherence, enabling unprecedented measurement precision. Recent advances include determination of the gravitational time dilation across a few hundred micrometers, and the use of spin entanglement for clock precision beyond the standard quantum limit at $1\text{x}10^{-18}$. Meanwhile, the combination of ultrafast optics and precision metrology has given us new tools for nuclear physics, leading to the recent breakthrough of quantum-state-resolved laser spectroscopy of Thorium-229 nuclear transition. The permeation of quantum metrology to all corners of physics sparks new ideas to probe the interface of gravity and quantum mechanics and search for new physics.

MOLECULAR LATTICE CLOCKS

T. Zelevinsky[a]

[a] Columbia University, USA

High-precision spectroscopy has long been central to advancing our understanding of the physical world. With the development of laser cooling techniques and atomic clock technologies, the field has entered a new era. These powerful methods can now be extended to more complex quantum systems, such as diatomic molecules. The ability to precisely measure molecular degrees of freedom, for example, nuclear vibrations, offers unprecedented insight into their subtle properties [1,2]. Furthermore, it opens up new opportunities to probe fundamental physical interactions at the nanometer scale, particularly through high-accuracy measurements of molecular vibrational isotope shifts [3].

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[1] S. S. Kondov, C.-H. Lee, K. H. Leung, C. Liedl, I. Majewska, R. Moszynski, and T. Zelevinsky **2019** *Nat. Phys.*, 15, 1118

[2] K. H. Leung, B. Iritani, E. Tiberi, I. Majewska, M. Borkowski, R. Moszynski, and T. Zelevinsky **2023** *Phys. Rev. X*, 13, 011047

[3] E. Tiberi, M. Borkowski, B. Iritani, R. Moszynski, and T. Zelevinsky **2024** *Phys. Rev. Res.*, 6, 033013

HIGHLY CHARGED ION CLOCKS TO TEST FUNDAMENTAL PHYSICS

Piet O. Schmidt[a,b]

[a] Physikalisch-Technische Bundesanstalt, Braunschweig, Germany
[b] Institut für Quantenoptik, Leibniz Universität Hannover, Hannover, Germany

The extreme electronic properties of highly charged ions (HCI) render them highly sensitive probes for testing fundamental physical theories[1]. The same properties reduce systematic frequency shifts, making HCI excellent optical clock candidates. The technical challenges that hindered the development of such clocks have now all been overcome, starting with their extraction from a hot plasma and sympathetic cooling in a linear Paul trap[2], readout of their internal state via quantum logic spectroscopy[3], and finally the preparation of the HCI in the ground state of motion of the trap[4]. Here, we present the first operation of an atomic clock based on an HCI (Ar^{13+} in our case) and a full evaluation of systematic frequency shifts of the employed $^2P_{1/2} - {}^2P_{3/2}$ fine-structure transition at 442 nm[5]. The achieved uncertainty is almost eight orders of magnitude lower than any previous frequency measurements using HCI and comparable to other optical clocks. One of the main features of quantum logic spectroscopy is the flexibility of the investigated species. This allowed us to perform isotope shift spectroscopy of the $^2P_0 - {}^2P_1$ fine-structure transition at 569 nm in Ca^{14+} ions. In a large theory-experiment collaboration, we combined this data with improved measurements of the Ca^+ $^2S_{1/2} - {}^2D_{5/2}$ clock transition at 729 nm, new isotope mass measurements, and highly accurate calculations of the 2nd order mass shift. The resulting King plot allows us to put the currently most stringent bound from isotope shifts on a hypothetical 5th force coupling neutrons and electrons, despite a large ($\sim 900\sigma$) residual nonlinearity, suspected to be dominated by nuclear polarizability[6]. This demonstrates the suitability of HCI as references for high-accuracy optical clocks and to probe for physics beyond the standard model.

A next-generation HCI optical clock may be based on Ni^{12+}, which offers a long excited state lifetime of > 10 s. By developing efficient search strategies with quantum logic techniques[7] and precise atomic structure calculations[8], we identified the logic and clock transitions in this species within just a few hours of searching.

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[1] M. G. Kozlov *et al.*, Rev. Mod. Phys. **90**, 045005 (2018). S. Schiller, Phys. Rev. Lett. **98**, 180801 (2007).

[2] L. Schmöger *et al.*, Science **347**, 1233–1236 (2015).

[3] P. Micke *et al.*, Nature **578**, 60–65 (2020).

[4] S. A. King *et al.*, Phys. Rev. X **11**, 041049 (2021).

[5] S. A. King *et al.*, Nature **611**, 43–47 (2022).

[6] A. Wilzewski *et al.*, accepted for publication in Phys. Rev. Lett., arXiv:2412.10277

[7] Chen *et al.*, Phy. Rev. Appl. **22**, 054059 (2024).

[8] Cheung *et al.*, arXiv:2502.05386

N-I: Contributed Talks

Thursday, August 28, 16:30
Hörsaal I

Chair: Neil Reilly

QUANTITATIVE ABSORPTION SPECTROSCOPY OF ACETYLENE IN THE BLUE REGION

H. Fleurbaey[a], G. Méjean[a], S. Kassi[a], and A. Campargue[a]

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We present an improved mode-locked cavity absorption spectrometer[1] coupling a tunable grating spectrograph and a femtosecond titanium-sapphire laser, whose second harmonic generation provides access to a spectral region from 340 to 540 nm. Presently designed to cover the blue region (385-435 nm), the system consists in injecting the laser light into a high-finesse cavity (finesse 43,000, 26 km effective path length) and recording, with a CCD camera, the transmitted light that has been dispersed with an exceptionally high-resolution (800,000) grating spectrograph. The absolute calibration of the absorption axis is obtained from the ring-down time of the empty cavity. Leveraging the properties of grating dispersion, frequency calibration of the blue spectra mainly relies on an iodine cell probed in the green region.

To assess the instrumental performance, we focused on an acetylene (C_2H_2) band that was detected four decades ago[2] using ultra-sensitive yet hardly quantitative photoacoustic spectroscopy. We have quantitatively studied the pressure dependence of the highly excited ro-vibrational overtone band ($7\nu_{CH} + \nu_2$) near 435 nm with unprecedented accuracy (Fig. 1), evidencing perturbations in the upper energy levels. Additionally, thanks to the high resolution (sub-GHz) and sensitivity (minimum absorption sensitivity of 3×10^{-10} cm^{-1}) of our setup, we could observe and analyze several C_2H_2 hot bands in the vicinity of the overtone, reaching energy levels well above what is reported in literature.

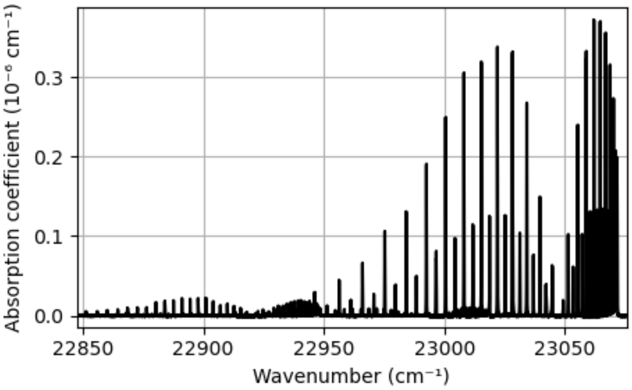

Figure 1: Spectrum of the $7\nu_{CH} + \nu_2$ band of C_2H_2 (ca. 435 nm) recorded at 60 Torr.

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[1] Gherman, T. and Romanini, D. **2002** *Opt. Express*, 10, 1033.

[2] Hall, R. R. PhD Thesis **1984** Rice University.

PRECISION SPECTROSCOPY AND FREQUENCY STABILIZATION USING A COMPACT DUAL-MODE CAVITY-ENHANCED ABSORPTION SPECTROMETER AT 1550 nm

W.-T. Wang[a], T.-P. Hua[b], Z.-T. Zhang[c], Z.-J. Yuan[a], Y.-R. Sun[b], A.-W. Liu[a,d], and S.-M. Hu[a,c]

[a] Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China
[b] Institute of Advanced Science Facilities, Shenzhen, 518107, China
[c] Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China
[d] State Key Laboratory of Molecular Reaction Dynamics, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

The development of precision frequency references at 1550 nm is limited by scarce molecular transition options for fiber-optic communications and coherent LiDAR applications. We identify the $(101)3_{21} \leftarrow (000)3_{12}$ rovibrational transition of $HD^{16}O$ at 1549.8639 nm as a metrologically viable candidate, offering complementary capabilities to existing BIPM-recommended standards. A compact dual-mode cavity-enhanced absorption spectrometer (30 cm × 30 cm footprint) employing spectral characterization and active locking enables precision spectroscopy and laser stabilization via differential piezoelectric transducer (PZT) feedback for cavity length control. Using wavelength-modulated cavity-enhanced saturated absorption spectroscopy with optical frequency comb calibration, we determine the absolute transition frequency to be 193,431,476,145.8(12) kHz. The system achieves 2×10^{-12} frequency stability at 512 s integration time and sustains <20 kHz frequency deviation over 10-hour continuous operation with a cavity leaking rate of 0.18 Pa/hour (Shown in Fig. 1) – performance rivaling conventional acetylene-based references in this spectral band. This work establishes $HD^{16}O$ transitions as practical frequency references for field-deployable wavelength stabilization in next-generation photonic systems operating at telecom wavelengths.

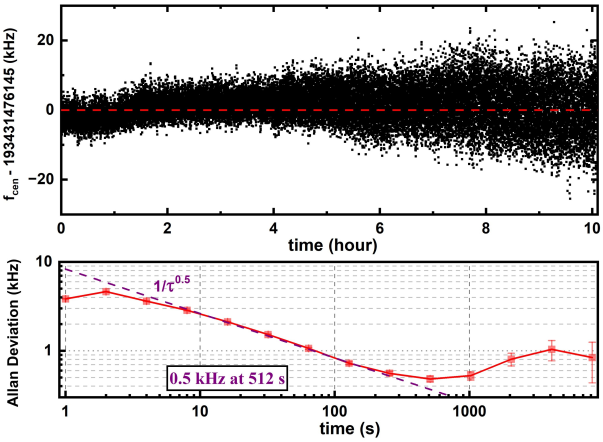

Figure 1: Frequency drift of the stabilized-laser at 1550 nm. Allan deviations are shown in the bottom panel.

SPECTROSCOPIC GAS TEMPERATURE AND CONCENTRATION DETERMINATION USING CARBON MONOXIDE LINE INTENSITIES

S. Wójtewicz[a], D. Lisak[a], V. D'Agostino[b], A. Cygan[a], M. Gibas[c], P. Wcisło[a], R. Ciuryło[a], K. Bielska[a]

[a] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziadzka 5, 87-100 Torun, Poland
[b] Department of Mathematics and Physics, Università degli Studi della Campania "Luigi Vanvitelli", Caserta, 81100, Italy
[c] Central Office of Measures, Physical Chemistry and Environment Department, Świętokrzyskie Laboratory Campus of the Central Office of Measures, Poland

The redefinition of the International System of Units (SI) distinguished unit definitions, now based on fixed physical constants, from their practical realizations, allowing flexibility in selecting physical equations that connect these constants to the measured quantities.[1] In the case of temperature, the accurate methods previously employed to determine the Boltzmann constant, k, can be used for primary thermometry. Among these methods, two optical spectroscopic techniques, namely Doppler broadening thermometry (DBT) and rovibrational line-intensity ratio thermometry (LRT), have undergone intense development in recent years. While the DBT has shown the best accuracy to date, the LRT can be applied in a considerably wider range of gas pressures.

Here we present an LRT-based calibration-free spectroscopic gas temperature and concentration measurement method based on cavity mode-dispersion spectroscopy (CMDS).[2,3] This technique links the spectrum derived from observed frequencies of high-finesse cavity resonances to the primary frequency standard. Using the LRT measurements of the CO (3–0) vibrational band lines and *ab initio* calculated line intensities,[4] we achieve a temperature uncertainty of 24 mK at 296 K (82 ppm).[5] This result is over an order of magnitude lower than any previously reported spectroscopic thermometry at gas pressures above 1.2 kPa. We also demonstrate sub-permille uncertainty (250 ppm) in absolute gas concentration measurements over a pressure range from 50 Pa to 20 kPa by using the spectroscopic temperature and integrated line areas from several CO lines with intensities differing by more than two orders of magnitude. Moreover, we adress current limitations and perspectives for improving the accuracy of spectroscopy[6] and the reference data[7] for the primary thermometry and amount of substance measurement.

The research was supported by: the European Partnership on Metrology project 22IEM03 PriSpecTemp; 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.

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[2] Cygan, A. et al., **2015** *Opt. Express* 23, 14472
[3] Cygan, A. et al., **2019** *Opt. Express* 27, 21810
[4] Bielska, K. et al., **2022** *Phys. Rev. Lett.* 129, 043002
[5] Lisak, D. et al., **2025** arXiv:2502.17660 [physics.optics]
[6] Cygan, A. et al., **2025** *Sci. Adv.* 11, eadp8556
[7] Hodges, J. T. et al., **2025** *Metrologia*, 62, 08006

LEAK-OUT SPECTROSCOPY OF RENNER-TELLER DISTORTED $HNCS^+$

M. Gerlach[a], J. van der Hulst[a], H. Kaur[a], G. C. Groenenboom[b] and S. Brünken[a]

[a] HFML-FELIX, Nijmegen, the Netherlands & Institute for Molecules and Materials, Radboud University, Nijmegen, the Netherlands
[b] Institute for Molecules and Materials, Radboud University, Nijmegen, the Netherlands

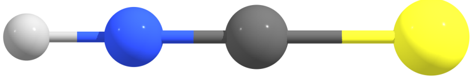

Figure 1: Structure of $HNCS^+$.

Neutral isothiocyanic, HNCS, was first detected in the interstellar medium (ISM) in 1979 in Sagittarius B2 by Frerking *et al.*[1] Since then it was also detected in the "sulphur factory" TMC-1 and the "rotten egg" Nebula OH231.8+4.2.[2][3] Positively charged isothiocyanic acid, $HNCS^+$, may be produced from neutral HNCS via cosmic ray ionization in the ISM. In addition, $HNCS^+$ is also a molecule of fundamental spectroscopic interest because of its linear and electronically degenerate $^2\Pi$ ground state. This leads to the Renner-Teller effect which constitutes a breakdown of the Born-Oppenheimer approximation due to the coupling of vibrational and electronic angular momenta. The consequences are experimental and computational challenges, which we addressed by using the novel leak-out spectroscopy (LOS) developed in Cologne[4] to measure the infrared action spectra, and an effective Hamiltonian approach developed in our group to describe Renner-Teller distorted systems.[5]

The experiments were conducted using FELion, a cryogenic 22-pole ion trap instrument[6] coupled to the infrared free electron lasers available at HFML-FELIX.[7] For these experiments FELIX-2 provided infrared photons in the range from 333 to 2200 cm^{-1}. Using LOS at 18K and Ne as a collision partner, we were able to measure the asymmetric NCS stretching mode as well as the low-lying Renner-Teller perturbed HNC and NCS bending modes. Our effective Hamiltonian approach then allowed us to fit the experimental spectrum and extract the Renner-Teller parameters.

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[1] M. A. Frerking, R. A. Linke, P. Thaddeus, *Astrophys. J.* **1979**, 234, L143-L145.

[2] L. Velilla Prieto, C. Sánchez Contreras, J. Cernicharo, M. Agúndez, G. Quintana-Lacaci, J. Alcolea, V. Bujarrabal, F. Herpin, K. M. Menten, F. Wyrowski, *Astron. Astrophys.* **2015**, 575, A84.

[3] G. R. Adande, D. T. Halfen, L. M. Ziurys, D. Quan, E. Herbst, *Astrophys. J.* **2010**, 725, 561-570.

[4] P. C. Schmid, O. Asvany, T. Salomon, S. Thorwirth, S. Schlemmer, *J. Phys. Chem. A* **2022**, 126, 8111-8117.

[5] K. Steenbakkers, T. van Boxtel, G. C. Groenenboom, O. Asvany, B. Redlich, S. Schlemmer, S. Brünken, *Phys. Chem. Chem. Phys.* **2024**, 26, 2692-2703.

[6] P. Jusko, S. Brünken, O. Asvany, S. Thorwirth, A. Stoffels, L. van der Meer, G. Berden, B. Redlich, J. Oomens, S. Schlemmer, *Faraday Discuss.* **2019**, 217, 172-202.

[7] https://hfml-felix.com/

JET-COOLED ETHYLENE SPECTROSCOPY IN THE 5880-6200 cm^{-1} REGION TO STUDY COLD AND HOT BAND TRANSITIONS

S. Perot[a,b], J. Lecomte[a], N. Suas-David[a], L. Rutkowski[a], M. Rey[c], S. Kassi[d], and R. Georges[a]

[a] IPR, UMR 6251, Université de Rennes, Rennes, France
[b] SQUARES, C.P.160/09, BLU-ULB Brussels Laboratory of the Universe, Université libre de Bruxelles, Brussels, Belgium
[c] GSMA, UMR 7331, Université de Reims, Reims, France
[d] LIPhy, UMR 5588, Université Grenoble Alpes, Saint Martin d'Hères, France

Small hydrocarbons are expected in the atmosphere of warm and hot Jupiter exoplanets and their detection relies on the availability of spectroscopic data at relevant temperatures. In the case of ethylene, the spectroscopic data available is very scarce, partly due to its 12 non-degenerate vibrational modes that lead to a highly congested spectrum, even at low temperatures.

In a first step, the rotational structure of the spectrum was simplified to enable spectral assignment of cold band transitions in the 5880-6200 cm^{-1} spectral region. To do so, jet-cooled absorption spectra of ethylene were recorded at three different rotational temperatures (6/8 K, 12 K, 38 K) using cavity ring-down spectroscopy (CRDS). Direct comparison with the TheoReTS variational line lists[1] lead to the identification of 320 rovibrational transitions in 20 interacting vibrational cold bands[2], among which 14 had never been observed before. This line by line assignement was confirmed using lower state combination differences (LSCD). 15 of the identified bands were fitted using PGOPHER[3] to determine their band center and rotational constants.

In a second step, ethylene was preheated to $T_0 = 650$ K and 850 K using a high enthalpy source (HES) prior to its expansion through a Laval nozzle[4] to investigate rotationally cold lines belonging to both hot and cold bands. Parts of the spectra recorded with $T_0 = 650$ K and 850 K are shown in the middle and lower pannels of Fig 1. A comparison with the spectrum at $T_0 = 300$ K and $T_{rot} = 12$ K (upper pannel) highlights the presence of hot band transitions. The analysis of the spectrum with $T_0 = 650$ K based on TheoReTS calculations revealed the presence of 812 transitions belonging to 22 cold bands and 218 lines in 5 hot bands. 53 lines belonging to two additional hot bands were identified in the spectrum at $T_0 = 850$ K, paving the way for ethylene detection on warm Jupiters.

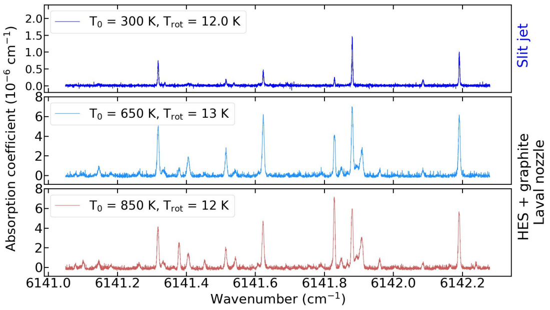

Figure 1: Rotationnally cold spectra of ethylene recorded from $T_0 = 300$ K (upper pannel),
$T_0 = 650$ K (middle pannel) and $T_0 = 850$ K (lower pannel).

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[1] Rey, M., *et al.*, **2016** *J. Mol. Spectrosc.* 327, 138
[2] Perot, S., *et al.*, **2024** *JQSRT* 324, 109065
[3] Western, C. M., **2017** *JQSRT* 186, 221
[4] Dudás, E., *et al.*, **2020** *J. Chem. Phys.* 152, 134201 ; Dudás, E., *et al.*, **2023** *ICARUS* 394, 115421

A VERSATILE INSTRUMENT TO STUDY THE REACTIVITY AND SPECTROSCOPY OF ISOMER-SELECTED MOLECULAR IONS

C. Rossi[a], A. P. Rasmussen[a,b], B. Gans[a], J. Jašík[c], J. Žabka[c], and U. Jacovella[a]

[a] Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay, France
[b] Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, 8000 Aarhus C, Denmark
[c] J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic

Distinguishing the chemical reactivity of isomers remains a fundamental challenge in chemistry, particularly in cluster chemistry, where the number of possible structures increases rapidly with cluster size. We present a novel instrument designed to measure the kinetics of ion-molecule reactions of laser-ablated species with isomer-specific resolution. This is achieved by combining drift-tube ion mobility spectrometry with mass spectrometry, enabling shape-based selection of ions prior to probing their chemical reactivity. The capabilities of this approach are demonstrated through the determination of isomer-specific reaction rate coefficients for the C_{40}^+ cluster, a system known to exhibit multiple coexisting isomers.[1]

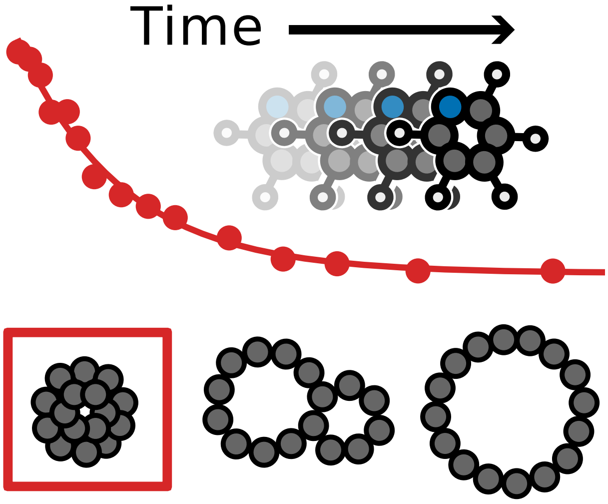

Figure 1: Illustration of our ability to study the reactivity of isomer-selected molecular ions.

In addition to kinetic measurements, the instrument also enables the acquisition of electronic spectra of cryogenically cooled molecular ions that have been both mass- and shape-selected. These spectra are recorded via action spectroscopy techniques and are particularly relevant for the ongoing effort to identify the carriers of the diffuse interstellar bands (DIBs)–a series of absorption features observed in the spectra of starlight passing through diffuse interstellar clouds. The ion mobility spectrometer serves a dual purpose: (i) it highlights "magic structures", particularly stable species that are likely to withstand the harsh ultraviolet conditions of the interstellar medium, and (ii) it enables isomer-specific electronic spectroscopy. The capabilities of the setup will be illustrated through the electronic spectra of carbon cluster rings, with results that reproduce previous experimental findings.[2,3] We will also hopefully present some promising new DIB candidates.

Figure 2: Using the DIBs to bridge the knowledge gap in the carbon life cycle.

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[1] Rossi *et al.*, **2025** *Chem. Methods* 2500013
[2] Marlton *et al.* **2023** *J. Phys. Chem. A.*, 127,1168
[3] Rademacher *et al.* **2022** *J. Phys. Chem. A.*, 126,2127

N-II: Contributed Talks

Thursday, August 28, 16:30
Hörsaal II

Chair: Sergey Yurchenko

CS^{2+}: A COMPLEX MODEL FOR SPECTROSCOPIC APPLICATIONS

L. Hrubcik[a], T. Uhlíková[a],

[a] Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Prague, Czech Republic

Sulfur plays a significant role in the chemistry of the interstellar medium (ISM). Despite the relatively low gas phase abundance of sulfur-bearing molecules, several small molecules were detected, such as CS, CS_2, SO, H_2S, OCS or CH_2CHCHS. Although physical conditions in the ISM are usually quite harsh (low pressure, high radiation), there are not many charged molecular species identified (roughly 15 % of the identified molecules (CDMS 26.6.2025)). There are just few theoretical studies, that focus on dications and even less experimental studies that could support those theoretical models. The reason may be that these molecules should theoretically not exist as they have dissociative potential curves. However, there is at least one positively detected dication CO^{2+} in the atmospere of Mars[1].

We choose to focus on an CS^{2+} ion as its neutral "brother" was already detected in the ISM. CS^{2+} could occur, for example, in the ionospheres of vulcanic planets, such as Venus. Our goal is to create a complex spectral model using highly precise ab initio calculations. Potential energy curves (PECs) for six lowest laying electronic states were calculated, alongside with dipole moment curves, transition dipole moment curves, spin-orbit coupling curves, and transition electronic angular momentum curves, using the multireference configuration interaction (MRCI) method with augmented V5Z-DK basis set including relativistic corrections. This model can be used to simulate spectra for variable conditions (temperature and pressure) to match those of experimentally studied objects, from planetary atmospheres to galactic coronas.

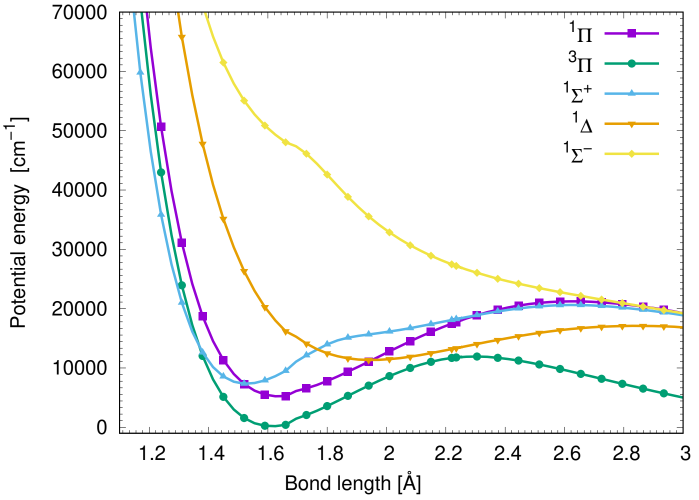

Figure 1: Potential energy curves of six lowest laying electronic states of CS^{2+} molecule

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[1] Beth, A., Altwegg, K., Balsiger, H., Berthelier, J.-J., et al., (**2020**) *Astronomy and Astrophysics*, 642, A27

TEMPERATURE-DEPENDENT PHOTODISSOCIATION CROSS SECTIONS AND RATES FOR H_2O AND H_2S

Armando N. Perri[a], Alexander O. Mitrushchenkov[b], Sergei N. Yurchenko[a], and Jonathan Tennyson[a]

[a] Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom
[b] MSME, Université Gustave Eiffel, CNRS UMR 8208, Univ Paris Est Creteil, F-77474 Marne-la-Vallée, France

The photodissociation of molecules impacts the composition and dynamics of many astronomical systems. The vacuum ultraviolet irradiation of an exoplanet by its host star, for instance, leads to complex photochemistry in its upper atmosphere. In the study of observable exoplanets and other hot astronomical bodies, it is thus critical to understand the effect of temperature on such processes. Water (H_2O) and hydrogen sulphide (H_2S) are important equilibrium species in exoplanetary atmospheres that yield many subsequent photochemical products. This is of particular importance with recent SO_2 detections using the James Webb Space Telescope (JWST). Accordingly, this work presents temperature-dependent photodissociation cross sections and rates for both H_2O and H_2S. All time-independent nuclear motion calculations were performed using the EVEREST program with an exact kinetic energy operator and *ab initio* potential energy, coupling and transition dipole moment surfaces. These data are compared to experimental measurements and photodissociation rates are analysed for important radiation fields.

THE INVERSION-INTERNAL ROTATION-ROTATION PROGRAMME FOR THE METHYLAMINE MOLECULE

M. Kręglewski and I. Gulaczyk

Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poland

Methylamine is considered as a model molecule that exhibits two different large-amplitude motions: CH_3 internal rotation and NH_2 inversion. These two large-amplitude motions are strongly coupled and give rise to a rich rotation-inversion-torsion structure in the vibrational states. In the current work, recent progress is reported on the development of the program to predict inversion-torsion-rotation energy levels and the fitting of the experimental data for methylamine. The program is built using a global approach based on a 2-dimensional model. Since the fit to a single state model based on the group theoretical formalism of Hougen and Ohashi [1] does not work for higher torsional excited states of methylamine, a global fit was performed from the inversion-torsion-rotation Hamiltonian for the ground state, four excited torsional states (first, second, third, and fourth) and inversion state. The best standard deviation of 0.27 cm^{-1} was obtained for a fit to 9500 transitions using 23 molecular parameters for J and K values up to 10 [paper in preparation]. To improve a quality of fit results, the parameters of higher-order terms of the inversion-torsion-rotation Hamiltonian need to be developed and implemented into the program. Thus, appropriate matrix elements were derived and coded. This work is in progress.

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[1] Ohashi, N., Hougen, J.T.,**1987** *J. Mol. Spectrosc.*, 121, 474.

AI-GENERATED SOFTWARE SUITE APPLIED TO RO-VIBRATIONAL ANALYSIS OF HIGH-RESOLUTION FTIR SPECTRA OF THE ^{13}C-ENRICHED MIXTURE OF CHClF$_2$ ISOTOPOLOGUES

E.O. Dobrolyubov[a,b], I.M. Efremov[a,b], S.V. Krasnoshchekov[a],
V.B. Laptev[c], S.A. Klimin[c], and O.V. Naumenko[d]

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[b] Emanuel Institute of Biochemical Physics of RAS, Kosygina ul. 4, 119334, Moscow (Russia)
[c] Institute of Spectroscopy, RAS, Fizicheskaya Ul. 5, 108840 Troitsk, Moscow (Russia)
[d] V.E. Zuev Institute of Atmospheric Optics, RAS, Acad. Zuev Sq. 1, 634055 Tomsk (Russia)

A vast majority of modern empirical analyses of high-resolution spectra are conducted using sophisticated program suites with such methods as combination differences and/or Loomis-Wood diagrams. Often such programs are developed in separate research teams by experienced programmers over a long period of time.

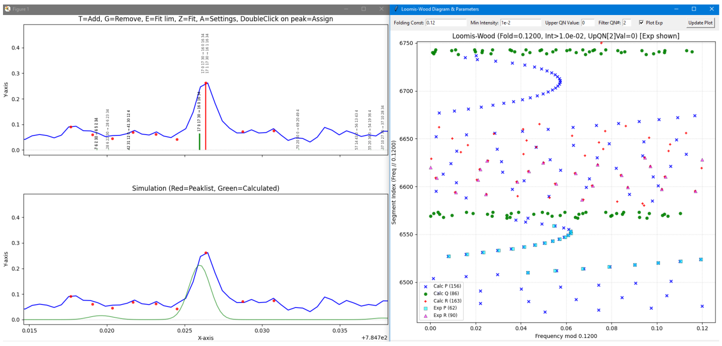

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Figure 1: An example of a graphical user interface of the AI-generated program.

Very recently, rapid advances in artificial intelligence (AI) tools have significantly reduced the time and made it accessible to a wide range of researchers to translate theoretical methods and algorithmic ideas into complex software using modern programming languages such as Python. In this report, we demonstrate an efficient solution of a dual problem: a seamless creation of a comprehensive new software using AI ‘vibe coding’ via sequential instructions (prompts) and its application to deciphering highly complex molecular spectra of a mixture of four HCFC-22 (CHClF$_2$) isotopologues, enriched in ^{13}C by 30%.

This chemical substance is an important atmospheric pollutant and its IR high-resolution spectra for most abundant isotopologues (^{35}Cl,^{37}Cl) were studied in a number of publications [1] [2] [3]. However, so far the high-resolution spectra of rovibrational bands of two ^{13}C isotopologues were not investigated. As a result of the analysis of the main and ^{13}CH^{35}ClF$_2$ substituted isotopologues, new line lists, empirical energy levels and spectroscopic parameters of effective Hamiltonians were obtained.

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METHYL INTERNAL ROTATION AND ^{14}N NUCLEAR QUADRUPOLE COUPLING EFFECTS IN THE MICROWAVE SPECTRUM OF 2-FLUORO-4-PICOLINE ANALYZED USING THE `WESTERFIT` PACKAGE

J.H. Westerfield[a], Mike Buttkus-Barth[a], and Ha Vinh Lam Nguyen[a]

[a] Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France

The microwave spectrum of 2-fluoro-4-picoline was previously measured in 2020 using a resonator-based Fourier-transform microwave spectrometer.[1] The presence of a methyl internal rotor introduces torsional splitting, while the nitrogen nucleus gives rise to a hyperfine structure. Only the A symmetry species could be assigned. We re-investigated the spectrum using the chirp-excitation mode of the newly developed Passage And Resonance In Synergy (PARIS) spectrometer in the range of 5–20 GHz,[2] adding in the E species transitions and bringing the final line count up to 846 transitions. The barrier to methyl internal rotation was determined to be 46.94154(82) cm^{-1}. Initial fits using the *XIAM*[3] program were performed but struggled to meet measurement accuracy of $\sim$4 kHz due to the low barrier height. This was later achieved using the `westerfit`[4] program. The spectrum has been fit in both the Rho Axis Method (RAM) and the reduced Principal Axis Method (PAM) with comparable root means square deviation between the two methods. The conversion of parameters between RAM, reduced PAM, and the traditional PAM will be discussed. Recent improvements and changes to the program will also be given.

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COLLISIONAL EFFECTS IN ATMOSPHERIC SPECTRA THROUGH RIGOROUS QUANTUM SCATTERING CALCULATIONS

M. Gancewski, H. Jóźwiak, A. Olejnik, J. Behrendt,
M. Żółtowski, and P. Wcisło

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The shapes of molecular spectra are modified by collisions within the studied gas sample. This introduces systematic errors in the analysis of both terrestrial and exoplanetary atmospheric measurements, as well as influences the accuracy of spectroscopy-based optical metrology. At the same time, the line-shape manifestation of collisional effects allows the accurate study of molecular interactions and quantum scattering, thus serving as an important tool for validating the high-quality theoretical calculations capable of providing fully *ab initio* line-shape parameters, the knowledge of which helps reducing the aforementioned systematic errors in atmospheric retrievals. We present our methodology and results concerning the fully quantum approach to the problem of collisional effects in the fine-structure, rotational, vibrational and electronic molecular spectra of atmospherically-relevant species — O_2 [1], CO [2,3], HCl [4], HF and HCN [5] — perturbed by collisions with N_2 and O_2, the two most abundant constituents of the Earth's atmosphere. We show that, despite the challenging nature of the quantum scattering problem involving atmospheric molecules, the *ab initio* calculations are capable of providing high-quality reference data which may be used for populating spectroscopic databases (such as HITRAN or GEISA), which was previously demonstrated for the simpler case of He–perturbed spectra of H_2 [6].

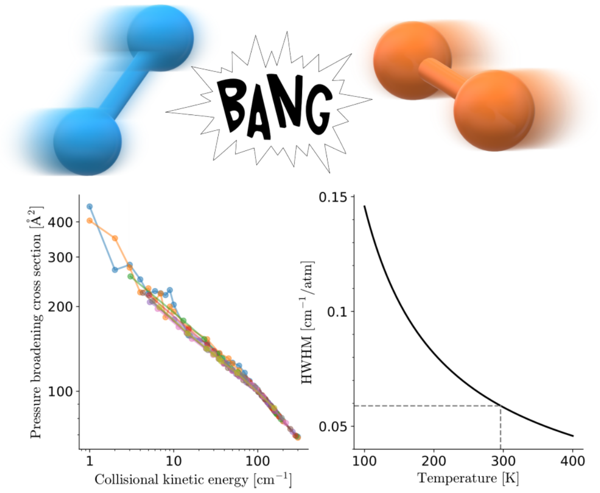

Figure 1: The effect of molecular collisions on the atmospheric spectra may be parametrized in terms of several line-shape parameters, such as pressure broadening and shift of the line, which in turn may be determined *ab initio* from the knowledge of the associated generalized scattering cross sections. A set of *ab initio* pressure broadening cross sections (shown above for the case of N_2–perturbed oxygen *A*-band) is used to obtain the temperature-dependence of the collisional half-widths (HWHM) of the given line.

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N-III: Contributed Talks

Thursday, August 28, 16:30
Hörsaal III

Chair: Guido Fuchs

HOT MOLECULES, COLD VALVE: ENHANCING MOLECULE VAPORIZATION FOR ASTRO-CHEMISTRY SEARCHES

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Polycyclic aromatic hydrocarbons (PAHs) are thought to deeply influence the chemical balance of the interstellar medium (ISM), making them a central focus of astrochemical research. Rotational spectroscopy is a powerful tool for producing spectral blueprints that are used as roadmaps to detect molecules in the ISM, having contributed to the identification of several PAHs in space [1] [2] [3] [4] [5] [6] [7]. These detections rely on prior laboratory measurements to obtain each molecule's unique spectroscopic signature in a controlled environment. But there is a major technical limitation related to sample vaporisation: the upper temperature limit of standard nozzles is $\sim 200^{o}$C, and surpassing it for extended periods of time will permanently damage the solenoid valve components that control sample delivery. This constraint restricts laboratory measurements to molecules with relatively low melting points, preventing access to an elusive library of candidate PAHs for detection in the ISM.

Instead of resorting to laser ablation techniques, we have designed and developed a new nozzle capable of sustaining higher setpoint temperatures without damaging the solenoid valve. With this setup, we measured the rotational spectrum of 1,8-Naphthalimide, a PAH with a melting point above 300^{o}C, and obtained a substantial improvement in the signal-to-noise ratio compared to conventional nozzle designs, as shown in Figure 1. In this contribution, we will present our findings and discuss their implications in the realm of future astrochemistry searches, rotational spectroscopy, and of other molecular jet expansion-based experiments.

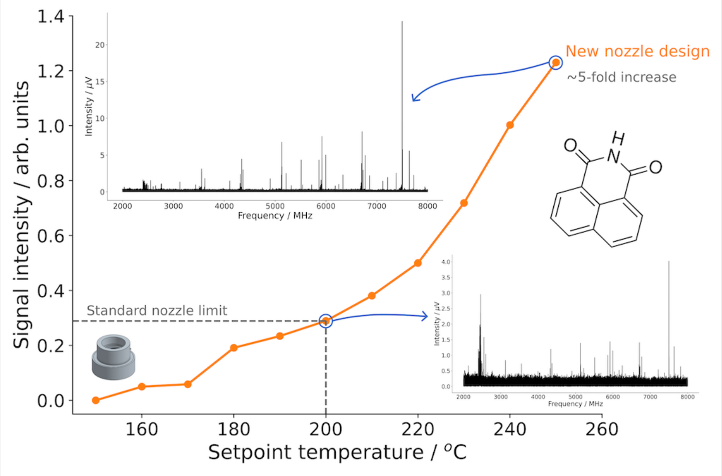

Figure 1: Rotational spectrum (60k FIDs) of 1,8-Naphthalimide obtained at 200^{o}C and 250^{o}C.

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TIME RESOLVED MID-INFRARED FREQUENCY COMB SPECTROSCOPY IN CO_2 PLASMA ENVIRONMENTS

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The study of pure and mixed CO_2 plasmas has gained renewed attention due to environmental concerns and the potential of non-thermal plasmas for CO_2 valorization via methanation, dry reforming, and methanol synthesis[1]. However, limited experimental data—particularly on vibrational temperatures—hinders the development of accurate kinetic models.

Optical frequency combs are a powerful tool for investigating the molecular dynamics in plasma environments [2] [3] [4].

Here, we introduce mid-infrared frequency comb Fourier transform spectroscopy[5] to perform kinetic studies in CO_2 containing plasma discharges. A DC, or pulsed glow plasma discharge is generated in a 60 cm-long tube at 40 mA with pressure ranging from 0.1 to 5 Torr. This type of plasma ensure a good axial homogeneity along the line of sight. We recorded spectra spanning 250 cm^{-1} around 2200 cm^{-1} with a resolution of 3×10^{-3} cm^{-1} at different total pressures, mixing ratios (with Ar and He), discharge current, and radial position in the tube. A typical recorded spectrum recorded in a DC discharge is shown in Figure 1 and compared with the spectrum obtained in the same conditions without the discharge. In addition to the fundamental absorption band of CO_2, many vibrationally excited transitions are observable, together with cold and hot bands of CO. To monitor in time the excitation dynamic, we performed time-resolved FTS, by triggering 1 ms-long discharge events with a regular optical path difference and recording interferograms with a 2 µs time resolution. This opens up for following the formation and dissociation of molecular species during plasma discharge. We will present the experimental setup and discuss the results.

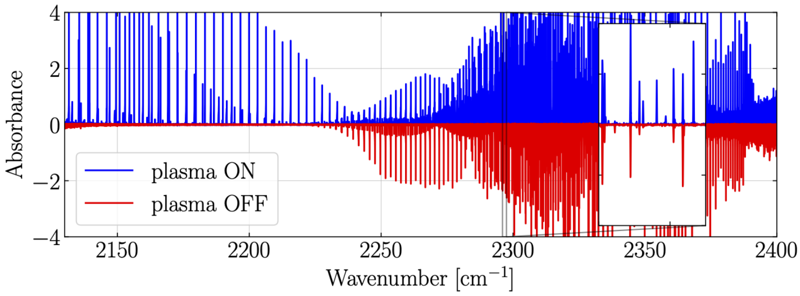

Figure 1: Experimental spectra of a CO_2 sample at 5 Torr, with and without (inverse, for clarity) plasma discharge.

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IR SPECTRA OF ASTROCHEMISTRY-RELATED RADICALS PRODUCED VIA HYDROGEN-ATOM REACTIONS USING *PARA*-HYDROGEN MATRIX ISOLATION

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[b] Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Taiwan

Solid *para*-hydrogen (p-H_2) exhibits unique quantum solid properties that enable applications beyond those achievable with noble-gas matrix-isolation.[1],[2],[3] Among them, efficient reactions involving hydrogen atoms facilitate hydrogen abstraction, hydrogen addition, and hydrogen-induced fragmentation. We employed a novel method to generate H atoms for reaction with guest molecules isolated in a p-H_2 matrix. By incorporating trace amount of Cl_2 and photodissociating it with light near 365 nm, we produced Cl atoms. These atoms remain stable in the p-H_2 due to the large barrier and endothermic nature of the Cl + H_2 reaction. Subsequent infrared (IR) irradiation induces $Cl + H_2 (\nu = 1) \rightarrow HCl + H$, generating H atoms that chemically tunnel through solid p-H_2 via consecutive H–H bond breaking and formation, promoting efficient H-atom reactions. Using this method, we investigated the H-reaction with acenaphthylene ($C_{12}H_8$) and report the IR spectra of four isomers of acenaphthylenyl radicals (2-, 3-, 4-, and 5-$H^\cdot C_{12}H_8$), produced via UV/IR irradiation of a $C_{12}H_8/Cl_2/p$-H_2 matrix at 3.2 K. Spectral lines of these radicals were grouped based on their photolysis behaviors at various wavelengths. Spectral assignments were confirmed by comparison with scaled harmonic vibrational wavenumbers and IR intensities of possible isomers predicted with quantum-chemical calculations using the B3PW91/6-311++G(d,p) method. Relative energies and interconversion pathways of all species were also calculated. The IR spectra of four conformers of $H^\cdot C_{12}H_8$ are newly reported. Additionally, we explored H-atom reactions with carbonyl derivatives. H-atom reactions involving glycolaldehyde [$HOCH_2C(O)H$] in two conformations exhibited diverse chemistry, leading to the formation of $HO^\cdot CHC(O)H$ and $HOCH2^\cdot CO$ via H-abstraction, $HOCH_2CH_2{}^\cdot O$ via H-addition, and $^\cdot CH_2CO + H_2CO$ via H-induced fragmentation.[4] In contrast, H-atom reactions with glycinamide [$H_2NCH_2C(O)NH_2$] in two conformations resulted in the formation of $H_2N^\cdot CHC(O)NH_2$ via H-abstraction on the CH_2 moiety. IR spectra of all radicals, except $^\cdot CH_2CO$, are newly reported.

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ROVIBRATIONAL COMPUTATIONS FOR THE $\mathbf{He_2}$ a $\mathbf{^3\Sigma_u^+}$, b $\mathbf{^3\Pi_g}$ AND c $\mathbf{^3\Sigma_g^+}$ STATES INCLUDING NON-ADIABATIC, RELATIVISTIC, AND QED CORRECTIONS AND COUPLINGS

Balázs Rácsai[a], Péter Jeszenszki[a], Ádám Margócsy[a], and Edit Mátyus[a]

[a] ELTE, Eötvös Loránd University, Institute of Chemistry

Relativistic, quantum electrodynamics, as well as non-adiabatic corrections and couplings, are computed for the a $^3\Sigma_\mathrm{u}^+$, b $^3\Pi_\mathrm{g}$ and c $^3\Sigma_\mathrm{g}^+$ electronic states of the helium dimer. The underlying Born-Oppenheimer potential energy curves are converged to 1 ppm $(1:10^6)$ relative precision using a variational explicitly correlated Gaussian approach. The quantum nuclear motion is computed over the 3-dimensional a $^3\Sigma_\mathrm{u}^+$ and the 9-(12-)dimensional b $^3\Pi_\mathrm{g}$–c $^3\Sigma_\mathrm{g}^+$ (and B $^1\Pi_\mathrm{g}$–C $^1\Sigma_\mathrm{g}^+$) electronic-spin subspace coupled by non-adiabatic and relativistic (magnetic) interactions. The electron's anomalous magnetic moment is also included; its effect is expected to be visible in high-resolution experiments. The computed rovibrational intervals and fine-structure splittings, spanning over several orders of magnitude in energy, are found to be in remarkable agreement with available high-resolution spectroscopy data. Fine-structure splittings are also predicted for the c $^3\Sigma_\mathrm{g}^+$ levels, which have not been fully resolved experimentally, yet.

INTEGRATED THEORETICAL AND EXPERIMENTAL INVESTIGATION: ACCURATE STRUCTURE OF NORCAMPHOR AND CONFORMATIONAL LANDSCAPE OF TIOPRONIN

L. Uribe[a,b], M. Mendolicchio[a], S. Mato[c], S. Municio[c], J.L. Alonso[c], E. R. Alonso[c], I. León[c], and V. Barone[d]

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[b] Scuola Superiore Meridionale, Largo San Marcellino 10, 80138 Napoli, Italy
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This study presents the first integrated theoretical and experimental analysis of norcamphor's and tiopronin's microwave spectra. High-resolution experimental measurements allowed precise determinations of ground-state rotational constants for the parent species, together with ^{13}C and ^{18}O isotopologues, in natural abundance for norcamphor and two tiopronin's conformers.

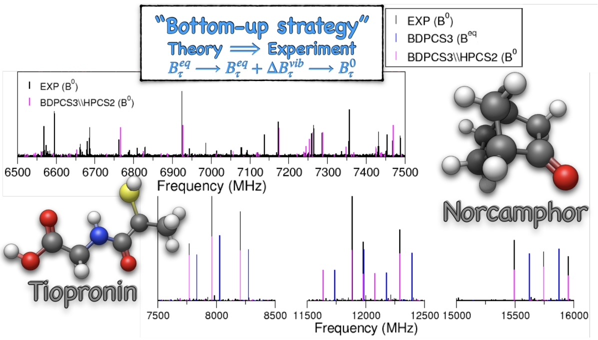

Figure 1: Comparison between the experimental and theoretical spectra of norcamphor and tiopronin.

The experimental rotational spectra of norcamphor and tiopronin were recorded using a Chirped-Fourier Transform Microwave (CP-FTMW) spectrometer[1,2] in combination with either a heating or laser ablation system. The BDPCS3//HPCS2[3,4] methodology provided highly accurate rotational constants, which served as starting points for the assignment of the experimental data. Deviations around 0.1% between computed and experimental results were achieved for rigid systems when vibrational corrections were taken into account. Although slightly larger errors are obtained for flexible systems, the accuracy of the proposed method is largely sufficient for assigment purposes. Further refinements were done for norcamphor by a novel tool implemented in the MSR program[5], overcoming the challenge of obtaining the semi-experimental equilibrium structure in the absence of deuterated species. This refinement protocol, designed to incorporate both computational and experimental data, substantially improved the reliability of the derived structural parameters.

This combined methodology demonstrated outstanding capability in determining spectroscopic parameters, enabling unambiguous spectral assignments.

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SPECTACLE – SPECTROSCOPY TAILORED ACTIVE LEARNING ALGORITHM FOR MACHINE LEARNING POTENTIALS

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With the evolution of quantum chemical methods and modern multicore computer architectures, it's now possible to simulate the infrared (IR) spectra of isolated molecules with accuracy parallel to established experimental methods which is on the order of a few cm-1. Theoretical IR spectroscopy therefore provides ideal conditions for rigorous benchmarking of novel methodologies, e.g. for constructing potential energy surfaces (PESs). Although it is mainly the multidimensional PES that controls the accuracy of these calculations, the subsequent vibrational structure calculations also need to be carefully converged to yield accurate results.[1][2]

In this contribution traditional approaches for representing a PES based on polynomial expansions will be compared to machine-learning based methods, specifically high-dimensional neural network potentials (HDNNPs).[3] While the former approach has been automated,[4] HDNNPs still require large data sets for training and a high amount of user control to achieve comparable accuracy.[5] Additionally, established methods for generating structures to be used for the data set like normal mode sampling[6] or random sampling from molecular dynamics trajectories[7] will be discussed and shown to be problematic when accurate vibrational calculations are to be performed.

Drawing ideas from the traditional methods, namely the well-known n-mode expansion, a physically motivated iterative active-learning workflow for the construction of machine-learning based PESs is presented. Benchmark results for molecules with increasing number of atoms will be presented, showing a more consistent construction of accurate HDNNPs and a reduction in the required amount of expensive training data. The presented workflow is formulated in a general manner making it applicable also to the construction of machine-learning based PESs for other purposes such as reaction modeling or condensed phase simulations.

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O: Posters

Friday, August 29, 9:00
Foyer

ROTATIONAL SPECTROSCOPY OF METHYLALLENE AND SEARCH FOR IT IN SPACE

H. S. P. Müller[a], J.-C. Guillemin[b], F. Lewen[a], and S. Schlemmer[a]

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[b] Univ Rennes, CNRS, ISCR−UMR 6226, 35000 Rennes, France

Several pure hydrocarbons have been detected in space recently, incuding 1-butyne, a C_4H_6 isomer, in the prototypical dark cloud TMC-1[1] and isobutene, a C_4H_8 isomer, in the cold and presumably shocked molecular cloud G+0.693−0.027[2]. Methylallene, also known as 1,2-butadiene, is a structural isomer of 1-butyne and hence a promising candidate for searches in space. Its detection in space may help through astrochemical modeling to quantify the abundances of other important small hydrocarbons lacking a permanent dipole moment, such as allene, 2-butyne, and the low-energy conformer of 1,3-butadiene.

Low-J microwave transition frequencies of methylallene of a-symmetry ($\mu_a = 0.40$ D) were reported with methyl internal rotation being frequently resolved[3]. We have started to record its rotational spectrum, thus far in the 36 to 117 GHz range. Observations of the much weaker b-type transitions ($\mu_b = 0.07$ D) gave access to transitions with fairly high values in J and K_a. We will present our investigations and intend to provide results from searches for this molecule in space.

We acknowledge support by the Deutsche Forschungsgemeinschaft via the collaborative research center SFB 1601 (project ID 500700252), subprojects A4 and Inf.

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ROTATIONAL SPECTROSCOPY OF CH_3C_3N: l-TYPE DOUBLING IN BENDING VIBRATIONS AND GROUND-STATE ANALYSIS OF ITS ISOTOPOLOGUES .

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Unsaturated carbon-chain molecules and nitriles are known for their relevance in astrochemistry. Methylcyanoacetylene (CH_3C_3N), a symmetric top molecule combining both structural motifs, was previously detected towards TMC-1[1] based on the ground-state laboratory data[2]. While earlier studies provided spectroscopic parameters only for the ground vibrational state and the lowest bending mode ν_{12}=1, our present work extends the characterization to additional low-lying vibrational states. We present the analysis of the ν_{12}=1, ν_{11}=1, and ν_{10}=1 bending modes of the linear part of the molecule. All three modes exhibit l-type doubling, characteristic feature due to their E symmetry. Using high-resolution rotational spectroscopy, we determine accurate spectroscopic constants for these states through global fitting including Coriolis interaction terms. In addition, we report new measurements and analysis of the ground-state rotational spectra of the singly substituted isotopologues ($^{13}CH_3C_3N$, $CH_3{}^{13}CC_2N$, $CH_3C^{13}CCN$, $CH_3C_2{}^{13}CN$, and $CH_3C_3{}^{15}N$) in natural abundance. These data provide refined molecular parameters, which will be used to determine the semi-experimental equilibrium structure of the molecule.

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BRANCHED ACYLIUM IONS: INFRARED ACTION-SPECTROSCOPIC STUDY OF $C_2H_3CO^+$ AND $C_2H_5CO^+$

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While linear and symmetric acylium ions have attracted some interest from the laboratory spectroscopy community recently because of their astronomical relevance, much less is known about branched acylium variants. In the present investigation we have now recorded mid-infrared spectra of propenoyl cation, $C_2H_3CO^+$, and propanoyl cation, $C_2H_5CO^+$, using infrared photodissociation of their weakly-bound Ne-complexes. Experiments were performed using the FELion 22-pole cryogenic ion trap apparatus connected to the Free Electron Laser for Infrared eXperiments, FELIX located at Radboud University (Nijmegen, The Netherlands). The study of $C_2H_3CO^+$ complements an earlier report of the IRPD spectrum employing CO-tagging[1] and extends the spectroscopic coverage down significantly to some 640 cm^{-1}. The infrared spectrum of $C_2H_5CO^+$ has been observed for the first time and covers the ranges from 700 to 1700 cm^{-1} and 2200 to 3150 cm^{-1}. Spectroscopic identification of vibrational bands has been performed on the basis of results of coupled cluster calculations performed at the CCSD(T) level of theory. Very good agreement between experiment and theory is found.

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ASAP & ASAP^2 ANALYSIS OF THE IR-SPECTRUM OF CYCLOPENTADIENE

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Vibrationally excited states of astronomical molecules are excellent temperature probes of the corresponding astronomical regions and are thought to be the origin of many unknown lines in astronomical survey spectra. Their rovibrational spectra provide accurate vibrational energies and can guide subsequent rotational studies. The *Automated Spectral Assignment Procedure*[1] (ASAP) greatly simplifies the rovibrational analysis when the rotational spectrum of either the upper or lower vibrational state is known with a high degree of accuracy (e.g., from a previous rotational analysis).

Here, we present a newly developed implementation of ASAP for the analysis of cyclopentadiene, a cyclic pure hydrocarbon which has already been detected astronomically toward the prototypical dark cloud TMC-1[2]. We recorded mid- and far-infrared high-resolution spectra of cyclopentadiene at the synchrotron facility SOLEIL and analyzed the ν_{21} fundamental with ASAP. In addition, the vibrational energies of all vibrational states below 800 cm^{-1} were determined with ASAP^2. ASAP^2 is an extension of ASAP to bands where the rotational structures of both the lower and upper state are known to high accuracy. Therefore, all transitions of said band can be cross-correlated to yield a single highly-precise value for the vibrational energy – even for hot or very weak bands. The agreement between our results and previous results from pure rotation[3] prove that our new ASAP implementation is efficient and reliable.

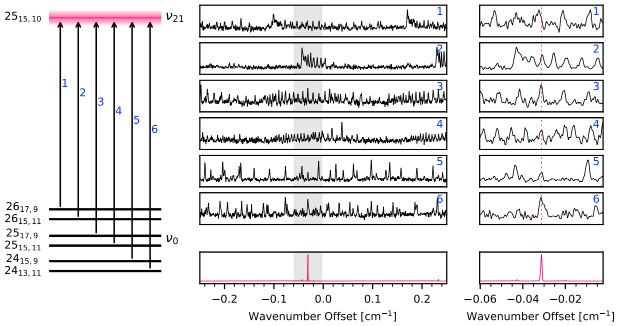

Figure 1: ASAP working principle at the example of the ν_{21} band of cyclopentadiene.

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$HOCS^+$ AND $HSCO^+$ SPECTROSCOPY

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The recent identification of the $HOCS^+$ ion in G+0.693[1] has awakened the interest in the spectroscopy of this species. *Ab-initio* calculations predict two structural isomers of protonated OCS, with the proton attached either to the O atom ($HOCS^+$) or to the S atom ($HSCO^+$), the latter being more stable by 27 kJ/mol. The rotational spectra of both species have been characterized[2,3,4] although $b-$type transitions of HOCS+ had not been measured until now. The only previous high resolution infrared study of $HOCS^+$ was that of the ν_1 band in a glow discharge, containing $a-$ and $b-$type transitions[5]. Unfortunately, the line-list of that work is no longer available, precluding a global fit of the rotational and the rovibrational transition frequencies of $HOCS^+$. Additionally, attempts to measure the IR spectrum of the $HSCO^+$ isomer had been unsuccessful[5],[6] up to now.

In this work, we present new measurements carried out in the cryogenic ion trap apparatus COLtrap, at the Universität zu Köln, using the leak-out spectroscopy technique (LOS). Both rovibrational and pure-rotational transitions of $HOCS^+$, specifically the hitherto unmeasured rotational $b-$type transitions of this almost linear asymmetric rotor ($\kappa = -0.9999$) have been recorded, as well as the $\nu_4 + \nu_2$ band of the elusive $HSCO^+$ isomer. The study has been extended using the difference frequency laser spectrometer and a hollow cathode discharge at IEM-CSIC, in Madrid, providing a new and accurate line list for the ν_1 band of $HOCS^+$. This experiment probes a more extensive range of rotational levels, allowing for a global fit and improving the accuracy of the distortion constants and the reliability of new predictions.

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DESIGN AND PERFORMANCES OF THE LILLE ICE TERAHERTZ EXPERIMENT (LITE)

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Rotational spectroscopy offers unmatched selectivity? for the identification of gas-phase molecules, making it a powerful tool for probing the chemical complexity of desorbed species from interstellar ice analogs. We present the Lille Ice Terahertz Experiment (LITE), a new setup designed to investigate desorption products resulting from thermal and photochemical processing of astrophysical ices. This experiment integrates chirped-pulse Fourier transform (CP-FT) spectroscopy in the millimeter/submillimeter-wave (terahertz) range, enabling broadband, sensitive detection of transient species under astrophysically relevant conditions. We will describe the design and capabilities of the LITE apparatus and its integration with the Lille terahertz emission spectrometer[1]. Preliminary results focusing on temperature-programmed desorption (TPD) experiments involving both pure and UV-irradiated ices will be presented. In the case of pure water ices (Fig. 1), we demonstrate the system high sensitivity, able to detect rotational transitions of desorbed species at number densities as low as 10^9 cm^{-3} with an integration time of just 20 seconds.

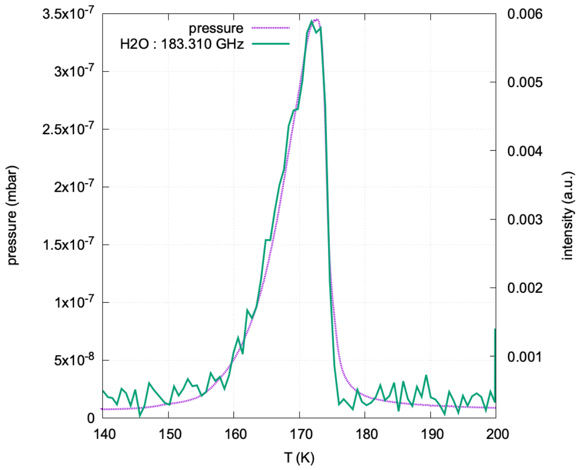

Figure 1: TPD profile measured using a pressure gauge and using $3_{1,3} \leftarrow 2_{2,0}$ transition of H_2O.

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INVESTIGATIONS ON ASTROPHYSICALLY RELEVANT NITRILES PRODUCED VIA DC PLATE DISCHARGE: TOWARDS HIGH-RESOLUTION REMPI SPECTROSCOPY OF AMINOACETONITRILE (NH_2CH_2CN)

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The astrophysical catalog of complex molecules in the interstellar medium or circumstellar environments is growing year by year with the advancement of observational and laboratory instruments and techniques. In particular, spectral investigation on prebiotic species like NH_2CH_2CN (AAN) are of high importance for the conception of the origin of life in stellar environments. AAN is a direct precursor to glycine and has already been detected in space at millimeter-wavelengths, towards the star-forming region Sagittarius B2 in 2008 by Belloche et al. [1] and recently in 2020 by Melosso et al.[2] Furthermore, the abundance of AAN in hot core stellar regions has been modeled and deduced computationally by Zhang et al.[3] In order to gain further insights into prebiotic chemistry in space, reference data from laboratory experiments performed under astrophysical conditions are mandatory. AAN has been studied extensively in the microwave and infrared regions [4], but spectral data of AAN in the UV and optical regions are rather scarce or non-existend, to the best of our knowledge. Exploring the interaction of such prebiotic molecules with UV and optical photons is essential for our comprehension of photochemistry in dense regions.

Here we present our first attempts at the *in-situ* production of AAN via DC plate discharge and observing the vibronic spectra of its corresponding mass via REMPI-mass-spectrometry. Chao He and Mark A. Smith measured the abundance of AAN produced in discharges of methane (CH_4) in nitrogen (N_2) mixtures, refering to the methane- and nitrogen-rich atmosphere of Titan, a moon of Saturn [5]. Following their suggestion of creating such prebiotic molecules in laboratory plasma, we expand a 10% CH_4 in N_2 mixture through a DC discharge nozzle, subsequently skimming a cold molecular beam from the supersonic expansion cone. First REMPI spectra of the neutral plasma products with vibronic resolution in the UV are obtained. The search for spectral features of AAN is supported by quantum chemical calculations on the time-dependent DFT level of theory using aug-cc-pV6Z basis sets in the computational environment of ORCA[6].

Examples of mass-selected spectra recorded in the range of (210-310) nm are presented in a 2 + 1 REMPI experiment.

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ROVIBRATIONAL OVERTONE AND COMBINATION BANDS OF THE HCNH$^+$ ION

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The HCNH$^+$ ion, a linear, closed-shell molecular ion, which plays a significant role in interstellar chemistry has been extensively studied in the laboratory. The latest spectroscopic study focused on the hyperfine-resolved pure rotational spectra[1], in this work we present the vibrational spectra in range of 6200 − 6900 cm^{-1}, i. e., the one of overtones and combination bands of the main N–H (ν_1) and C–H (ν_2) stretches. We present the rovibrationaly resolved spectra of the first overtones $2\nu_1$ and $2\nu_2$, its combination band $\nu_1+\nu_2$, and a combination band $\nu_2+\nu_3+2\nu_5^0$, where ν_3 is the C–N stretch, and ν_5 is the HNC bend[2]. This combination band has a calculated intensity of only 0.06 km mol^{-1} and is cca. 10^4 times weaker than the ν_1 fundamental band (482 km mol^{-1}). This sensitivity has been achived using our "kick-out" enhanced multi step laser induced reaction (LIR) scheme[3]. The endothermic reaction with C_2H_4 has been used, with the caveat, that the products reacted further with C_2H_4 up to $C_5H_7{}^+$ ion, which has been monitored as the spectroscopic signal (see Figure 1). The experimental data are supported by calculations at the CCSD(T)-F12b/cc-pCVQZ-F12 level of theory.

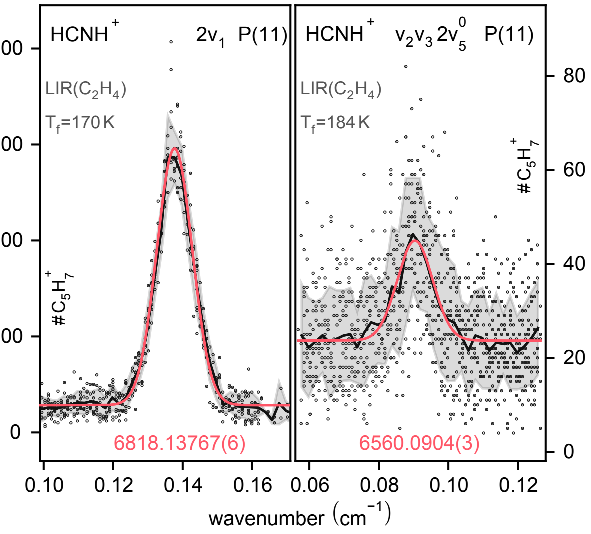

Figure 1: Spectra of overtone band $2\nu_1$ (left) and combination band $\nu_2\nu_3 2\nu_5^0$ (right) of HCNH$^+$.

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NO^{2+} DICATION SPECTRAL MODEL FOR ANY KIND OF SPECTROSCOPIC USAGE

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Understanding natural phenomena through observation and analysis has always been central to scientific progress. In astrophysics, spectroscopic methods play a key role in revealing the physicochemical conditions of distant celestial bodies. This research focuses on the theoretical investigation of the rovibronic spectra of molecular probes, with a particular emphasis on the NO^{2+} dication.

Using the DUO[1] and Molpro[2] [3] [4] computational program packages, the spectroscopic properties of NO^{2+} were systematically predicted under astrophysically relevant conditions. The resulting global spectral model provides an important tool for identifying NO^{2+} in various astronomical environments.

The DUO computational program was used for calculating ideal geometry of NO^{2+}, whereas Molpro was used to simulate rovibronic spectra of said molecular ion.

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COMPARISON OF ETHYLENE SPECTRA AT 10 μm RECORDED BY FOURIER TRANSFORM AND FREQUENCY COMB SPECTROMETERS

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The atmospheres of various astrophysical objects mainly consist of molecular species such as hydrogen and hydrocarbons. Among all these hydrocarbons, ethylene is highly important in various domains such as planetological and astrophysical applications. For example, hydrocarbons are considered to be standard building blocks for carbon-rich atmospheres of many exoplanets. The upper atmosphere of such exoplanets can be efficiently probed by transit techniques and transmission spectroscopy, which are excellent diagnostic tools for understanding physical chemistry. Moreover, in the Earth's atmosphere, ethylene is known as a pollutant produced by forest fires, volcanic emissions, road traffic, and plants, affecting the ozone concentration. Chemical destruction of ethylene within the atmosphere leads to enhanced production of carbon monoxide and formaldehyde.

In order to improve the knowledge of this molecule, ethylene spectra have been recorded in the 10 μm region by two spectrometers. The first one is a commercial Fourier Transform Spectrometer (Bruker IFS 125 HR). Fourier Transform spectroscopy is a well-established technique that permits the study of complete bands of molecules[1]. The main disadvantages of this type of spectrometer are a non-negligible apparatus function and a quite long recording time. Thus, spectroscopic studies are usually limited to intensities and air-broadening coefficients. On the opposite, diode laser spectrometers have no apparatus function and spectra can be recorded in a few milliseconds[1]. Unfortunately, their tunability is often limited to a few cm^{-1}. Nowadays, frequency comb spectrometers appear to be the ultimate solution to provide rapid and very high-resolution molecular spectra over a relatively wide wavelength region[2].

The Reims group has a new instrument, a tabletop mid-infrared dual-comb spectrometer emitting in the 10 μm region. The resolution of the wavenumber axis is increased by stepwise tuning and accurate measurement of the laser center wavelength and repetition frequency. The covered range is approximately 50 cm^{-1}. The wavelength range of the Fourier Transform spectrometer was selected to be comparable to that of the comb instrument. Preliminary spectra will be presented and compared to HITRAN data.

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MEASUREMENTS OF SELF-PERTURBED METHANE LINES IN THE ν_4 BAND BY DUAL-COMB SPECTROSCOPY

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Methane is one of the most potent greenhouse gases in Earth's atmosphere. It is also present in trace amounts in planetary atmospheres such as Venus or in larger amounts on Titan. The analysis of atmospheric spectra relies on the computation of radiative transfer models that require accurate knowledge of spectroscopic parameters. Among them, the most important are the line positions and intensities. Line-shape parameters, such as broadening and collisional narrowing coefficients, are some of the least known despite their importance in spectral inversion processes.

In this work, we determine the line positions, intensities, self-broadening and collisional narrowing coefficients of pure methane lines in the ν_4 band around 1300 cm^{-1}. Absorption spectra were recorded by a high-resolution dual-comb spectrometer operating in the 1280-1340 cm^{-1} spectral range. The methane gas was contained in a White-type cell with optical path lengths up to 8.17 m. The measurements were made at room temperature and at pressures below 10 mbar. Experimental spectra were fitted using a multi-spectrum procedure with the Voigt and Rautian profiles. A total of 1094 lines belonging to the fundamental ν_4 band and several weak hot bands of the $^{12}CH_4$, $^{13}CH_4$ and CH_3D isotopologues were studied, with J values up to 22. Many of these lines are studied experimentally for the first time in this particularly dense spectral region. Significant and systematic differences with the literature are found for line positions, intensities, and self-broadening coefficients especially at higher J values. Almost all discrepancies with the literature can be explained due to limitations in theoretical models predicting line positions and intensities, or due to the use of the Voigt profile to determine collisional parameters.

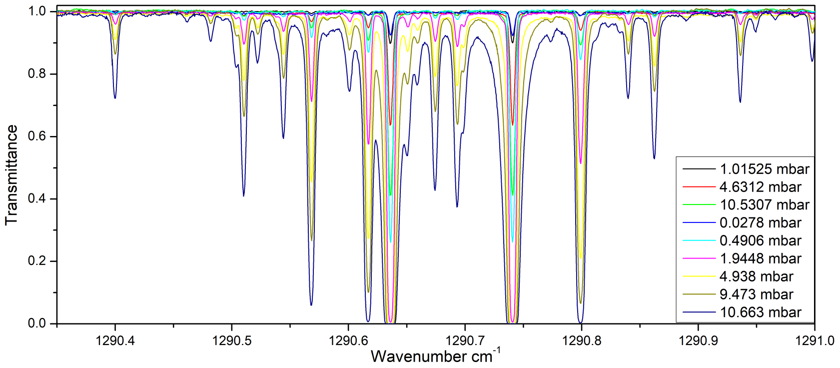

Figure 1: Zoomed section of pure methane absorption spectra recorded at various pressures and absorption path lengths.

MEASUREMENTS OF THE INFRARED CROSS-SECTIONS OF POTENTIAL EXOPLANETARY BIOSIGNATURES: CHLOROIODOMETHANE AND 2-IODOPROPANE

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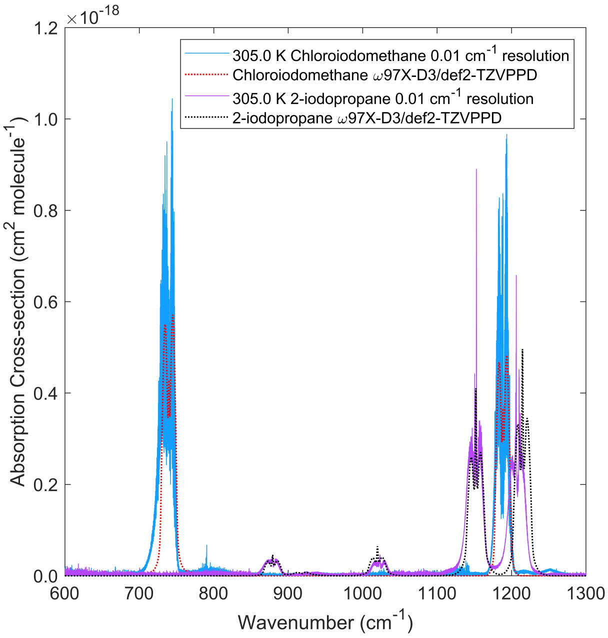
[c] Institute for Quantum Computing, University of Waterloo



Iodocarbons, such as chloroiodomethane and 2-iodopropane, contribute to the cycling of iodine between the ocean and the atmosphere. Atmospheric iodine can lead to the formation of atmospheric aerosol[1] and contribute to ozone loss[2]. Chloroiodomethane and 2-iodopropane, in particular, are produced from biogenic sources, such as marine algae[3], and, together with other methylated halogens, have been proposed as capstone biosignatures to help confirm the presence of the primary biosignature O_2[4].

There is limited infrared spectral information on chloroiodomethane and 2-iodopropane, and to our knowledge, there are no absorption cross-section measurements for either molecule. We provide experimental absorption cross-sections for both molecules from 515 to 1800 cm^{-1} at 305, 320, and 340 K at 0.01 cm^{-1} resolution. The rotational structure is partially resolved for chloroiodomethane at this resolution, as shown in the figure. Calculations using density functional theory at the ω97X-D3/def2-TZVPPD level, combined with PGOPHER, provide scaled theoretical cross-sections (the dotted lines in the figure) that are in reasonable agreement with experimental data. Our experimental cross-sections agree with vibrational assignments from past studies for chloroiodomethane[5] and 2-iodopropane[6].

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QUANTITATIVE FTIR SPECTROSCOPY OF CORROSIVE AND UNSTABLE ATMOSPHERIC GASES : APPLICATION TO HNO_3, HONO AND HOBr

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Nitric acid (HNO_3), nitrous acid (HONO), or hypobromous acid (HOBr) are known to play an important role in the complex chemical reactions that occur in the Earth atmosphere. Remote IR sensing satellites such as IASI, its successor IASI-NG, and FORUM[1] can, possibly, provide quantitative identifications on these species. However, to take full advantage of the spectra recorded by these satellite measurements, it is necessary to have at one's disposal high-quality spectroscopic parameters for these molecules. These data are achieved with theoretical investigation of high-quality laboratory spectra. However, getting "absolute" line intensities is quite a challenge for chemically unstable or highly reactive molecules like those investigated here.

In recent years, the far-infrared (FIR) and THz spectroscopy AILES beamline at Synchrotron SOLEIL has developed equipment dedicated to the study of such unstable molecules. The beamline couples the high-brilliance IR beam from the synchrotron to a high-resolution Bruker IFS125HR FTIR spectrometer whose ultimate spectral resolution is 0.001 cm^{-1}. The sample gas environment installed on the spectrometer consists in a White optical system embedded in a three-walled coolable glass cell.[2] Its non-glass parts in contact with the gas are carefully protected in order to prevent reactions at their surface. As a result, corrosive gas samples can be held as long as needed for averaging long high-resolution FTIR measurements. On the other hand, a special dual-channel detector[3] capable of recording two simultaneous spectra in the FIR and mid-infrared (MIR) regions has been designed for dealing with (polar) molecules in a mixture like HONO and HOBr. Provided the dipole moment of the target molecule is known, the pure rotational spectrum in the FIR region gives access to its partial pressure in the mixture. Hence, the relationship between the latter and the intensities of bands recorded simultaneously in the MIR region can be determined.

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SIMPLIFIED MODELING OF ETHYLENE: IMPACT OF SYMMETRIC-TOP APPROXIMATION ON COLLISIONAL LINE BROADENING

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Ethylene C_2H_4 is a significant atmospheric pollutant, widely emitted in combustion processes, and contributing to ozone formation and disrupting plant growth. Therefore, its high-resolution spectroscopic characterization is essential for both environmental monitoring and combustion diagnostics. However, its complex asymmetric-top structure leads to dense rovibrational spectra (Fig. 1[1]) which are extremely difficult to analyze experimentally to get isolated line shape parameters. Theoretical modelling is also not straightforward and computationally expensive due to line overlapping effects.

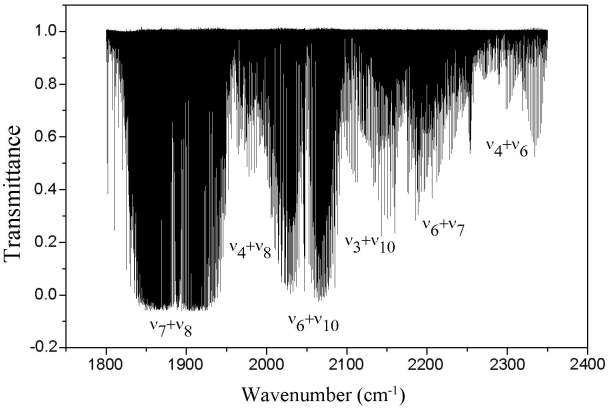

Figure 1: Overview of the absorption spectrum of pure C_2H_4 between 1800 and 2400 cm^{-1}

Many semi-classical theoricals approachs to pressure-boradening linewidth calculations simplified C_2H_4 to a symmetric-top [2] or even to a linear molecule [3] based on the fact that C_2H_4 is nearly a prolate symmetric top, with an asymmetry parameter $\kappa = 0.91$ [4]. The present work investigates the impact of this simplification in the frame of a semi-empirical method [5].

This trade-off between computational efficiency and spectral fidelity is discussed in the context of high-temperature diagnostics and the treatment of line overlapping. Although less accurate, the symmetric-top modeling offers the prospect of including line-mixing effects [6] over a wide range of thermodynamic conditions encountered in ethylene combustion diagnostics.

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THEORETICAL SPECTROSCOPIC STUDY OF ISOPRENE AND AMYLENE

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Highly correlated ab initio methods are performed to obtain very accurate structural and spectroscopic properties of 2-methyl-1,3-butadiene (isoprene) and 2-methyl-2-butene (amylene), with an emphasis in the far infrared region. In isoprene, the effects of the non-rigidity on spectra measured in different spectral ranges, are determined. In amylene, that contains 3 interacting methyl groups, four different isotopic varieties are studied and compared to help assignments.

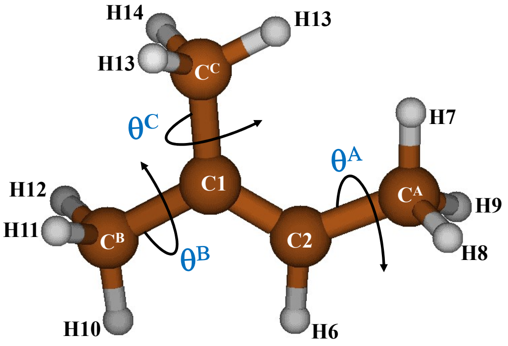

Figure 1: The most stable geometry of amylene

The search of conformers produced two stable forms trans (t) and gauche (g) for isoprene and a unique stable form for amylene. The ground state potential energy surfaces of isoprene and amylene show a total of 9 and 27 minima, respectively. Rovibrational parameters, infrared anharmonic band centers and internal rotation barriers, are provided. The barriers hindering the inter-conversions of isoprene have been computed to be 1994 cm^{-1} and 272 cm^{-1}.

The methyl internal rotation barriers V_3 have been estimated to be 917.6 cm^{-1} (t-isoprene), 696.1 cm^{-1} (g-isoprene). In the case of amylene, 3 barriers of 194.9 cm^{-1}, 806.2 cm^{-1} and 316.0 cm^{-1} were obtained for the 3 internal rotations. A variational procedure of reduced dimensionality is employed to explore the far infrared region. A A/E splitting lower than 10^{-3} cm^{-1} is obtained for the ground vibrational state of t-isoprene, whereas the (0 0) level splits into four components at 0.000 cm^{-1}, 0.001 cm^{-1}, 0.022 cm^{-1} and 0.022 cm^{-1} in g-isoprene. For amylene. The three fundamentals (1 0 0), (0 0 1) and (0 1 0) were computed to be 93.375 cm^{-1}, 118.538 cm^{-1}, and 180.604 cm^{-1}. The (0 0 0) level subcomponents are distributed in groups through 0.000 cmcm^{-1}, 0.030 cm^{-1}, 0.221 cm^{-1} and 0.251 cm^{-1}. [1] [2]

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PREDICTION OF N_2-BROADENED LINE-SHAPE PARAMETERS OF CO_2 LINES USING REQUANTIZED CLASSICAL MOLECULAR DYNAMICS SIMULATIONS (rCMDS)

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Remote sensing is a crucial tool to study Earth and planetary atmospheres. Radiative transfer models rely on the knowledge of various spectroscopic parameters. Among them, the line-shape parameters and their temperature dependencies are the least known. On Earth, carbon dioxide is the second most significant greenhouse gas, making its study at atmospheric temperatures necessary. Accurate determination of CO_2 line-shape parameters at higher temperatures is also crucial, expanding their application to combustion processes and studies of planetary and exoplanetary atmospheres.

In this work, broadening coefficients and high-order line-shape parameters, including the speed dependence of the line width, Dicke narrowing and first-order line-mixing parameters, are predicted for N_2-broadened CO_2 lines over a temperature range from 100 K to 1000 K using requantized molecular dynamics simulations (rCMDS). By employing an intermolecular potential, classical equations of motion and a requantization procedure, rCMDS enable the calculations of N_2-broadened CO_2 spectra across a wide temperature range without use of any adjustable parameters. For each considered temperature, line-shape parameters were retrieved from fits of the rCMDS spectra using the Voigt, speed-dependent Voigt, Nelkin-Ghatak and speed-dependent Nelkin-Ghatak profiles, with first-order line mixing accounted for. The obtained parameters and their temperature dependencies were compared with experimental data available in the literature for various temperatures, showing excellent agreements. We demonstrate that the line-shape parameters and their temperature dependencies obtained at Earth's atmospheric temperatures cannot be used to deduce with accuracy those at higher temperatures, relevant for studies of exoplanetary atmospheres and combustion media. Comparisons with databases show that several parameters and their temperature dependencies need to be updated by incorporating accurate high-temperature data to correctly simulate the absorption spectra of N_2-broadened CO_2 from low to high temperatures.

LINEAR OPTICAL FEEDBACK CAVITY RING-DOWN SPECTROSCOPY AT 3-μm WAVELENGTH: MEASURING RESIDUAL GASES IN AN ULTRA-HIGH VACUUM ENVIRONMENT

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One of the most demanding challenge for the Einstein Telescope (ET) vacuum system concerns the control of the residual partial pressure of hydrocarbons. For these species, a stringent limit of 10^{-14} mbar is required, as stated in the ET design report[1].

However, the accurate determination of the hydrocarbon partial pressure under Ultra High Vacuum (UHV) conditions is quite complicated. The conventional technique relies on the use of a Residual Gas Analyzer (RGA), but the interpretation of its outputs is challenging because of a mass degeneration in the spectral contributions of different molecular species. This limitation can be easily overcome if a highly-selective and intrinsically absolute laser-based technique, such as Cavity Ring-Down Spectroscopy (CRDS), is employed[2].

Here, we report on a novel Optical Feedback Cavity Ring-Down Spectrometer (OF-CRDS) operating in UHV conditions, designed for light hydrocarbon (<100 amu) detection at extremely high-sensitivity. To exploit the particularly strong absorption features of hydrocarbons in the mid-infrared (MIR) spectral region, the system employs an Interband Cascade Laser (ICL) operating at 3 µm. Furthermore, exploiting the optical feedback from the high-finesse linear cavity, the ICL emission linewidth could be drastically narrowed, thus leading to a strong enhancement of the light coupled into the cavity and, in turn, of the transmission signal[3,4].

A preliminary characterization of the setup has demonstrated that an empty cavity ring-down time of about 7.2 μs can be reached. We could determine a cavity finesse of about 15000, while the cavity-mode width was 22 kHz. An Allan-Werle analysis, performed at a fixed ICL frequency, allowed us to reach a minimum detectable absorption coefficient of 4×10^{-10} cm^{-1} for an integration time of approximately 1.5 hours.

Finally, we report on preliminary results targeting for the partial C_2H_2 residual pressure determination. To the best of our knowledge, this represents the first implementation of CRDS in an UHV environment.

This work was supported by the ETIC Project within the PNRR program.

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FIGURES OF MERIT QUANTIFYING PRECISION AND BIAS IN MULTISPECTRUM LEAST-SQUARES ANALYSES OF MEASURED SPECTRA

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The multi-spectrum fitting (MSF) method of spectroscopic analysis has revolutionized the measurement of line-shape parameters since its original application by Carlotti [1] in the late 1980s; while today MSF with global constraints serves as a pivotal tool in the most precise measurements of beyond-Voigt line-shape parameters. Since this seminal work, line-shape measurements with exceptionally high signal-to-noise ratios (SNRs) at the $104 - 105$ level are now widely available. These advances have motivated new metrics such as the often-used quality-of-fit (QF) parameter introduced by Cygan [2], and they have revealed connections between SNR and parameter correlation in multi-spectrum retrievals of line-shape parameters [3]. However, careful analysis of the literature today shows discrepancies in how QF is treated when doing MSF with global constraints. Here we generalize the definition of QF in the multi-spectrum case, and we introduce an additional metric, the systematic bias (SB), which characterizes the non-statistical deviations between model and experiment which are observable above the noise floor. As a case study, we evaluate these and other fit metrics for beyond-Voigt multi-spectrum analysis of spectra in the $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ (0,0) band O_2, which also incorporate the effects of intensity depletion.

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NON-EMPIRICAL DERIVATION OF AN EFFECTIVE DIPOLE MOMENT OPERATOR FOR ASYMMETRIC TOPS

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Effective Hamiltonians in Watson or other forms are widely used in interpreting and describing rotational structures of rovibrational bands both due to their ability to describe observable transitions with an experimental accuracy and a possibility to derive them *ab initio*. For instance, it is possible to solve the molecular Schrödinger equation with vibration-rotation Hamiltonian applying Van Vleck operator perturbation theory (CVPT) to vibrational operators, followed by the rotational reduction. The resulting effective Hamiltonians are fully compatible with their traditional empirical forms and depending on the order of vibrational CVPT may coincide with empirical values rather accurately.[1] Alternatively, it is possible to solve direct problem variationally and then fit constants of an effective operator to theoretical energies.[2]

In contrast, while effective dipole moment operators are commonly employed in empirical spectral analysis, it appears that there is no well-established fundamental approach for deriving such operators exclusively from ab initio methods.

In this report, we propose a theoretical systematic method of deriving effective dipole moment operators using the CVPT, which includes accounting of fine effects introduced by rotational S-generators:

$$ {}^{rot}\tilde{\mu}^{(1)}_{vib_{i\to j}} = {}^{vib}\tilde{\mu}^{(1)}_{vib_{i\to j}} - i\left({}^{rot}S^{(1)}_{\boldsymbol{i}} \cdot {}^{vib}\tilde{\mu}^{(0)}_{vib_{i\to j}} - {}^{vib}\tilde{\mu}^{(0)}_{vib_{i\to j}} \cdot {}^{rot}S^{(1)}_{\boldsymbol{j}}\right), $$

where i, j are labels of a pair of vibrational states.

Also, we propose their standardized form:

$$ \hat{\mu} = \left\{D^{1}_{0,\varepsilon}, (\mathbf{J}^2)^a \{J_z^b, J_+^c + J_-^c\}\right\}, \quad \varepsilon = -1, 0, +1, $$

where $D^{1}_{0,\varepsilon}$ is the Wigner function.

Some numerical examples are considered.

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VIBRATIONAL SPECTRA, RESONANCES AND POLYADS OF C_2H_4 AND C_2D_4 PREDICTED BY THE FOURTH ORDER VIBRATIONAL OPERATOR PERTURBATION THEORY CVPT(4) AND THE A-VCI

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Predicting anharmonic vibrational spectra poses a significant computational challenge for large molecules, requiring a balance between accuracy and available resources. The two complementary quantum mechanical approaches, perturbative and variational, offer distinct pros and cons depending on the specific application. The Second-order vibrational perturbation theory (VPT2) treats weak couplings and strong resonances separately, using criteria that can be considered artificial. In contrast, the more precise yet computationally demanding variational configuration interaction (VCI) method treats all couplings universally. The active ongoing development in solving vibrational problems necessitates updated comparative benchmarks to guide the selection of optimal theoretical tools.

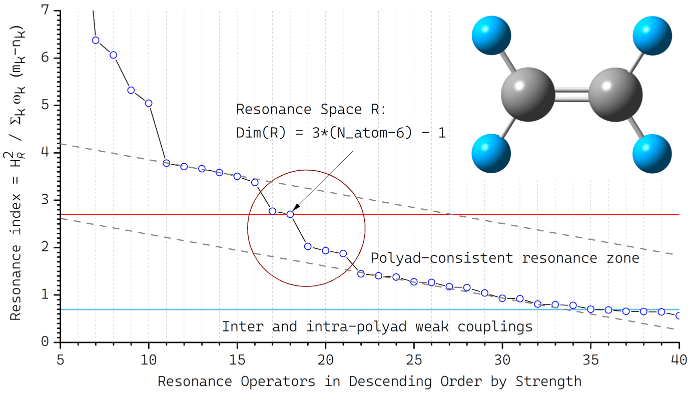

Figure 1: CVPT(2) resonance index X_k for C_2H_4. Horizontal red line indicates an approximate point of the resonance vector space reaching $(M-1)$-dimensionality $(M = 3 \times N_{atom} - 6)$.

In this work, we compare the performance of two modern methods: the second and fourth-order operator canonical perturbation theory (CVPT(2,4)) and an adaptive vibrational configuration interaction method (A-VCI).[1] Two practically important C_2H_4 and C_2D_4 molecules and an accurate CCSD(T)/cc-pVQZ four-body sextic normal mode PES were employed for benchmarking. The comprehensive picture of vibrational resonances and the polyad formula was revealed in the form: $P[C_2H_4] = 4(\nu_1+\nu_5+\nu_9+\nu_{11}) + 2(\nu_2+\nu_3+\nu_6+\nu_{12}) + \nu_4+\nu_7+\nu_8+\nu_{10}$.

A new quadratic resonance criterion $X_j = \left|V_j^2 / \left(\sum_k (n_k - m_k)\omega_k\right)\right|$ is proposed and its efficiency in elucidating polyad structures is demonstrated. A striking observation was made that CVPT(2) often produces better predictions of fundamental frequencies (e.g., RMSD for C_2H_4 fundamentals is 2.7 cm^{-1}, and for C_2D_4 is 1.9 cm^{-1}), whereas CVPT(4) demonstrates excellent correlation with A-VCI results for both fundamental and two-quanta states.

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RELATIVISTIC QED CORRECTIONS TO THE CORRELATED NO-PAIR DIRAC–COULOMB(–BREIT) ENERGY

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The equal-time Bethe-Salpeter (Salpeter-Sucher) relativistic QED wave equation is used to describe two-electron systems, *e.g.*, helium-like systems or the hydrogen molecule. The equation containing only the instantaneous part of the interaction is the with-pair Dirac-Coulomb(-Breit) equation (wpDC(B)), which includes the double-pair interaction in addition to the no-pair DC(B) Hamiltonian (npDC(B)). The npDC(B) energy can be converged within ppb to ppt relative precision using an explicitly correlated Gaussian basis set approach[1,2]. While the double-pair correction is a nonhermitian but 'algebraic' term that leaves the DC(B) equation linear in energy, the irreducible crossed-Coulomb and the single-transverse-photon exchange interaction kernels appear within a complicated, energy-dependent operator in the Salpeter-Sucher equation[3]. Including the transverse, the crossed-Coulomb, and further interactions (3) or radiative irreducible interaction kernels (5) through this term renders the wave equation non-linear in energy. Therefore, a novel perturbative approach[4,5] is under development for treating these contributions, using the npDC(B) and wpDC(B) results as high-precision correlated relativistic reference energies and wave functions. The numerical results are extensively tested with respect to the known fine-structure constant orders, α^n, of the non-relativistic QED (nrQED) scheme (and related precision spectroscopy experiments). Our results are not limited to the lowest Z nuclear charge number values and include a partial resummation in $Z\alpha$.

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AN ANALYSIS AND AN INTERPRETATION OF THE PHOTO-ELECTRON SPECTRA OF THE NITRATE ANION, NO_3^-

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The traditional photo-electron (PE) spectra and the spectra measured by adopting a modern PE spectroscopical method, slow photo-electron velocity-map imaging of cryogenically cooled ion (cryo-SEVI), of the nitrate anion, NO_3^-, reported by Neumark group [1] have been concurrently analyzed on the bases of traditional theories. According to Wigner threshold law [2] , electron kinetic energy (ϵ) dependences on the anisotropy parameter, $\beta(\epsilon)$, and on the photo-detachment (PD) cross-section, $\sigma(\epsilon)$, have been able to be analyzed consistently. The $\beta(\epsilon)$ observed are analyzed using Cooper-Zare (CZ) [3] and Wigner-Bethe-Cooper-Zare (WBCZ) formulations [4], the latter of which is one derived from the CZ formulation and Wigner threshold law. The analyses show that the PE of the bands terminating to the vibrationless and ν_4 fundamental levels of the NO_3 $\tilde{X}\ ^2A_2'$ system have *d*- and *s*-wave characters, respectively (i.e. l = 2 and = 0 components, respectively), as the major component of the ejected PE behaviors, while the band terminating to the ν_1 fundamental region, $\sim$ 1050 cm^{-1}, has both of the characters, *d*- and *s*-waves. The *d*- and *s*-wave characters are consistent with the selection rule, $\Delta l = \pm 1$, and with the characteristic of the highest occupied molecular orbital (HOMO) of the anion, NO_3^-, which is that the non-bonding MO, $1a_2'$, mostly consists of in-plane $2p$ atomic orbital (AO) of the three O's, and of little contribution of that of the central N. The mixed characteristic of the band including the ν_1 fundamental is consistent with results from the laser spectroscopy of the $\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$ electronic transition of the NO_3 neutral radical [5,6,7,8], where it has been found that the $3\nu_4$ (a_1') overtone with $l = \pm 3$ closely lies near the ν_1 fundamental.

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BROADBAND MID-INFRARED SPECTROSCOPY IN A $CH_4 + O_2$ PLASMA GLOW DISCHARGE

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Plasma in CH_4 and O_2 mixtures are known to generate a complex chemistry [1]. High resolution and broadband spectroscopy in the infrared spectral range in such environments can lead to the detection of the multiple products as well as transient species[2].

Here, we performed mid-infrared frequency comb Fourier transform spectroscopy[3] in a $CH_4 + O_2$ DC glow plasma discharge. We employed a commercial mid-infrared frequency comb source, based on an Er:doped fiber laser that is non-linearly converted to mid-infrared using difference frequency generation. This comb source provides a broadband optical spectrum of 200 cm^{-1} with a center wavelength tunable from 3 to 5 µm. To enhance the absorption sensitivity, the optical beam was passing five times through the 60 cm-long discharge tube. The spectra were recorded using a home-made Fourier transform spectrometer with a resolution of 3×10^{-3} cm^{-1} equipped with balanced detection. The spectral range corresponding to the R transitions of CH_4 is shown in Figure 1, with 3% (upper part, blue curve) and 20% (lower part, red curve, inverted for clarity) O_2 mixing, respectively. The transitions belonging to the fundamental CH_4 band absorb 100% of the comb light and are clipped on both spectra. Differences in vibrational excitation of CH_4 and density of observable species appears clearly when comparing the two spectra, but remain to be quantified. We will present the experimental setup, and the ongoing spectroscopic analysis of the retrieved data.

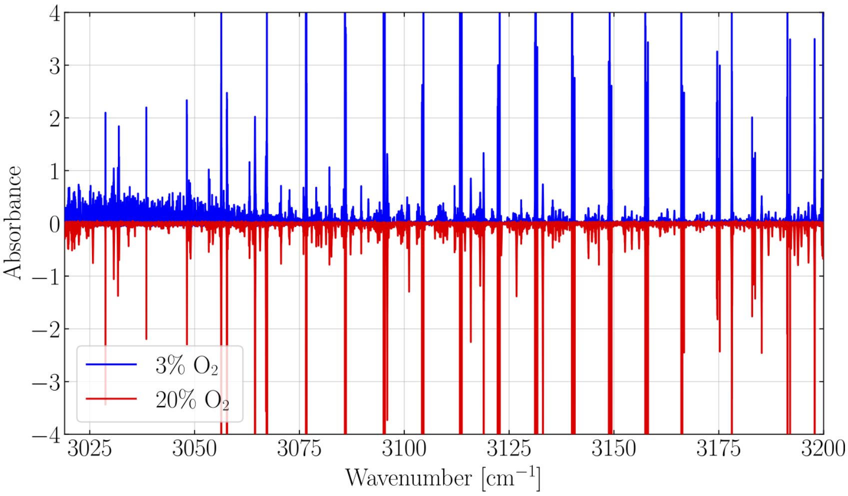

Figure 1: Measured absorbance spectra of 20% CH_4, with 3% O_2 and 77% Ar (upper part, blue curve); or 20% CH_4, with 20% O_2 and 60% Ar (lower part, red curve, inverted for clarity). The plasma discharge was generated at a total pressure of 5 Torr and a current 50 mA.

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TOWARDS THE MEASUREMENT OF ORBITAL ANGULAR MOMENTUM-ENABLED TRANSITIONS IN MOLECULES

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Orbital angular momentum (OAM) represents a unique and independent property of light that has enabled progress in diverse fields such as optical tweezers, multiplexing, and microscopy. Despite these advancements, the role of OAM in spectroscopy primarily remains unexplored. Recent theoretical work has predicted that OAM-carrying light can significantly influence molecular transition amplitudes.[1] In this work, we present the design and implementation of an experiment that aims to verify these theoretical predictions

Our approach combines OAM-carrying light, in the form of Laguerre Gaussian (LG) modes with high-resolution mid-infrared spectroscopy, utilizing an optical frequency comb and a high-resolution Fourier transform spectrometer. The Gaussian beam of the comb is transformed into a LG mode and send inside a high-finesse cavity. Embedded in the cavity lies the buffer gas cell, which limits Doppler broadening.

To resolve the degenerate dipole and quadrupole molecular transitions, we apply a strong, homogeneous electric field. Additionally, the symmetry axis of the LG beam defines the specified axis and sets the direction of the electrical field. Thus, we need a unique plate configuration that creates a homogeneous electric field along the beam axis.

We discuss the simulation results and the design considerations that enable the development of an optimized buffer gas cell, emphasizing the importance of field homogeneity for high-resolution measurements. This experimental platform provides a robust tool for probing the interactions between OAM carrying light and molecules.

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DEVELOPMENT OF SINGLE-PHOTON DOPPLER-FREE VUV/XUV SPECTROSCOPY EXPERIMENT

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The ionisation energies of many atoms and molecules lie in the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) parts of the electromagnetic spectrum, which correspond to wavelengths (frequencies) of light of < 200 nm ($> 1.5 \times 10^{15}$ Hz) and < 105 nm ($> 2.9 \times 10^{15}$ Hz) respectively.[1] Laser radiation generated at these wavelengths can therefore be utilised to perform single-photon excitation from the ground electronic state of an atom or molecule to highly excited electronic states, including direct excitation to Rydberg states with a large value of the principal quantum number, n.[1] However, although VUV/XUV laser sources with < 250 MHz bandwidths have been achieved,[2−6] large Doppler broadening of transitions at VUV/XUV wavelengths (with Doppler widths typically > 100 MHz) often limit the achievable resolution of single-photon VUV/XUV spectroscopy. Additionally, large Doppler shifts can result in $>$100 MHz systematic shifts of measured transition frequencies in the VUV/XUV. Here we present the development of a new experimental apparatus for performing Doppler-free spectroscopy at VUV/XUV frequencies. This method is based on combining an imaging-assisted single-photon Doppler-free spectroscopic technique, recently developed for precision Rydberg-state spectroscopy,[7] with a long-pulse-length ($\sim$ 100 ns) narrow-bandwidth VUV/XUV laser. The initial aim of such an experiment is to generate laser radiation with a wavelength of $\sim$ 80 nm, for use in precision single-photon XUV spectroscopy of H_2 molecules excited to high-n ($n > 30$) Rydberg states from the ground $X\,^1\Sigma_g^+$ state.

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MOLECULAR SPECTROSCOPY EXPLOITING RESONANT FREQUENCIES OF AN OPTICAL CAVITY

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Laser spectroscopy techniques used to quantitatively determine gas amount and composition rely on precise measurements of reference line intensities and collisional line profiles. Such data must be extremely accurate, especially in atmospheric studies of greenhouse gases, where line intensities need to be known with uncertainties at the permille level. Equally stringent or even tighter uncertainty levels are essential for developing optical standards for gas quantity, concentration, and temperature[1]. These efforts benefit from the recent redefinition of the SI units, which allowed flexibility in linking fundamental constants to measurable quantities.

Here, we present precise measurements of line intensities and profiles for carbon monoxide[2,3,4,5] and hydrogen[5] molecules, achieved by integrating cavity-enhanced absorption and dispersion spectroscopy methods, cross-validation between independent laboratories, and theoretical *ab initio* calculations. We further demonstrate that achieving permille-level accuracy for hydrogen line intensities necessitates the use of an advanced collisional line shape model – the speed-dependent billiard-ball profile (SDBBP)[6] that goes beyond conventional database representations of spectral line shapes.

Our measurements were carried out using cavity ring-down spectroscopy, cavity mode-dispersion spectroscopy (CMDS)[7], and the recently introduced heterodyne cavity ring-down spectroscopy (HCRDS)[5]. These techniques utilize the resonant frequencies of optical cavities, obtained from stationary[7] or
transient[5,8] cavity transmission signals, to perform high-resolution molecular absorption and dispersion measurements, leading to spectra that are directly traceable to the primary frequency standard.

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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DIABATIC AND ADIABATIC APPROXIMATION

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Exotic shapes of potential curves are due to electrostatic interactions that cause repulsion between states with the same symmetry and avoid intersection. When the electrostatic interactions are negligible, the diabatic approximation is more appropriate and the resulting diabatic potential curves of the same symmetry may cross. When these interactions are significant – the adiabatic approximation is more appropriate. It is the adiabatic curves which often have exotic shapes due to the avoided crossing. In 1985, Dressler introduced a parameter[1] $\gamma = \frac{\Delta H}{\omega}$ to qualitatively indicate the cases in which each approximation is preferable. The diabatic approximation is better when $\gamma << 1$, and at $\gamma >> 1$ – the adiabatic approximation is more appropriate.

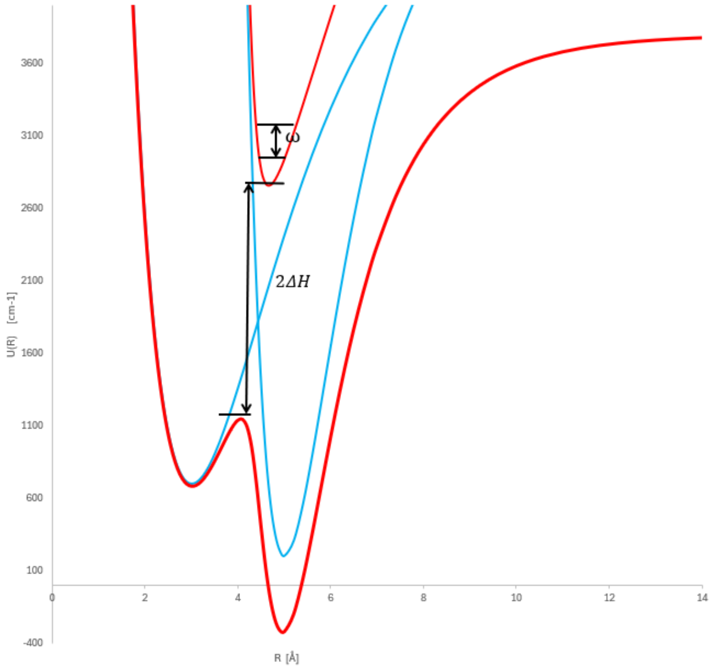

Figure 1: Correspondence between adiabatic and diabatic curves coupled by electrostatic interaction ΔH.

Our goal is to explore the limits of applicability of the two approximations and to provide a quantitative estimate for the quality of each approximation. The goal will be realized by a Monte Carlo simulation where a wide variety of coupled diabatic pairs of states will be simulated and their energy levels will be fitted within the single channel adiabatic approximation. The correlation between the quality of the fit and the Dressler parameter will be studied.

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EXPERIMENTAL AND THEORETICAL STUDY OF THE GROUND AND LOWEST EXCITED STATES OF THE NaSr MOLECULE

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We report the first spectroscopic characterisation of the open-shell, doubly polar diatomic molecule NaSr, using two different experimental approaches: thermoluminescence and laser induced fluorescence. At frequencies around 10000 cm^{-1} we identify transitions between the electronic ground state $X(1)^2\Sigma^+$ and the second excited state $B(2)^2\Sigma^+$, involving the lowest vibrational levels of each state. This assignment is based on electronic structure calculations performed by two methods that differ mainly in the way the correlation between valence and core electrons is treated. Comparison with theoretical results allows to interpret the experimental spectra and to deduce the salient molecular constants of the $X(1)^2\Sigma^+$ and $B(2)^2\Sigma^+$ states. The reliability of the employed theoretical methods is tested.

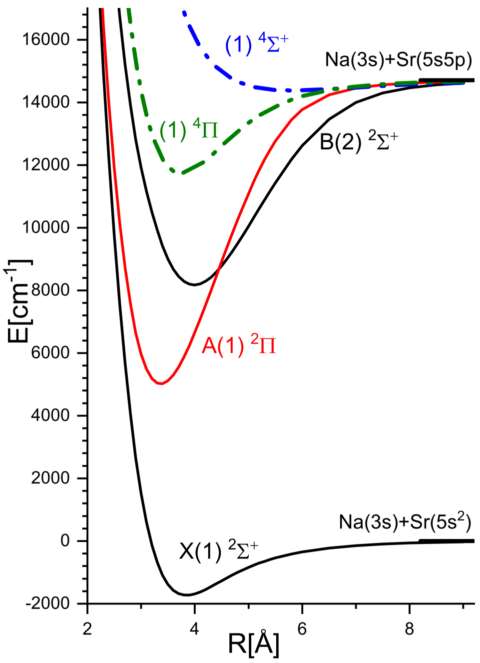

Figure 1: PECs of the electronic states of NaSr correlated to the two lowest atomic asymptotes.

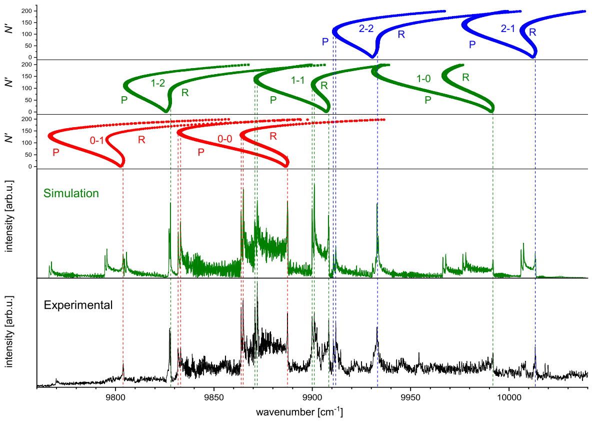

Figure 2: Comparison of the experimental spectrum (lower, black) with the one simulated using theoretical PECs obtained in this work (upper, olive). The uppermost part of the Figure illustrates formation of multiple band heads in the spectrum. Vertical dashed lines indicate band heads identified during spectrum analysis.

LOW-TEMPERATURE ABSORPTION SPECTROSCOPY FOR SIMULTANEOUS RETRIEVAL OF VAPOR PRESSURE AND TRANSITION INTENSITIES.

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This work presents a novel methodology for the simultaneous retrieval of saturated vapor pressure and absorption line intensities from low-temperature absorption spectra. The primary focus is on small hydrogenated molecules, such as ammonia. Ammonia, in particular, is known for its challenging behavior due to interactions with cell surfaces, which complicates accurate retrieval of transition intensities (Fig. 1)[1][2][3].

The core principle of the method lies in exploiting the differing temperature dependencies of vapor pressure and line intensity to enable their decoupled extraction from experimental data. In this study, we present a detailed evaluation and testing of the method's performance.

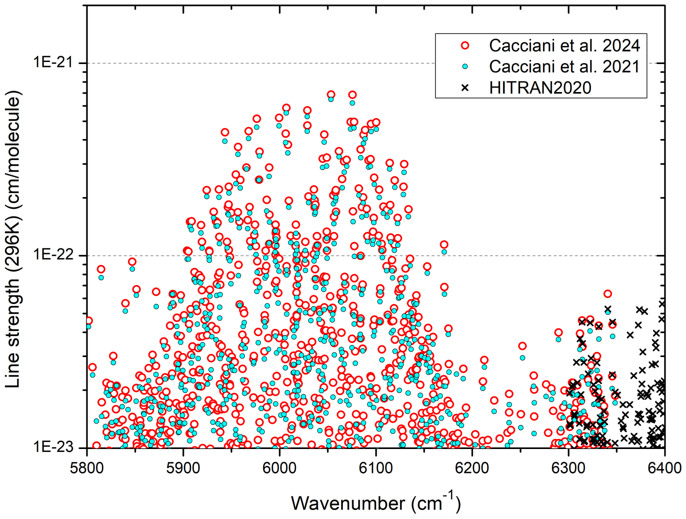

Figure 1: Intensity variation of Ammonia spectra from 3 different sources.[1,2,3]

In the first stage, a virtual model was developed to assess the retrieval capabilities using synthetic spectra. This step focused on verifying the convergence toward true parameter values, thus ensuring the proper separation of vapor pressure and transition strength contributions in temperature-dependent line intensities. In the second stage, the method was applied to low-temperature methane spectra, with the retrieved parameters compared to known values [4]. Finally, the methodology was tested on ammonia by measuring line intensities and vapor pressure for four transitions around 6049 cm^{-1}. As no vapor pressure data are available in the literature for this spectral region, the focus is placed on comparing the retrieved line intensities with available reference sources.

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FOURIER TRANSFORM CAVITY RING-DOWN SPECTROSCOPY: PRECISE RETRIEVAL OF CO-AR LINE PROFILES

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Cavity ring-down spectroscopy (CRDS) is a well-established technique in modern spectroscopy, offering high sensitivity and not requiring calibration. These advantages enable precise detection of weak absorption lines. However, conventional continuous-wave (cw) laser-based approaches often involve sequential acquisition of spectral elements, which makes experimental data determination prone to temperature variations in the sample and extends acquisition times. This limitation highlighted the need for a broadband, parallel acquisition method capable of delivering multiplexed spectra with equivalent resolution and sensitivity. The first broadband CRDS relying on mechanical Fourier transform spectroscopy (FTS) demonstration conducted by Engeln and Meijer [1], using a pulsed dye lasers and a step-scan time-resolved FTS. In 2022, two innovative techniques emerged to enhance resolution and speed: combining CRDS with dual-comb interferometric detection[2], and employing time-resolved Fourier transform spectroscopy using a single optical frequency comb[3]. Very recently, Liang et al.[4] demonstrated a related method with mid-infrared experiments. This work introduces an approach based on direct frequency comb fast scanning FTS with updates incorporating recent advancements[5]. Key improvements include a redesigned frequency stabilization method allowing extended extinction of comb light without losing the comb-cavity lock. A cw-laser serves as an intermediary between the comb and the cavity. The principle of the acquisition is depicted in Figure 1: ring-down events are triggered as the FTS is scanning at regular optical path difference values, to obtain a three dimensional interferogram which in turn gives access to the spectral variation of the cavity decay. The experimental setup's performance was validated through absorption measurements of CO mixed with Ar, showcasing high signal-to-noise ratios and confirming the impact of speed-dependent effects on absorption line profiles.

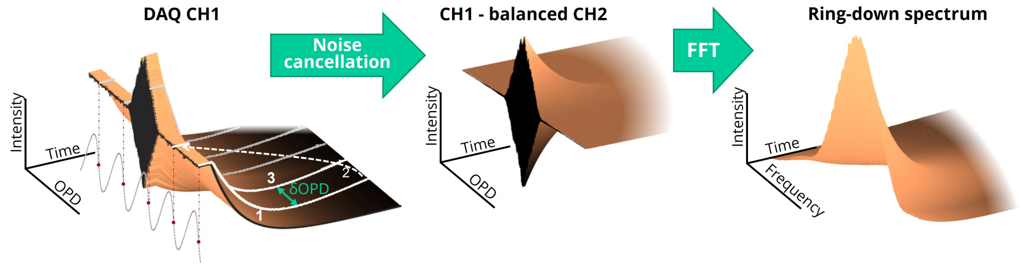

Figure 1: Principle of Fourier transform cavity ring-down spectroscopy.

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TOWARDS THE DETECTION OF ENANTIOMERIC EXCESS OF CHIRAL MOLECULES USING PHOTOELECTRON CIRCULAR DICHROISM IN A MOLECULAR BEAM

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Chirality is a fundamental aspect in nature with broad relevance in biology, chemistry and physics. Enantiomeric molecules are identical in mass, energy levels and most spectroscopic observables, distinguishing them demands observables that are sensitive to parity. Photoelectron circular dichroism (PECD) arises when circularly polarized light ionizes chiral molecules. The resulting forward/backward angular distribution of outgoing electrons acquires an asymmetry that reverses sign between enantiomers, making PECD an exceptionally sensitive method for the detection of enantiomeric excess.

Axial transient chiral species e.g. HSOH are known for the rapid tunneling motion of their ligands resulting in quick transitions between their chiral states. Substituting these ligands with suitable heavier atoms or isotopes can alter the barrier height between these states, hence reducing the speed of their tunneling motion. Under ambient conditions, the tunneling motion as well the high reactivity impose experimental challenges on the setup, therefore a cold collision-free environment for these species is required. Employing an Even-Lavie valve with a custom discharge nozzle enables the production of both stable and transient species at low rotational and translational temperatures. This cold, pulsed molecular beam provides the ideal environment for coherent manipulation of chiral states. Within the beam, we implement a resonant three-wave mixing scheme using phase-locked mid-infrared pulses to drive enantio-selective population transfer between vibrational states. A time-delayed depletion pulse is then used to selectively remove one enantiomer from the beam, resulting in an enantiomeric enrichment of the other.

To quantify this enantio-selective manipulation, the processed beam is interrogated using a velocity-map imaging spectrometer in combination with circularly polarized laser pulses. By measuring the resulting photoelectron circular dichroism, we obtain a direct and highly sensitive readout of the enantiomeric excess induced by the three-wave mixing process. This setup enables us not only to verify enantio-separation in a state-resolved manner, but also to explore the dynamics of chiral control in reactive or short-lived species under isolated conditions.

ACCURATE MEASUREMENT OF TRACE MOISTURE IN GAS USING LASER-WAVELENGTH-TUNED CRDS

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The measurement and control of trace water vapor (trace moisture) in gases at nmol/mol (ppb) levels in amount-of-substance fraction (mole fraction) is important in the semiconductor industry. This is because the yield and product performance of semiconductor devices are adversely affected by the presence of the residual trace-moisture in the high-purity gases used in the manufacturing processes. Various types of humidity sensors have been used to measure and control humidity. Among them, cavity ring-down spectroscopy (CRDS) is a powerful technique for measuring trace moisture [1].

In CRDS, the frequency of the probe laser must be coupled to a resonance frequency of the cavity (a cavity mode). For accurate control of both the probe laser and resonant frequencies, various techniques have been developed such as comb-locked CRDS [2], which requires advanced laser control techniques using optical frequency comb, Pound-Drever-Hall technique, high-performance electronics for high-speed locking, and so on. In this study, I developed a relatively simple technique for laser control and frequency coupling, referred to as "laser-wavelength-tuned CRDS." In this technique, the laser is tuned to a measurement wavelength using the built-in function of the wavelength meter, the resonant frequencies are modulated to match the laser frequency, and the ring-down time at the wavelength is measured. By changing the wavelength, a spectrum of trace water is acquired. The mole fraction of trace moisture can be determined by analyzing the spectrum.

An optical cavity made of stainless steel with a cavity length of 60 cm was constructed using two highly reflective mirrors with a reflectivity of 99.9993 % at a wavelength of 1.393 µm. The cavity length was modulated using a piezoelectric element introduced inside the mirror mount on one side. The wavelength of a DFB laser was measured with a wavelength meter, and the driving current of the DFB laser was PID-controlled to tune the laser wavelength to a measurement point near the absorption line (7181.145 cm^{-1}) of water in nitrogen at 1 atm using the built-in function of the wavelength meter. The measurement results with uncertainty obtained using a primary trace-moisture standard at National Metrology Institute of Japan will be presented.

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HIGH-RESOLUTION UV SPECTROSCOPY OF CHIRAL CANDIDATES FOR ESST APPLICATIONS

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Recent advances in chiral research have enabled the study of isolated gas-phase chiral molecules with higher chirality sensitivity. An intriguing development in this field is enantiomer-specific state transfer (ESST), a method that allows for enantiomer separation in different rotational states. Theoretically, ESST can achieve 100% efficiency using three mutually orthogonally, linearly polarized microwave fields. However, early studies reported only modest efficiencies [1,2] due to the thermal population and orientational degeneracy of rotational states [3]. In our recent work, we achieved near-complete quantum state control of chiral molecules for a triad of rotational states that includes the absolute ground state ($J = 0$), by employing a novel experimental approach that combines UV and microwave radiation to mitigate the adverse effect of thermal population [4].

While our approach is broadly applicable to all C_1-symmetric chiral molecules, our current hardware and experimental setup can achieve maximum efficiency only with molecules that possess a UV chromophore and have well-characterized rotational structures in both ground (S_0) and electronically excited (S_1) states. For many candidate molecules, while their ground state rotational constants are known from microwave spectroscopy, their excited state rotational energy level structures remain unknown. To address this gap, we perform high-resolution UV spectroscopic studies of potential chiral candidates in a jet-cooled condition. We investigated the S_0 - S_1 electronic transition of 1-indanol using resonance-enhanced multi-photon ionization (REMPI) and laser-induced fluorescence (LIF) spectroscopy [5]. Additionally, we measured the lifetime of the S_1 excited state. In this presentation, I will present our ESST results of 1-indanol and demonstrate how the spectroscopic information we acquired was used for our ESST studies. Additionally, I will share our recent high-resolution spectroscopic studies of two promising chiral candidate molecules: 1-phenylethanol and styrene oxide.

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NUCLEAR SPIN ISOMER SELECTION VIA LEAK-OUT SPECTROSCOPY

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Leak-out spectroscopy (LOS[1]) is an efficient action spectroscopic method typically applied to molecular ions stored in a cryogenically cooled ion trap. As this method is based on ejecting the stored ions from the trap based on their rotationally resolved transitions, and because different nuclear spin isomers have disjunct spectroscopic fingerprints, it can be used to eject all molecules of one nuclear spin isomer. For instance, the molecular ion H_2O^+ has two identical protons and followingly two nuclear spin isomers called ortho ($I = 1$) and para ($I = 0$) with a ratio of 3:1. If one now addresses, e.g., an ortho-transition, eventually all ortho species can be ejected, leaving only para species in the trap. This approach may be used to prepare a pure spin modification (e.g. para) for subsequent spin-specific reaction experiments or to measure the nuclear spin ratio. While the latter may be trivial for the given two-proton example, it may be highly diagnostic for other systems.

In this poster, we present results for the ion CH_3^+, including its isotopomers CH_2D^+ and CD_2H^+, as well as CH_5^+, presenting systems with two, three, and five fermions (protons), as well as a system with two bosons (deuterons). Their nuclear spin weights are known to be ortho:para=1:1 for CH_3^+, ortho:para=3:1 for CH_2D^+, ortho:meta:para=8:5:3 for CH_5^+, as well as ortho:para=2:1 for CD_2H^+ [2,3]. For all named ions, the given nuclear spin ratios have been confirmed by our novel experimental method. For CH_5^+, the fact that all three nuclear spin isomers have different statistical weights (8:5:3) can be used to distinguish them. This allows to disentangle the unassigned and chaotic high-resolution spectrum of CH_5^+, measured 10 years ago[4], and link different transitions with the corresponding spin isomer for the first time.

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LARGE AMPLITUDE MOTION AND GEOMETRY INVESTIGATION FOR SIMILAR COMPLEXES OF 3-PHENYLPROPIONALDEHYDE-H_2O AND 3-PHENYLPROPIONALDEHYDE-H_2S

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[b] Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Hannover 30167, Germany
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Lone pair$\cdots\pi$-hole interactions, $\pi\cdots\pi$ stacking, and H$\cdots\pi$ interactions, play crucial roles in various chemical and biological processes, and can be studied using aromatic molecules as a probe. In particular, when a molecule possesses an extended side chain, it may create a complex chemical environment that introduces unpredictability in the formation of non-covalent interactions (NCIs). 3-phenylpropionaldehyde is the derivative of the simplest aromatic aldehyde (benzaldehyde) towards longer carbon chains. Its structural flexibility enhances the potential for competition between NCIs.

As adjacent Group VI_A elements in the periodic table, oxygen and sulfur exhibit similar but distinct physical and chemical properties. H_2O and H_2S can serve as an ideal model system for investigating how these subtle variations in atomic characteristics influence the NCIs, large amplitude motion (LAM), and geometry of their complex formed with an identical partner molecule. For example, similar geometries were observed or predicted between the H_2O and the H_2S complexes of benzene,[1,2] naphthalene,[3] and indole,[4] while the structure of phenylacetylene-H_2O[5] was found to be distinct from that of phenylacetylene-H_2S.[6] This raises a question: how do H_2O and H_2S differ in their binding behavior when interacting with an identical molecule that offers multiple potential binding sites? Besides, the presence of LAM caused by different property of H_2O and H_2S in their similar complexes remain insufficiently explored. At these purposes, the two title complexes have been investigated using broadband rotational spectroscopy in frequency range of 2-8 GHz.

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PRECISION SPECTROSCOPY OF THE FINE-STRUCTURE IN THE $a\,^3\Sigma_u^+(v=0)$ AND $c\,^3\Sigma_g^+(v=4)$ STATES OF THE HELIUM DIMER

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The helium dimer (He_2), having only four electrons, no nuclear spin and being the prototypical example of a Rydberg molecule[1], serves as a benchmark system for testing *ab initio* calculations. In recent years, highly accurate calculations from first principles including relativistic and quantum-electrodynamical effects of molecular three- and four-electron systems have become feasible [2,3,4,5]. Accurate experimental data on the lowest-lying electronic states of He_2 are needed to validate the current level of theory, but are scarce in the literature. Especially the fine structure in the triplet manifold, arising from the spin-spin and spin-rotation interactions, has only been measured for a few rovibrational levels in the $a\,^3\Sigma_u^+$ state [6,7,8,9,10,11] and for only three rovibrational levels ($v=4, N\in\{8,10,12\}$) in the $c\,^3\Sigma_g^+$ state[8].

We report on a high-resolution spectroscopic study of the fine structure of the $a\,^3\Sigma_u^+(v=0)$ and $c\,^3\Sigma_g^+(v=4)$ states of He_2 including all rotational levels of the $c\,^3\Sigma_g^+(v=4)$ state up to $N=10$. The experiments combined a dense cold supersonic beam of He_2 in the $a\,^3\Sigma_u^+$ metastable state generated by a cryogenic pulsed valve, and single-mode laser radiation in a geometric arrangement optimized to suppress Doppler shifts. Measurements were performed using a two-color resonant two-photon ionization scheme. A narrowband continuous-wave laser was used drive transitions from the fine-structure levels of the $a\,^3\Sigma_u^+(v=0)$ to those of the $c\,^3\Sigma_g^+(v=4)$ state. The c-state levels were then photoionized with a pulsed dye laser for background-free detection.

The absolute level positions of the $a\,^3\Sigma_u^+(v=0)$ and $c\,^3\Sigma_g^+(v=4)$ fine-structure levels could be determined to within 1 MHz and better in a linear-least squares fit including the transition frequencies of Ref. 8 and fine-structure intervals of Ref. 11.

The rotational, spin-spin and spin-rotation constants with their respective centrifugal distortions and the band origin were fitted in a global weighted nonlinear least-squares fit to the measured transition frequencies, again including the measurements of Refs. 8 and 11. Significant improvements in the precision of the molecular constants were achieved compared to the previous measurements.

The $c\,^3\Sigma_g^+$ state is of particular interest also because its potential-energy curve exhibits a local maximum and its high vibrational levels ($v=3$ and 4) undergo tunneling predissociation. The high spectral resolution enabled the characterization of the rotational-state-dependent tunneling dynamics through the observation of line broadening. The broadening was found to be in good agreement with calculated values, which were obtained by determining the energy dependence of the phase-shift of the scattering wavefunctions.

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P: Plenary

Friday, August 29, 11:00
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COHERENT CONTROL OF CHIRAL MOLECULES

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Chiral molecules are important in many biological and chemical processes and are ubiquitous in nature. Over the last two decades there have been important developments in fundamental chiral research and new experimental methods have emerged. Controlling the internal quantum states of chiral molecules for a selected enantiomer has a wide range of fundamental applications from collision and reaction studies, quantum information to precision spectroscopy. In my presentation, I will introduce recent developments in the experimental quantum state control of chiral molecules using Enantiomer-Specific State Transfer (ESST). Beyond chiral analysis, ESST enables the control and manipulation of chiral molecules at the quantum level. Using tailored microwave fields, a chosen rotational state can be enriched for a selected enantiomer. This enables rapid switching between samples of different enantiomers in a given state, holding great promise, for instance, for measuring parity violation in chiral molecules. In theory, ESST can reach 100% transfer efficiency. However, early studies on ESST reported only modest state-specific enantiomeric enrichment, limited to a few percent [1,2]. This is primarily due to the thermal population of rotational states and the spatial degeneracy of these states. To mitigate the effect of thermal population, we developed a new experimental approach utilizing both ultraviolet and microwave radiation to deplete one of the rotational states before the ESST process [3,4], thereby significantly enhancing the transfer efficiency. In this way we are able to perform quantitative studies of ESST, increasing our understanding of the underlying physical effects. Recently, we realized near-ideal conditions by emptying two of three rotational states prior to ESST, overcoming both the limitations of thermal population and spatial degeneracy in rotational states[5]. I will present details of our recent work together with discussions of the dependence of ESST on various experimental parameters.

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RECENT ADVANCES IN THE QUANTUM-CHEMICAL CALCULATIONS OF SPECTROSCOPIC PARAMETERS FOR ROVIBRATIONAL SPECTROSCOPY

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Recent developments in quantum chemistry concerning the accurate and reliable prediction of rotational and rovibrational spectra are reviewed. The focus will be on advances concerning (a) the treatment of larger molecules, (b) the inclusion of relativistic effects, and (c) hyperfine interactions. The accuracy of state-of-the-art quantum-chemical calculations is shown in benchmark calculations, and the power of the interplay of theory and experiment is demonstrated by several examples.

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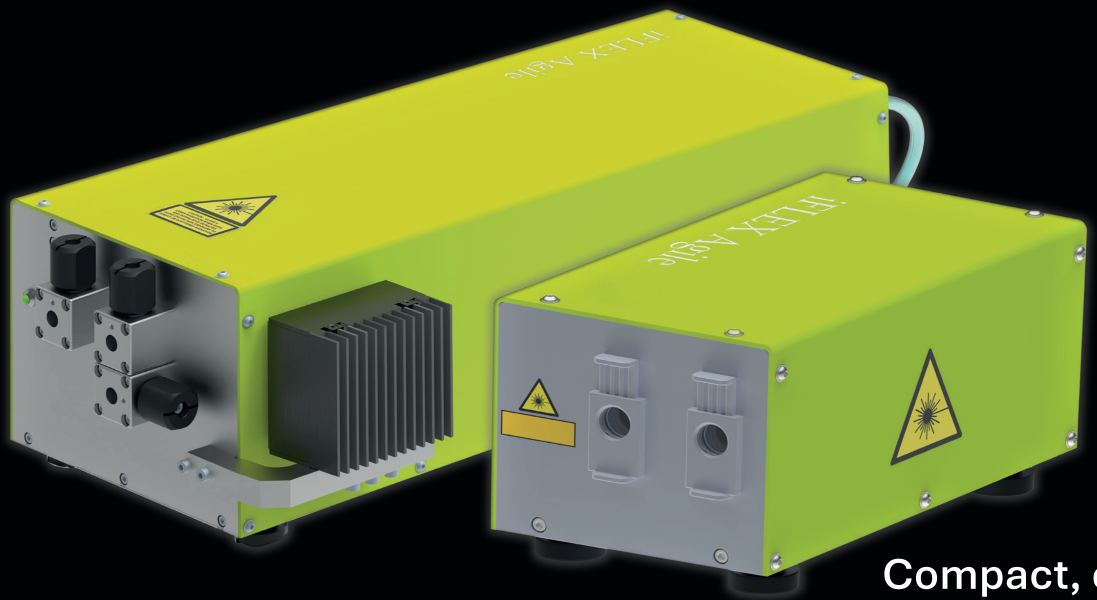

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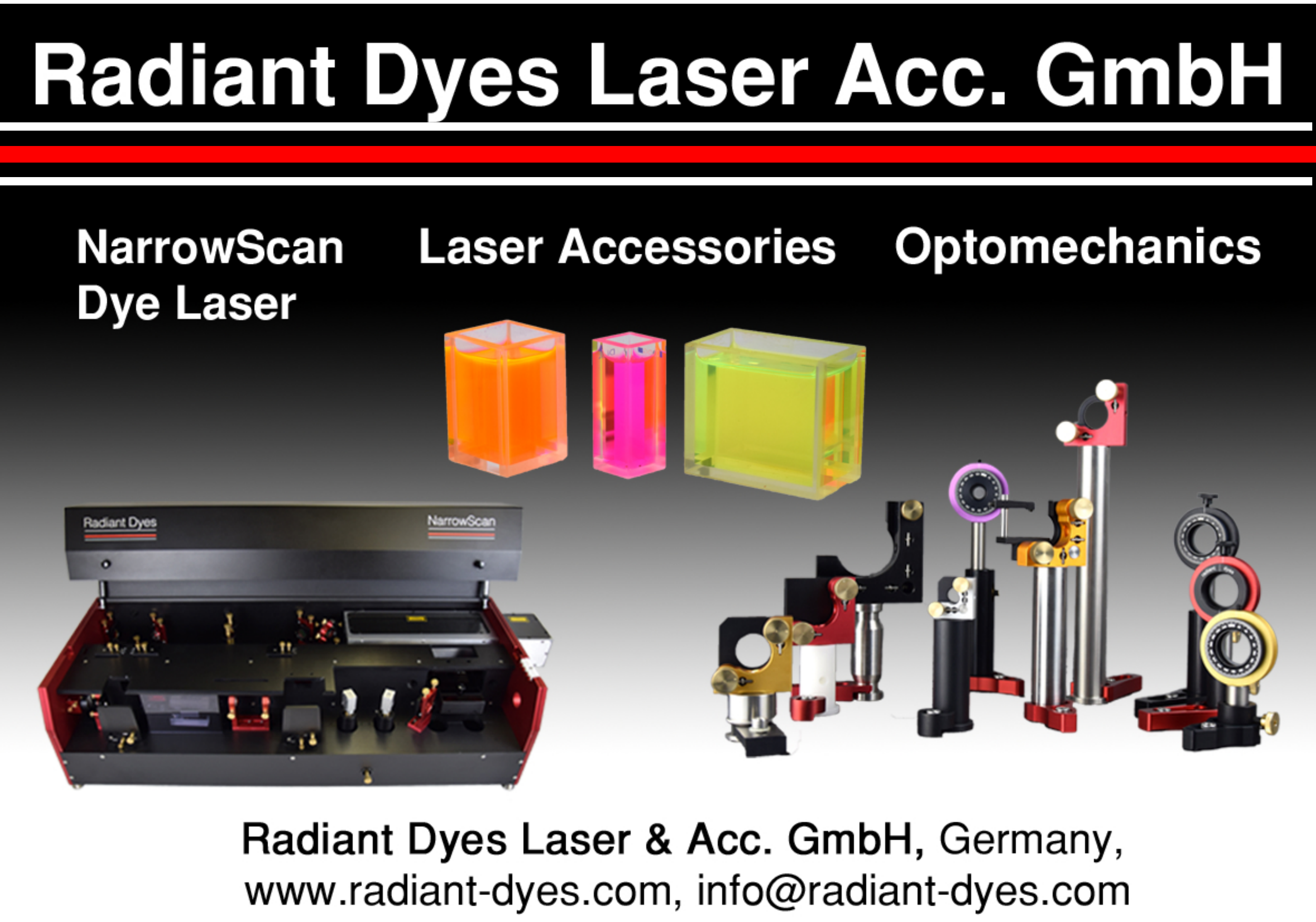

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Benefits:

- ▲ PT401: 210 (193) nm to 2.3 μm @ 100 Hz or 1 kHz
- ▲ PT501: 2.3 - 16 μm @ 100 Hz
- ▲ High pulse energy up to 200 μJ
- ▲ Narrow linewidth of < 4 cm^{-1}
- ▲ High laser stability, exact motorized tuning
- ▲ Fully air-cooled

Other performance features include low beam divergence and a short pulse duration of 8 - 30 ps. This makes the laser system an excellent choice for applications such as time-resolved fluorescence spectroscopy, pump-probe spectroscopy or laser-induced fluorescence.

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