International Workshop: New Developments in High Resolution Molecular Spectroscopy and outreach to modern applications May 29th - June 3rd 2022 Les Houches, France

New Developments in High Resolution Molecular Spectroscopy and outreach to modern applications

Les Houches school of physics, Haute Savoie, France

May 29th to June 3rd 2022

Book of Abstracts

Scientific rationale

The French and German Molecular Spectroscopy community is well recognized internationally for its expertise in both theoretical and experimental research, and benefits from extensive connections and international collaborations. This has favored interactions between individual groups using cutting-edge and specific high-resolution techniques. Resources and related expertise have been shared to tackle and solve complex problems in fundamental molecular physics and its applications in astrophysics, the environmental and life sciences, and even more in industry.

This workshop will share this wealth of experience with graduate students on a larger scale. We consider particularly important the establishment of new career opportunities for the numerous PhD students and postdocs working in the discipline. These students are mainly (but not only) working in fundamental research. New connections between fundamental and applied research are therefore of high interest for the young researchers as well as for the whole spectroscopy community. We will therefore unite experts at the forefront of our discipline to present their latest developments with those from the various applications fields of molecular spectroscopy. The latter will communicate on the specific needs and interests of theirs fields.

For example, in astrophysics, modern telescopes using highly advanced spectrometers are being built constantly, with ever-increasing performances. They are aiming to study the physical chemistry of astrophysical objects. This evolution is driven by the enthusiasm of the society to explore the Universe more and more deeply. In order to fully exploit the enormous quantities of available data and to interpret the astrophysical observations in depth, molecular spectroscopy has to be developed in parallel since the precision requirements on spectral data (frequency and intensity) are extremely challenging. This has led to the establishment of the flourishing field of "Laboratory Astrophysics". Yet, it is our opinion that connections between spectroscopists and astronomers have to be improved continuously taking into account the most recent technological progress.

These developments are mirrored in the studies of Earth's atmosphere where ambitious space missions are undertaken to measure atmospheric mixing ratios of greenhouse gases and air pollutants such as ozone, NO_x and volatile organic compounds (VOCs), by means of remote sensing. In this context we mention the OCO-2 (orbiting carbon observatory), MERLIN (Methane Remote Sensing Lidar) and the IASI-NG (Infrared Atmospheric Sounding Interferometer-next generation) missions. Spectroscopic insitu measurements are aiming to understand the influence of free radicals and very low-concentration VOCs on air quality and, in the long term, on climate change. There is always demand for precise spectroscopic parameters beyond the limit of current knowledge.

The development of high-sensitivity, target-specific and rapid spectroscopic techniques adapted to trace gas detection is leading to multiple applications in life sciences, and is implemented in real-time surveillance of environments ranging from clean rooms to petrochemical industry installations or incineration plants. The molecular spectroscopy community is also clearly linked to progress in photonics, and the development of new laser sources.

The main goal of this workshop is to create long-lasting bridges between our future PhD degree holders in bio- chemical- geo- physics and the socio-economic world, so that they can navigate efficiently towards their post-university environment, and nurture a positive perception of fundamental science there. Another important objective is to enhance academia's awareness of specific problems and demands from the various application fields, and to allow industry to appreciate the specific strengths of the academic scientific community. New links forged between industry and Science will therefore be of strong mutual benefit.

Scientific advisory committee

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Sylviane AUDET BONNEAU, Faculté des Sciences & Technologie, Université Paris-Est Créteil. Communication.

List of Speakers and lecture titles, by discipline

Spectroscopy and photonics:

<u>Prof. Jérôme FAIST</u>, Quantum Optoelectronics group, ETH Zürich: *Progress in the development of QCL sources*.

<u>Dr. Bernd FISCHER</u>, Head of Division IV "Protection Technologies, Security, Situational Awareness", Institut Franco-Allemand des recherches de Saint Louis: *Use of THz radiation for strategic issues (explosives, pharmaceuticals, drugs and counterfeiting).*

Dr. Rysvan MALECK, Société OQO: Pursuing a career in the photonics industry: experience sharing.

Spectroscopy and Astrophysics:

<u>Prof. Svetlana BERDYUGINA</u>, Director Kiepenheuer Institut für Sonnenphysik (KIS), Chair for Astrophysics, Universität Freiburg: *Current advances in stellar physics, astrobiology and exoplanetary science*.

Dr. José CERNICHARO, Director Molecular astrophysics group, Instituto de Ciencia de Materiales de Madrid - ICMM – CSIC: *Exploration of objects of the interstellar medium: molecules, spectroscopy and challenges*.

<u>Dr. Isabelle KLEINER</u>, Laboratoire Interuniversitaire des Systèmes Atmosphérique (UMR 7583 CNRS), Université Paris-Est Créteil: *Theoretical methods to interpret interstellar surveys in the microwave and sub-mm spectral regime*.

<u>Dr. Michael REY</u>, Groupe de Spectrométrie Moléculaire et Atmosphérique (UMR CNRS 7331), Université de Reims Champagne Ardenne: *Theroretical methods for describing highly excited rovibrational states and applications to planetary atmospheres*.

Spectroscopy and Atmospheric Science:

<u>Prof. Ulrich PLATT</u>, Institut für Umweltphysik, Universität Heidelberg: *Current questions in atmospheric chemistry and their relation to air pollution and climate*.

<u>Prof. Patrick RAIROUX</u>, Institut Lumière Matière (UMR CNRS 5306), Université de Lyon: *Overview and challenges in current LIDAR missions (space born and from ground).*

Dr. Ann Carine VANDAELE, Head of Planetary Aeronomy Division, Royal Belgian Institute for Space Aeronomy (BIRA-IASB): *Overview and challenges in current solar system exploration missions includung Earth.*

Dr. Samir KASSI, Laboratoire Interdisciplinaire de Physique (UMR CNRS 5588), Université Grenoble Alpes: *Current developments and applications of high finesse optical cavities*.

<u>Prof. Weidong CHEN</u>, Laboratoire de Physico-chimie de l'Atmosphère (LPCA), Université du Littoral Côte d'Opale: *Developments of photonic instrumentation for applied spectroscopy, optical sensing and metrology of atmospheric species*.

Dr. Pierre ASSELIN, Laboratoire Molécules, et Nanoobjets : Réactivité, Interactions & Spectroscopie (MONARIS UMR CNRS 8233), Sorbonne Université: *Infrared spectroscopy of jet-cooled molecules using QCL sources and atmospheric applications*.

<u>Jean DECKER</u>, Laboratoire de Physico-chimie de l'Atmosphère (LPCA), Université du Littoral Côte d'Opale: *THz spectroscopy of pollutant emissions in a waste recovery center*.

Spectroscopy and Life Science:

<u>Dr. Isabelle COMPAGNON</u>, Institut Lumière Matière (UMR CNRS 5306), Université de Lyon: *Platform IRoGlyph: deciphering molecular structure and carbohydrate sequence*.

<u>Prof. Kevin PAGEL</u>, Institute of Chemistry and Biochemistry, Freie Universität Berlin: *Ion Mobility-Mass Spectrometry and Spectroscopy of Biomolecules*.

Dr. Irène VENTRILLARD, Laboratoire Interdisciplinaire de Physique (UMR CNRS 5588), Université Grnoble Alpes: *Real-time laser spectroscopy of exhaled air and its use in medical applications*.

<u>Baptiste MOGE</u>, Institut Lumière Matière (UMR CNRS 5306), Université de Lyon: *IRMPD* spectroscopy in analytical chemistry.

Spectroscopy @ **Dynamics**

Dr. Pierre Caraçabal, Institut des Sciences Moléculaires (ISMO), Université Paris-Saclay. Dr Carçabal will present the <u>GdR EMIE (*Edifices moléculaires isolés et Environnés*)</u>

International Workshop: "New developments in High Resolution Molecular Spectroscopy and outreach to modern applications"

Preliminary program 2022 (last update May 24, 2022), subject to slight changes

Sunday May 29th : reception from 15h on (rooms can be taken), a meal is served in the evening

	Monday, May 30th	Tuesday, May 31st	Wednesday, June 1st	Thursday, June 2nd	Friday, June 3rd					
	Spectroscopy & Atmospheric science	Spectroscopy & Atmospheric science & Astrophysics	Spectroscopy & Astrophysics	Spectroscopy & Life Science	Spectroscopy & Photonics					
Morning session 1 9h-10h30	Ulrich Platt: Current questions in atmospheric chemistry and their relation to air pollution and climate (~40 min).	h Platt: Current questions in atmospheric nistry and their relation to air pollution climate (~40 min).Pierre Asselin: Infrared spectroscopy of jet- cooled molecules using QCL sources and atmospheric applications (~40 min).		Isabelle Compagnon: Platform IRoGlyph: deciphering molecular structure and carbohydrate sequence (~40 min)	Jerome Faist : Current advances in the development of quantum cascade laser sources and photonics (~60 min).					
	Weidong Chen: Developments of photonic instrumentation for applied spectroscopy, optical sensing and metrology of atmospheric species (~40 min).	Svetlana Berdyugina: Current advances in stellar physics, astrobiology and exoplanetary Science (~45 min).	Ann Carine Vandaele : Overview and challenges in current solar system exploration missions (~40 min).	Kevin Pagel: Ion Mobility-Mass Spectrometry and Spectroscopy of Biomolecules (~40 min).	Bernd Fischer: Use of THz radiation for strategic issues (explosives, pharmaceuticals, drugs and counterfeiting) (~40 min).					
	Coffee break 10h30 - 10h50									
Morning	Samir Kassi : Development and applications of high finesse optical cavities (~60 min).	José Cernicharo : Exploration of objects of the interstellar medium: molecules, spectroscopy and challenges (~50 min).	Michael Rey : Theroretical methods for describing highly excited rovibrational states and applications to planetary atmospheres (~40 min).	Baptiste Moge : IRMPD spectroscopy in analytical chemistry (~20 min).	Irène Ventrillard: Real-time laser spectroscopy of exhaled air and its use in medical applications (~30 min). Restituion of practical work by participants					
session2			Spectroscopy & Dynamics:	Rysvan Maleck : Pursuing a career in the	lean Decker: THz spectroscopy of					
101150-121120	Flash presentations of participants (A, B1) come to my poster ! (~30 min)	Flash presentations of participants (B2,C) <i>come</i> to my poster ! (~30 min)	Pierre Carçabal: The GdR EMIE - Isolated and Surrounded Molecular buildings (~30 min).	photonics industry: experience sharing (~40 min).	pollutant emissions in a waste recovery center (20 min).					
	Lunch Break	12h30 to 14h		Lunch Break 12h30 to 14h						
Afternoon	Irène Ventrillard: Introduction to practical works (OFCEAS) (Tutorial ~45 min)				Departure					
session 1 14h-16h	Patrick Rairoux: Overview and challenges in current LIDAR missions (space born and from ground) (~60 min).	Practical work : Group A, B1: OFCEAS	Liking Evenueion	Practical work : Group B2,C: OFCEAS						
	Coffee brea	k 16h-16h20		Coffee break						
Afternoon session 2	Vincent Boudon Introduction to practical works (astronomical observations) (Tutorial ~40 min)	Poster session		Practical work / tutorials						
16h20-18h30	Poster session & Welcome Coktail (19h)			,						
		Dinner 19h30								
Evening session 21H30-24h	Practical work : Group A: Astronomical observations ; Groups B1&2, C: free.	Practical work: Group B1&2: Astronomical observations ; Groups A,C: free.	Practical work : Group C: Astronomical observations ; Groups A,B1&2: free.	Savoyard evening						

Speakers' résumés (received by May 24th; in alphabetical order).

Rovibrational spectroscopy of jet-cooled molecules using Fourier Transform and QCL methods: applications in atmospheric science and astrophysics

Pierre Asselin, Sorbonne Université, MONARIS UMR 8233 CNRS, Paris, France

Infrared spectroscopy is a standard method largely used in chemistry to identify chemical substances from the identification of functional group or characteristic molecular vibrations. In the field of molecular spectroscopy, high resolution Fourier Transform Infrared (FTIR) spectrometers coupled to long path absorption gas cells at room temperature has proven to resolve in some cases the rovibrational spectrum of small polyatomic molecules but this approach reaches its limits in the case of larger molecular systems having low lying vibrational levels and/or small rotational constants. To overcome these limitations, the supersonic jet technique turns out the diluted matter environment suitable for gas phase high resolution infrared spectroscopy.

During this talk, I will enlarge two experimental set-ups combining supersonic jets and high resolution infrared spectroscopy implemented at the AILES beamline of the SOLEIL synchrotron (Jet-AILES) and at MONARIS laboratory (SPIRALES).

To illustrate the performances and the complementarities between both jet-cooled devices, three examples of atmospheric studies involving sulphur dimethyl, methoxyphenols and a furan compound, the furfural molecule will be presented and last, the long story of a PAH model molecule, the naphthalene investigated with Jet-AILES then SPIRALES over ten last years.

Pierre Çarçabal^{1*}

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Abstract

The mission of the « Isolated and interacting molecular assemblies » research network (EMIE) is to bring together the French community of physicists and chemists working on molecular systems, and covering a wide range of size and complexity. The objects under scrutiny are either isolated in the gas phase or surrounded by a controlled environment. Building upon fundamental aspects of experimental and theoretical molecular physics, our community is naturally inclined to benefit from interactions with other disciplines (chemistry, biology) and to extend its fields of applications to other scientific domains with timely societal impacts (biology, atmosphere).

Two transverse axes

- Experimental methods and instrumentation
- Theoretical approaches

Four Interdisciplinary themes

- Atmospheric and Universe sciences
- Excited states and energy
- Biomolecules
- Environment effects.

THz spectroscopy of pollutant emissions in a waste recovery center

<u>Jean Decker</u>^{1*}, Frank Hindle¹, Eric Fertein¹, Nicolas Houzel¹, Patrick Augustin¹, Marc Fourmentin¹, Yamina Allouche², Fabrice Cazier², Frédéric Desmedt³, Marion Philippon⁴, Julien Dumont³ and Arnaud Cuisset¹

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Abstract

Dunkirk waste recovery center continuously treats all the household waste of the urban community by transforming it into electrical and thermal energy through incineration. These activities are carried out with a control of the environmental impact (ISO 14001 certification), based on the continuous improvement of detection techniques. The TeraWaste project explores the potential of high-resolution TeraHertz spectroscopy for the monitoring of gaseous emissions, by developing an in-situ diagnostic unit. The selectivity as well as the ability to detect in scattering media of THz radiation make it an alternative of choice to current solutions [1-4]. A new sub-millimetre source, acquired for this project and allowing the detection of trace gases, has been characterised. The prototype of the in-situ spectrometer was developed and the detection limits of the regulated compounds were determined. Measurements on real process and emission gases were performed and compared to standard analytical chemistry methods. Using pre-concentration [5], a multi-species time-resolved mapping and quantification, extended to all polar compounds absorbing sub-millimeter waves of the pole's gaseous emissions, will allow the operator to better meet current standards and future normative evolutions. Finally, by correlating environmental measurements in the emission plume with LIDAR measurements, the impact of atmospheric emissions can be directly assessed.

Acknowledgments We thanks all its sponsors for their support.

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Theroretical methods to interpret laboratory surveys in the microwave and (sub)-millimeter spectral region for molecules of interstellar interest

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Abstract

Recently, more than 200 molecules have been detected in the interstellar medium (ISM), a third of them are complex organic molecules (COMs).

The key point for the detection of new molecular species in space is the precise knowledge of the rotational spectra for a number of complex molecules, which can be gained by laboratory spectroscopy assisted by appropriate theoretical models. One of the most efficient strategy is to combine experimental microwave, millimeter and sub-millimeter-wave spectroscopy, followed by analysis of these spectra using appropriate effective quantum mechanical Hamiltonians, sometimes coupled with theoretical studies using also ab initio calculations. In the microwave spectral range through the THz, all the data is accessible to the astronomy community thanks to the well-known spectroscopic databases (JPL [1], CDMS [2], SPATALOG [3], the Lovas NIST databasis [4], the Toyama databasis [5] etc). Databases are built up from intensive spectroscopic studies both experimental and theoretical.

The present class is focused on the theoretical methods used to analyze the laboratory spectra in the microwave and (sub) millimeter-wave spectral range [6-7]. After a short introduction, I will give the basics of rotational spectroscopy, and the strategy used in the laboratory analysis with certain specific Hamiltonian codes which can model quadrupole effects or large amplitude motions and I will finish with a few examples of spectra for interstellar internal rotor molecules.

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Abstract

E. Coli infection is a major challenge in animal breeding because it is responsible for a high post weaning mortality rate, with disastrous impact for animal well-being, human safety, as well as economically and environmentally ¹. In this public/private cooperation, our industrial partner Elicityl performed the synthesis of a glycoconjugate that prevent infection, without the use of antibiotics, thus avoiding antibioresistance. This synthetic compound and its potential impurities and co-products must be fully characterized before it is authorized to be placed on the market. Impurities are expected to be oligosaccharidic compounds. Oligosaccharides respond to vital functions in living organisms. Despite their great importance, structural characterization of oligosaccharides remains not perfect with current analytical methods (MS or NMR) due to their structural complexity and dynamic range in samples. This lack of knowledge constitutes a bottleneck for a better knowledge of the nature and function of such species. The structural characterization of the glycoconjugate is no less challenging, but will not be presented here for confidentiality reasons.

Gas phase InfraRed spectroscopy has emerged from the Physical Chemistry community has a gamechanging tool for Analytical Chemistry. This interest is the case, particularly concerning isomeric compounds such as carbohydrates. We propose an innovative method to study the impurities (unknown oligosaccharides) generated by the glycoconjugate synthesis. InfraRed MultiPhoton Dissociation spectroscopy (IRMPD), as Cryogenic IR spectroscopy and Messenger Tagging IR spectroscopy is one of the three gas phase IR spectroscopies, they all have proved their usefulness concerning carbohydrate structural characterization².

In this context, my goal as a PhD student is to characterize the glycoconjugate and its impurities and coproducts. IRMPD spectroscopy will be used to decipher intrinsic the complexity of oligosaccharides (regiochemistry, stereochemistry of the glycosidic bonds, nature of the monosaccharides...). Effort are being made to automate and facilitate data acquisition, data process and data interpretation. Therefore, IRMPD spectroscopy can be widespread in analytical laboratories of industrial companies. Identification of unknown oligosaccharides by the mean of a homemade database and the newest developments of the method will be discussed.



Fig. 1: Fragmentation spectra of two protonated Lewis species that are not significantly different, generated fragments are the same (left panels) They results from cleavage of glyosidic bond. and IRMPD spectra of fragment at m/z = 384 allowing unambiguously distinction between these two species (right panels).

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Theoretical methods for describing highly excited rovibrational states and applications to planetary atmospheres

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Precise knowledge of high-energy molecular states and absorption spectra is of primary importance because it gives access to the determination of the physical properties of various planetary object and clearly demonstrates the necessity of having consistent line-byline molecular databases (e.g. like HITRAN or GEISA for the modelling of the Earth's atmosphere). The interpretation of strong spectral features requires the use of sophisticated and robust theoretical models (i) for an accurate quantum-mechanical description of highly excited molecular states and (ii) for the prediction of line intensities for reliable opacity calculations. Although empirical effective Hamiltonians have greatly contributed to the "golden age" of the high-resolution molecular spectroscopy, extensive firstprinciples quantum mechanical calculations are generally preferred for planetary and astrophysical applications because of their completeness.

The first necessary ingredient in variational calculations is the construction of accurate intra-molecular potential energy and dipole moment surfaces in a large range of nuclear displacements. The second one lies in the development of efficient computational methods using adapted coordinates to solve the Schrödinger equation for medium-sized molecules. We will see in a pedagogical way how to reduce "dimensionality" of a problem using relevant symmetry-adapted reduction-contraction methods and how to choose appropriate eigensolvers for computing high energy eigenstates involved in hot spectra calculations.

In a second part, a novel methodology will be presented for the construction of "global" *ab initio* effective rotation-vibration spectroscopic models. The current researches in the study of various planetary atmospheres require knowledge of increasingly complex molecular systems over wide wavenumber and temperature ranges. Unfortunately, the empirical models are beginning to reach their limits for studying molecules with complex rovibrational energy-level structures and for which the successive polyads contain many vibrational bands and numerous degeneracies and quasi-degeneracies. Modelling of the « dark states » which are not directly observable is one of the major obstacles in the empirical effective approach. The model we propose turns out to be a clear alternative to the rather involved Van Vleck perturbation method. We will see how to transform first-principles calculations into a set of spectroscopic parameters to be further refined on experiment. It will be demonstrated that crucial information is provided within a very short time compared to more traditional spectroscopic models (*few hours, days or weeks against few months, years or decades*). Undoubtedly, this approach brings a new insight into high-resolution spectra analysis and will be of great help, not only in current or future infrared spectra analyses of polyatomic molecules but also in the modelling of hot atmospheres for which completeness is crucial.

Real-time laser spectroscopy of exhaled air and its use in medical applications

Irène Ventrillard

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Abstract

The sense of smell is one of the oldest diagnostic tools in the practice of medicine. In the last decades, exhaled air analysis for non-invasive medical diagnosis has seen a growing interest. There are a thousand species present at very low concentrations in exhaled air, of which around thirty have been identified as markers of physiological processes and of various pathologies [1]. Among the different analysis methods, tunable diode laser spectroscopy appears to be very attractive. It allows very low detection limits together with good selectivity, in real time. Numerous laboratory demonstrations have been carried out with different techniques based on absorption spectroscopy in multi-pass cells or with resonant cavities [2,3]. Today, we are at a turning point where some state-of-the-art analyzers developed in the laboratory are finding well-identified medical applications, thanks to close collaborations between physicists and doctors engaged in clinical studies.

After a general presentation, we will illustrate the potential benefits of real-time laser analysis by focusing on a technique developed in our group: Optical Feedback Cavity-Enhanced Absorption Spectroscopy (OF-CEAS [4]). Firstly, we will present clinical studies which fall within the context of lung transplantation. The final objective is to propose new markers to assess the quality of lung grafts in order to increase the number of grafts available [4,6]. Real-time measurements of the production of CO, NO and CO_2 by an ex-vivo lung graft are carried out by OF-CEAS (figure 1). Secondly, this lecture will end with short presentations given by workshop participants who will be asked to perform breath analysis measurements during the week, using an OF-CEAS analyzer studied during one of the practical sessions.



Fig. 1: Continuous measurements of nitric oxide (a), carbon monoxide (b) and carbon dioxide (c) concentrations obtained in real time by OFCEAS. Regular respiratory cycles of 6 s duration are imposed by a ventilator with an inspiration (I) to expiration (E) ratio: I/E = I/2 [5].

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COMPREHENSIVE ROTATIONAL SPECTROSCOPY OF METHYL CYANOACETATE FOR ASTRONOMICAL SEARCHES

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Abstract

Out of more than 200 individual molecular species already identified in the interstellar medium (ISM), nearly 16% of the molecules contain a cyano functional group (CDMS)*. An interesting extension to this is studying molecules that contain an additional functional group. We present a comprehensive study on methyl cyanoacetate (MCA) whose condensed formula is NCCH₂COOCH₃. It is a molecule whose both functional groups (cyano, -CN, and ester, -COO) have already been identified individually in various molecules in the ISM, making it a promising candidate to be detected.

The rotational spectrum of MCA was obtained in the frequency range of 2-110 GHz using three chirpedpulse Fourier transform microwave (CP-FTMW) spectrometers, namely the COMPACT (2-18 GHz)¹, the K- band (18-26 GHz)², and the W-band (75-110 GHz)³ spectrometer. Two low energy conformers, MCA_1, and MCA_2 were assigned in the rotational spectra, with MCA_1⁴ being the lowest energy conformer. Both conformers of MCA show hyperfine splitting (HFS) due to ¹⁴N nuclear quadrupole coupling and internal rotational splitting in the rotational transitions. Each transition is first split into A and E component due to the internal rotation of the methyl group, followed by HFS due to the interaction of *I*=1 spin of ¹⁴N with the electric field gradient averaged over the molecular rotation. During the course of analysis, it was observed that the transitions from the second conformer, MCA_2, are more intense than the lowest energy conformer, MCA_1, owing to its high dipole moment. The calculated intensity ratio based on the Gibbs energies and the dipole moment suggests that MCA_2 can be a better candidate for astronomical searches in various regions of ISM.

Apart from the assignment of the parent species, singly-substituted ¹³C and ¹⁵N isotopologues for both conformers of MCA were also assigned in natural abundance. In conclusion, the precise determination of the rotational parameters presented in this study, can facilitate searches for both conformers of MCA with the help of various radio observatories, for example, the Jansky Very Large Array (JVLA) and the Radio Telescope Effelsberg.



Figure 1: Rotational spectrum of MCA recorded with the *K*- band spectrometer in the 18-26 GHz region. The upper black trace is the experimental spectrum, the lower colored traces are the simulated spectra based on the fitted rotational constants at 3 K for both conformers of MCA. The zoom-in illustrates the assignment and the intensity ratio of the two conformers. The rotational transition7₀₇ - 6_{06} , is marked with an asterisk to highlight for the difference in the intensity for MCA_1 and MCA_2.

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Characterization of *sec*-Butoxytrimethylsilane by Chirped-Pulse Fourier-Transform Microwave Spectroscopy

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Abstract

Silicon chemistry is an extensive research topic due to its importance for industry and technology, and because of its natural abundance on earth. Silicon is a versatile element; its applications range from pure silicon to compounds. To understand the physical and chemical properties of silicon-containing molecules it is essential to characterize their gas-phase structures.

The rotational spectrum and structural analysis of sec-butoxytrimethylsilane (sBTMS) will be presented. The spectrum of sBTMS has been recorded using the Hamburg COMPACT spectrometer, which is a chirped-pulse Fourier transform microwave spectrometer, operated in the 2 - 8 GHz frequency range. Quantum-chemical calculations have been carried out to study the conformational flexibility of sBTMS, and the measured rotational spectrum was examined for the lowest energy conformers. The spectrum is complicated due to the fact that three of the five methyl groups in sBTMS have a rotational barrier lower than 7 kJ/mol, leading to internal rotation splitting. Despite this, the lowest energy conformer is prominent in the spectrum and has been successfully assigned. In addition, weak signals of the conformers second and third lowest in energy are present. On this poster, the conformational flexibility of sBTMS will be presented as well as its internal motion analysed and compared to previous work on silicon-containing molecules with three methyl groups, which in contrast exhibit an overall $C_{3\nu}$ symmetry [1].



Conformer 1

Conformer 2



Fig. 1: Left side: Zoom-in of the rotational spectrum of sBTMS; the upper trace in black shows the experimental spectrum, the lower traces show the simulated spectra based on the fitted rotational constants. Red: conformer 1, blue: conformer 2, green: conformer 3; the structures of the different conformers are depicted on the right side.

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MILLIMETER-WAVE SPECTROSCOPY OF METHYLFURAN ISOMERS: LOCAL vs GLOBAL TREATMENT OF THE INTERNAL ROTATION

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Abstract

Methylfurans (MF) are methylated aromatic heterocyclic volatile organic compounds (VOCs) and primary or secondary pollutants in the atmosphere due to their capability to form atmospheric particles such as secondary organic aerosols (SOAs)^[1]. MFs are produced by cracking biomass such as wood combustion and the pyrolysis of biomass, lignin and cellulose^[2]. Therefore there is a fundamental interest to monitor these molecules in the gas phase. The high resolution spectroscopic studies of methylated furan compounds, except 2- MF^[3], are generally limited to pure rotational spectroscopy in the ground state. This might be explained by the difficulties arisen from the internal rotation with a medium barrier and the complexity of the vibrationally excited state rotational spectra. As Finneran et al. for 2-MF, we faced the same difficulties for 3-MF to treat the first torsional levels given by the BELGI code^[5], was used. This gave us access to the V₆ term characterizing the anharmonicity of the potential, together with some higher order perturbation and coupling terms. Carrying out a BELGI global fit of $v_t = 0$ and $v_t = 1$ states using our new assignment for 3-MF and the assigned transitions of Finneran et al. for 2-MF enabled us to compare the molecular parameters of these two isomers.

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Spectroscopic study of intermolecular interactions between mannose and receptor models

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Abstract

Sugars are one of the most important families of biomolecules. They act as mediators of molecular recognition processes. Among the possible biomedical applications, one example is the addition of mannosides to photosensitizers used in PhotoDynamic Therapy, targeting Mannose Receptor (MR) proteins on pathogenic cells. A precise description of the structural basis of Mannose-MR local and direct interplay, which can be provided by gas phase spectroscopy, critically lacks to design PSs with improved selectivity.

In the gas phase, combining experimental mass resolved and conformer selective double resonance vibrational spectroscopy and theoretical chemistry studies, [1] we have already been able to observe several complexes between sugars and peptide models. [2,3] We can now also observe such complexes with a controlled number of water molecules (Figure 1). Our most recent results on complexes of mannose with various peptide models, either hydrated or not, allow resolving the nature of the interactions between the molecules, for each donor and acceptor molecular group involved in the non-covalent bonds governing the complexes. These results reveal the multiple interaction preferences of sugar-peptide complexes. In particular, the study of the complexes formed with few water molecules may highlight the role of water in molecular recognition processes in an unprecedented manner.



Fig. 1: Experimental (top) and computed (bottom) vibrational spectra of the Alanine-Mannose-water ternary complex.

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Abstract

More than 30% of molecules detected in space are free radicals or their ions¹, and they are also important intermediates in many chemical reactions. However, their study in the lab is a challenge due to their high reactivity. In order to produce *in situ* free radicals molecules in an abundant and controlled way and study their photoionization spectroscopy, several radical sources can be coupled to our VULCAIM (VUv Laser for Considering Astrophysical and Isolated Molecules)² set-up: pyrolysis, electric discharge, chemical reaction as well as photolysis. So far, we have carried out the coupling of VULCAIM with a radical source by pyrolysis and by electric discharge. With pyrolysis, the methyl radical (CH₃) was generated using the precursor CH₃NO₂ and its photoelectron spectrum was recorded thanks to our tunable VUV (Vacuum UltraViolet) laser. With the pulsed electric discharge source³, we have successfully observed CH_x (x=1-3) radicals and NH_y (y=1,2) radicals signal using the precursors CH₄ and NH₃ respectively. In this poster, I will present several examples of radicals produced by different radical sources and I will provide details on their internal energies.



Fig. 1: PFI-ZEKE experimental (black) and simulated (red) spectra of the $X^{+1}A_{1} \leftarrow X^{2}A_{2}^{"}$ transition of CH₃ radical produced by pyrolysis.

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All fiber-coupled mini-multipass cell based dense spot pattern for ppb-level methane detection

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Abstract

Tunable diode laser absorption spectroscopy (TDLAS) based on multi-pass cell (MPC) [1-4] is a powerful analytical tool for field applications in air quality monitoring, industrial process control and medical diagnostics. However, the conventional MPC as a core component in TDLAS devices has a large size, low utilization efficiency of the mirror surfaces and tight optical alignment tolerances [5]. Design of miniaturized long-path MPC for the development of handheld portable high sensitivity sensing devices is one of the mainstream trends nowadays.

In this work, we designed and fabricated a mini-MPC with an effective optical absorption path length of 4.2 m and dimensions of $4 \times 4 \times 6$ cm³, which to our best knowledge is the current smallest MPC in terms of the same optical path length. The mini-MPC generates a seven-nonintersecting-circle dense spot pattern on two 25.4 mm spherical mirror surfaces providing a high fill factor of 21 cm⁻² as shown in Fig.1. A fiber-coupled collimator and an InGaAs photodetector are integrated into the mini-MPC via a high-resolution 3D-printed frame, hence removing the requirement of active optical alignment. This setup as shown in Fig.1 (e). Using a 1.65 µm distributed-feedback laser, the performance of this mini-MPC for methane detection was evaluated in terms of linearity, flow response time, stability, minimum detectable limit and measurement precision. The developed mini-MPC has a fill factor of 21 cm⁻², achieving a RNF of $\sim 10^{-7}$ cm²•Hz^{-1/2}. A side-by-side comparison of RNFs for the mini-MPC based CH₄ sensor and those current state-of-the-art MPC based CH₄ sensors. This mini-MPC based CH₄ sensor has the best RNF value due to the large value of the fill factor and the small value of the NEA. Continuous measurements of methane near a sewer and in the atmosphere were performed to demonstrate the stability and robustness of the highly integrated mini-MPC based gas sensor. The results as shown in Fig. 2. This work paves the way towards a sensitive, low-cost, miniature trace gas sensor inherently suitable for large-scale deployment of distributed sensor networks and for handheld mobile devices.



Fig. 1: (a) Photograph of an open mini-MPC with a seven-nonintersecting circle spot pattern shown on the exit spherical mirror sur-face;
(b) Photograph of the ray trajectories between two spherical mirrors; (c) Photograph of a closed mini-MPC with a gas inlet and an outlet;
(d) Top view of the closed mini-MPC without the cap; (e) Schematic diagram of the developed CH4 sensor.



Fig. 2: Continuous monitoring of CH4 concentrations (a) measured from Apr. 6, 2019 to Apr. 18, 2019 near sewers and (c) measured from Apr. 28, 2019 to May 8, 2019 far away from sewers on the Shanxi University campus, China; Diurnal variations of CH4 mixing rations (b) near sewers and (d) far away from sewers. Bottom whisker, bottom box line, and top whisker in (b) and (d) indicate the 10th ,25th, 75th, and 90th percentiles, respectively. Line inside the boxes and continuous solid line in (b) and (d) represent the hourly median and mean of the data, respectively.

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VIS/UV Dual Comb Spectroscopy for Environmental Sensing

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Abstract

Dual Comb Spectroscopy (DCS) combines the advantages of conventional Fourier transform spectroscopy (FTS), a high spectral resolution and at the same time a broad spectral range, with the high accuracy of laser spectrometers and short measurement times (one million times shorter than conventional FTS). In addition, a long interaction path length can be used to increase the sensitivity of the measurement method [1, 2].

Two coherent frequency comb lasers are used in an interference set-up to down convert the optical frequencies into a measureable radio frequency signal. This down conversion allows an easy detection with a photo diode and at the same time it provides a high signal-to-noise ratio [2, 3]. Two frequency comb lasers with slightly different repetition rates are spatially overlapped and the time dependent interference pattern is recorded. For the evaluation, a Fourier transform in addition to a mathematical up-conversion is used to obtain the optical spectrum of the lasers.

Absorption data can be used to determine not only the type of sample but also the concentration via quantitative absorption measurements. This allows the investigation of several trace gases in air. Most importantly, nitrogen dioxide (NO₂) and ozone (O₃) play an important part in photochemical reactions. DCS allows reproducible measurements with a high sensitivity and over long path lengths [3-5], and therefore provides ideal conditions for long path length measurements.

For the experiments, two lasers with a centre wavelength of 1035 nm and a repetition rate of 80 MHz are used. The repetition rates of the lasers are locked with the possibility to adjust the repetition rate of one laser to a slight detuning. In the current set-up, the carrier envelope offset is free-running. With a second harmonic generation set-up, the infrared radiation is converted into visible light with a centre wavelength of 517 nm.

For the atmospheric measurements, several absorption paths around the physics building in Graz were established. A compact and portable version of the dual comb set-up was realized to conduct experiments at multiple locations outside of the laboratory. In order to increase the absorption length, a multi-pass configuration is implemented. Figure 1 shows a photograph of a field experiment, in which the laser is pointed from the physics building at the Graz University of Technology towards a retroreflector, mounted on a neighbouring building. Current measurement paths are around 100 m for a single pass. With multiple reflections, distances of up to 600 m are currently under investigation.

Complementary to the first experiments outside, a NO₂ gas absorption cell was designed and realized. This cell serves as a reference and is used to determine the detection limit of our mobile dual comb spectrometer by applying different NO₂ gas concentrations. At a later state, different concentration ratios of complex gas mixtures will be investigated exploiting DCS' broad spectral coverage and high spectral resolution. Figure 2 shows recent measurements using DCS and an Optical Spectrum Analyser (OSA), in comparison to adapted literature data from 2004, Nizkorodov et al. [6] with a spectral resolution of 0.0005 nm. For these experiments, the absorption length is about 80 cm, with 500 ppm NO₂ in artificial air and a pressure inside the cell of 500 mbar. The spectral resolution of the OSA is 0.2 nm whereas the resolution of the DCS measurements is currently 0.01 nm but it can be improved by several orders of magnitude with carrier envelope offset stabilization to improve the averaging process [2].



Fig. 1: Photo from a field measurement at night from the physics building of Graz University of Technology to a neighbouring building.



Fig. 2: Preliminary laboratory measurements of a nitrogen dioxide gas cell filled with 500 mbar NO₂ /air mixture (NO₂ concentration 500 ppm). Transmitted intensity of NO₂, measured with OSA (green data, linearly shifted for better comparison), 15 averaged single DCS transmission spectra (orange line and right axis) compared with adapted data from 2004, Nizkorodov [6] (blue line).

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Abstract

We present a unique setup consisting of a doubly resonant Bow–Tie Cavity, both at 780 and 1560 nm which permits to load and cool atoms inside a deep optical dipole trap using gray molasses. High–finesse at 780 nm in turn allows for collective strong atom-cavity coupling via frequency doubling of the 1560 nm source which is locked to the cavity resonance. Interactions between counter-propagating modes and BECs could reveal the existence of different phases of matter which we would like to explore in the future.



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Abstract

Accurate knowledge of the absorption by a gas mixture of CO_2 and water is very important for planetary sciences, as it enables a better modeling of the atmospheres of rocky planets, e.g. improving our understanding of the early climate of Mars or why Venus and the Earth have evolved so differently. The absorption spectrum of such a gas mixture includes monomer lines (localized resonances whose areas are proportional to the density of each species) and binary absorption features varying more smoothly with frequency: self-continuum absorption, proportional to the squared density, and "crossed" absorption involving both species and scaling as the density product $\rho_{CO2}\rho_{H2O}$. We used highly sensitive spectroscopy techniques (CRDS and OFCEAS) to measure the absorption spectrum of H₂O+CO₂ gas mixtures in various spectral regions situated in transparency windows where the monomer absorption of both species is weak (1.5-1.53 µm, 1.68-1.75 µm, 2.06 µm, 2.2-2.35 µm, 3.5 µm). For both water and CO₂, the monomer lines, modeled using HITRAN parameters, and the self-continuum absorption, calculated from literature values or measured in dedicated experiments, were subtracted from the measured absorption. The obtained "crossed binary absorption" coefficients are compared to the only available empirical model based on far wings of line shape profiles scaled by γ -factors [1]. A broad absorption peak centered at about 6000 cm⁻¹ was attributed to a collision-induced simultaneous transition of H₂O and CO₂ through the v_1 and v_3 modes, respectively. This assignment was confirmed using humidified ¹³CO₂, where a similar band was observed at a lower wavenumber due to the isotopic spectral shift of the v₃ band of CO₂. Classical molecular dynamics simulations (CMDS) of the considered collision-induced absorption were conducted and are found in good agreement with the experiment [2].

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Dust climatology from NOMAD UVIS channel

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Introduction:

Aerosols present in the atmosphere of Mars have a major effect on it. They are mainly composed of dust, water ice or CO_2 ice. Dust is confined to lower altitudes during the aphelion season and can reach higher altitudes during the perihelion, especially during dust storms that frequently arise on Mars. These storms can sometime grow up to cover the entire planet and are then called a global dust storm.

The NOMAD ("Nadir and Occultation for MArs Discovery") spectrometer suite on board the ExoMars Trace Gas Orbiter (TGO) is composed of three spectrometers, two in IR (LNO and SO) and one in UV-visible (UVIS). The UVIS channel spectral range extends from 200nm to 650nm with a spectral resolution about 1.5nm. UVIS can operate in nadir and occultation modes. In this work, we use observations taken in occultation mode to investigate the vertical distribution of aerosols.

Method:

To compute aerosol's extinction, from the transmittances of UVIS. We use first the ASIMUT code (Vandaele, et al., 2006.) to make a fit on ozone and Rayleigh scattering and then subtract them from the original transmittances. In the result should remain only the background of the spectra. Extinction can be computed from the transmittance after subtraction of ASIMUT's fit using the formula from (Wilquet et al., 2012): $\tau = -\ln(T) = \ln(I/I_0)$ and $\beta_n(\lambda) = \frac{\tau - \sum_{i=1}^{N-1} dz \beta_i(\lambda, z)}{dz_n}$. With τ the optical depth , T the transmittance, I the solar irradiance attenuated through the atmosphere and I₀ the reference irradiance of the solar spectrum outside the atmosphere. β represents the extinction and N the number of layer above the current layer n. λ represents the wavelength and dZ represents the pathlength of light through the atmosphere to the point and i represent the upper layer.

The extinction is fitted using the refractive index for Mars dust from (Wolff et al., 2009). The extinction efficiency, Q_{ext} is computed using a Mie code (Bohren, et al., 1998) with a log normal size distribution. Given the Q_{ext} for each size distribution, the number density "n" is fitted using the relation $\beta = n * Q_{ext}$, with β the extinction derived from the UVIS spectra. The fit is made for each effective radius and each standard deviation. The best fit finally selected will be the one with the smallest reduced chi square. The number density error is calcultated based on the extinction error with a Monte Carlo algorithm.

Results:

Using only the spectral range of UVIS, the dust, water ice and CO_2 ice cannot be differentiated because the three aerosols have similar spectral features in the UV-visible. Therefore, only dust will be assumed in this work. Detection of CO_2 and water ice will be investigated in a future work. Dust in the Martian atmosphere is sensitive to seasonal variations. During perihelion (LS 250), the atmosphere of Mars becomes warmer, and dust can be transported to higher altitudes. In the contrary, at the aphelion (LS 70) dust remains confined at lower altitudes.



Figure 1: Dust vertical extinction profiles versus solar longitude for Mars year 34 to 36

We can see on Figure 4 that at the perihelion dust is present at higher altitudes and the extinction is stronger than during the aphelion. In this work we will further compare the vertical distribution of dust for Mars year 34 (with global dust storm) and Mars year 35 (without global dust strom), as well as latitudinal variations.

Acknowledgements:

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Spectroscopic signatures of C60 and its derivative in the gas phase

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Abstract

Although discovered a hundred years ago [1], the Diffuse Interstellar Bands (DIBs) remain mysterious in astrochemistry. Their origin and nature is still an open question, and several candidates are under investigation. Best candidates are gas phase carbon with an high number of atoms like fullerenes (C60 and its derivatives). For more than 10 years, C60 has been observed around various astronomical objects such as planetary nebulae, diffuse clouds and star forming regions. The challenge consists in measuring its gas phase spectrum, on Earth, over a wide range of wavelengths. This challenge was taken up by P. Bryan Changala [2] in 2019, who succeeded in measuring the fundamental vibrational absorption band around 8.5 microns. But many spectral regions remain to be explored.

The CRDS [3] technique is an highly sensitive optical technique which consists in injecting photons into a high finesse optical cavity composed of very high reflectivity mirrors (R>99.95%). Thanks to an Acousto-Optic Modulator (AOM), it is possible to interrupt the photon injection and mesure the exponential light decay at cavity output. The photon lifetime depends on the reflectivity of the mirrors (considered constant), together with intracavity losses arising from an absorbing gas. Measuring these losses as a function of wavelength provides the absorption spectrum of the considered gas.

In the interstellar medium, C60 is extremely cold (a few K) and only its fundamental vibrational level is populated. On earth, C60 is a solid powder up to several hundreds of K. Reaching such low thermal condition in a cell is thus very challenging. The best option to date appears to be the buffer gas cooling technique [4], which makes it possible to cool the C60 molecules well below the first vibrationnally excited states (<150 K) through collisions with a cold buffer gas (cold Argon at 77 K). A simulation shows that after 55 collisions with cold Argon buffer gas, the C60 is cooled down to less than 5% of the buffer temperature.

By combining the cooling capability of buffer gas cooling and the extreme sensitivity of the CRDS, routinely aquiring C60 absorption spectrum becomes realistic. Initially the spectral region around 8.5 microns will be probed, in order to validate the cooling technique and serve the purpose of tuning experimental conditions. In parallel, measurements with a supersonic jet cooling system will be performed at the Institute of Physics in Rennes, taking benefits of these developments.

Finally, after validation of the various experimental devices, spectral zones beyond the middle infrared will be explored.



Figure 1: Schematic representation of the expected experimental device.

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Dual Comb Spectroscopy in the Ultraviolet Spectral Region

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Abstract

Dual comb (DC) spectroscopy enables high resolution and short acquisition time simultaneously and substantiated its potential for molecular fingerprinting. So far, DC techniques operate mainly in the infrared spectral region due to the availability of suitable laser sources. However, the visible and especially the ultraviolet (UV) spectral regions remain underexplored [1]. Many atmospheric and astrophysically relevant gases, e.g. formaldehyde and iodomethane, exhibit strong and congested absorption features in the wavelength range 50-550 nm [2,3]. For example, formaldehyde is important in cities with smog issues and exposes a plethora of narrow absorption lines around 340 nm with an absorption cross section of up to 0.2 Mb [4]. This project aims at developing the world's first UV DC spectrometer allowing the investigation of these gases and their electronic transitions at high resolution [5].

Here, we utilize two frequency comb outputs amplified by a pulse picking chirped pulse amplifier scheme at MHz repetition rate and subsequently reduce the central wavelength by nonlinear frequency up conversion. In a first step, we employ second and third harmonic generation in nonlinear crystals to approach the visible and near UV, respectively. The efficiency of nonlinear frequency conversion scales inversely with the pulse duration of the driving pulse. Therefore, the output power of the upconverted light can be increased by temporal compression of the fundamental pulses. This is achieved by spectral broadening in an all solid-state Herriott-type multi-pass cell (MPC). The highly-reflective mirrors of the MPC operate in the negative dispersion regime to compensate the group delay dispersion introduced by the broadening medium and air [6]. Besides the increased conversion efficiency, the broadened spectrum can be used to tune the center wavelength of the generated harmonic light by choosing different phase-matching angles. We then superpose the upconverted light of both lasers and send it through a gas cell containing the sample gas. After this, we record the time-domain interferogram using a fast photodetector and an oscilloscope with sufficient bandwidth, from which we can retrieve spectral information of the sample after Fourier transformation.

We achieved a spectral bandwidth of 997-1055 nm at the -10 dB level using the multi-pass geometry with a 10 MHz repetition rate seed laser (see Fig. 1). The broadened spectrum supports pulse durations down to 62 fs and at the same time featuring a high power transmission of up to 85 %. This enables high peak intensities for efficient nonlinear frequency conversion. Figure 2 depicts the generated third harmonic spectrum using two beta barium borate crystals. It covers one branch of the formaldehyde absorption spectrum. Utilizing two such near UV light beams can be employed for high-resolution DC spectroscopy of gaseous formaldehyde. This DC spectroscopy scheme will improve the resolution of state-of-the-art measurements, achieving GHz resolution, by more than one order of magnitude [7]. It will facilitate MHz spectral resolution at an acquisition time of few seconds.

In the future, we will use our first near UV DC spectrometer to perform absorption spectroscopy in the UV region with unprecedented resolution to investigate the transition line width and the absolute absorption cross section of formaldehyde. We will further develop a high-power, few-fs pulse duration laser source at MHz repetition rate and employ high-harmonic generation in a gas jet for experiments deeper in the UV (λ <300 nm). This spectrometric system will be able to investigate important gas species of earth atmospheric relevance. It will improve our understanding of photochemical reactions and their electron dynamics that play an essential part in chemical processes induced by solar UV radiation. Those insights could contribute to the development of abatement strategies of the global climate change.



Fig. 1: MPC pulse compression. (A) MPC output spectrum at different amplifier pump currents using a 10 MHz repetition rate seed laser. The blue curve has similar bandwidth to the seed spectrum. The red curve spans from 997-1055 nm at the -10 dB level and supports pulse durations down to 62 fs. (B) Measured autocorrelation curve for 35 A pump current (black) and theoretical sech²-pulse with 62 fs pulse duration (orange) at an input pulse duration of 250 fs.



Fig. 2: Ultraviolet dual-comb absorption spectroscopy experiment. Left y-axis: Absorption Cross Section of formaldehyde (Data adapted from [4]). Right y-axis: Near ultraviolet spectrum generated via third harmonic generation in nonlinear crystals. The generated spectrum covers one branch of the formaldehyde absorption spectrum and can be tuned via the phase-matching angle of the crystals.

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Rotational Spectrum of Methylamine in the First and Second Excited Torsional States

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Abstract

We present the assignment of the pure rotational transitions in first ($v_{i}=1$) and second ($v_{i}=2$) excited torsional states of methylamine. The assignments were made based on new measurements of the rotational spectrum of methylamine in the frequency range 150 to 1520 GHz using the Lille THz spectrometer. The methylamine exhibits two large amplitude motions. The methyl group CH_3 group is associated with internal-rotation large-amplitude motion and amine group NH₂ group is associated with inversion large-amplitude motion. The analysis is based on the "hybrid" model [1] that can fit rotational levels in molecules with two large-amplitude motions. The dataset used to calculate the predictions already contains around 3000 MW and 26848 FIR transitions of $v_t = 0$, 1 and 2 of CH₃NH₂, which are fit to a weighted standard deviation of 1.75 using 102 parameters. In the THz spectra, the rotational transitions of v_t =1-1 state were easily located within few MHz vicinity of their predicted positions. The assignment of the rotational transitions in $v_t=2-2$ state was more complicated due to somewhat higher shifts between predicted and measured frequencies. In this case, to confirm the assignments we used Loomis-Wood type diagrams. In total, more than 3500 new rotational transitions of methylamine in v_t =1-1 and around 2200 new rotational transitions of methylamine in v_t =2-2 states were assigned and added to the existing dataset. The latest results of the global fitting of MW and FIR data will be presented.

Acknowledgments

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Universal PAH fragmentation: Searching for Universal Molecular Building Blocks

The chemical link between the diffuse interstellar medium and molecular clouds and planetary systems is not well characterized. This is in part because the century old mystery of the Diffuse Interstellar Bands (DIBs) is still unsolved, as it could hold the keys to unlocking which are the most important molecules capable of surviving in the diffuse interstellar medium for aeons. By studying the radiation-induced fragmentation of several PAH species of different symmetry and different sizes, this work shows that PAHs appear to follow very similar fragmentation pathways, giving rise to ionized magic number carbon clusters. These could be ideal candidates as products of PAH destruction in PDRs and other astrophysical regions that ungergo significant energetic processing. If this scenario is taken to the extreme, these clusters might survive in the diffuse interstellar medium for a long enough period to form the first chemical seeds of molecular clouds and planetary systems.

The effects of methyl internal rotations and ¹⁴N quadrupole coupling in 4methyl-5-vinylthiazole and 2,4-dimethylthiazole investigated by microwave spectroscopy and quantum chemical calculations

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Abstract

Thiazoles and its derivatives are five-membered heterocyclic compounds that contain a sulfur atom and a nitrogen atom in the ring. They are characterized by their aromatic ring with π -electron delocalization. Thiazoles form one of the most important classes of the five-membered heterocycles. Their molecular characterizations are therefore of particular interest. Thiazoles derivatives containing methyl groups are important in astrophysical observations for the detection of aromatic heterocycles in the interstellar medium. The methyl torsional barriers are influenced by other substituents attached to the thiazole ring. We recorded the microwave spectra of 4-methyl-5-vinylthiazole (MVT) [1] and 2,4-dimethylthiazole (24DMTA) with a molecular jet Fourier transform microwave spectrometer operating from 2 to 26.5 GHz [2]. To support the experimental observations, quantum chemical calculations were carried out. The MVT and 24DMTA spectra have been assigned, including splittings arising from methyl internal rotation and the ¹⁴N quadrupole coupling effects, and analyzed using the program *XIAM* [3,4] and *BELGI* [5-7].



Fig. 1: Molecular structure of 4-methyl-5-vinylthiazole and 2,4-dimethylthiazole.

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Abstract

The study of the vibrational-rotational spectra of the german molecule and the extraction of highprecision spectroscopic information about the characteristics of the spectral lines from experimental data is an urgent problem that has been solved for many years. Namely, until the mid-seventies, there was little progress in our knowledge of the composition of the atmospheres of the solar system's planets. Thanks to the rapid development of earth infrared technologies, many hydrogen-bonded molecular compounds have been discovered in the atmospheres of the solar system's planets, and among all this diversity was the GeH₄ molecule. In particular, the study of Saturn's composition of the atmosphere was carried out based on remote sensing using earth and near-earth telescopes and interplanetary orbital spacecraft. These studies played an important role in studying the chemical composition of the stratosphere and upper layers of the troposphere of Saturn and made it possible to establish the presence of the german molecule and its isotope-substituted modifications ^[1,2]. This molecule was also found in the atmosphere of Jupiter ^[3,4] and a small amount in the atmosphere of Mars ^[5].



Fig. 1. Overview spectra of the $^{72}GeH_4$ and $^{74}GeH_4$ molecules in the region 2350–2750 cm⁻¹

The high-resolution spectra of the ⁷²GeH₄ and ⁷⁴GeH₄ molecules were recorded on a Bruker IFS125 HR Fourier spectrometer with an optical resolution of 0.003 cm⁻¹ (see Fig. 1). The line positions in the range 2350–2750 cm⁻¹ were analyzed for ten interacting vibrational–rotational bands $3v_4$ ($1F_2$, F_1 , $2F_2$), $v_2 + 2v_4$ (1E, F_1 , F_2 , 2E), and $2v_2 + v_4$ ($1F_2$, F_1 , $2F_2$). As a result of the analysis, 1726 and 1924 experimental lines with the maximum quantum number $J^{\text{max}} = 17$ and $J^{\text{max}} = 18$ were identified for ⁷²GeH₄ and ⁷⁴GeH₄, respectively. The obtained data were used in the fitting procedure with the effective Hamiltonian, which made it possible to determine the spectroscopic parameters, namely, the centrifugal distortion parameters, resonance interactions, and tetrahedral splittings. The resulting sets of spectroscopic parameters (35 parameters for ⁷²Ge piece and 37 for ⁷⁴Ge piece) make it possible to reproduce initial experimental line positions with $d_{\text{rms}} = 7.5 \times 10^{-4}$ cm⁻¹ and $d_{\text{rms}} = 7.8 \times 10^{-4}$ cm⁻¹. To illustrate the quality of the obtained results, Fig.2 represents a fragment of the experimental lines.



Fig. 2. A small part of the experimental spectrum of the ⁷²*GeH*⁴ *molecule of the* 3v₄ *band (upper part of the figure). On the bottom chart the corresponding simulated spectral lines of the* 3v₄ *band are shown.*

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All-PM ultrafast fiber laser based on artificial saturable absorber at 1.55 µm

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Abstract

During the more than sixty years since the creation of the first laser in 1960, their enormous potential for applications has been exploited in fundamental scientific research, industry, and biomedicine. Their property to emit a spectrally narrow line that can be targeted to a specific spectral line of the molecule has made laser spectroscopy a prolific part of the spectroscopy. For continuous-wave (CW) lasers, the ability to tune to and within a small range around the absorption line of interest allows the detection of single lines of a given molecule at a time. By the use of electronics driving the laser through a feedback loop, the laser parameters can be controlled. In semiconductor lasers, it is usually accomplished by the modulation of the driving current of the laser diode and the range of control depends on the structure of the cavity [1]. Alternatively, a laser source containing many spectral lines (broad spectrum) can be used. In the time domain, such laser can produce sub picosecond optical pulses, which additionally can have relatively high peak powers in comparison to CW lasers. This allows such sources to be used for timeresolved spectroscopic measurements [2], and the high peak power can be exploited in laser-induced breakdown spectroscopy [3]. Broadband detection schemes incorporating broadband light sources such as Fourier-transform spectroscopy, dual-comb spectroscopy, Vernier cavity filtering, and virtually imaged phased array have been proposed to date [4]. Most often, a mode-locked laser that is stabilized to an external source constituting an optical frequency comb (OFC) is employed for this task. As a phase-locking element between longitudinal modes, such lasers uses saturable absorbers. These absorbers are characterized by a directly proportional increase in the transmittance of light through them as its intensity increases [5]. For spectroscopy applications, many aspects of the laser itself translate into measurement results. Especially in precision and high-resolution measurements, it is important to pay attention to how stable the source is. To meet the challenges posed by spectroscopy, the development of ultrafast lasers is breaking new records and constantly looking for optimal solutions for a given application [6,7]. The stability of the pulsed laser output depends on many factors but the use of optical fibers that maintain the polarization state provides a linearly polarized output beam, resistance to bending, shock, and vibrations. The use of mode-locked fiber lasers that employ birefringent fibers may be one of the key elements in the journey toward an ideal source for broadand spectra research, but inherent noise of the laser is mostly raised from saturable absorber itself [8]. To minimize intrinsic noise, the use of artificial saturable absorbers has been proposed, whose response time is much faster than natural saturable absorbers, making their noise characteristics much more affordable [9]. One such absorber is the nonlinear amplifying loop mirror (NALM) which is taking advantages of nonlinear effects and does not require any other materials other than optical fibers themselves [10].



Fig. 1: Schematic of the all-fiber femtosecond laser (a). Measured optical spectra from three outputs recorded for a repetition rate of 43.74 MHz (b).

We present the design of an all-fiber femtosecond laser operating at a central wavelength of 1560 nm. As a saturable absorber, we used a system based on a nonlinear Sagnac interferometer along with a reflective phase shifter that shifts the curve of the saturable absorber to facilitate self-pulsed operation [7,11,12]. The replacement of the volumetric phase shifter by an integrated fiber optic component results in reduced system dimensions and improves system stability to environmental conditions. Pulse generation occurs due to the interference at the 50/50 coupler of two beams propagating in opposite directions, which experience different nonlinear phase shifts due to the asymmetric arrangement of the active fiber. In the loop part of the laser, we placed additional couplers with different values (e. g. 70/30) of the splitting ratio, which allows for monitoring the pulses propagating inside the laser cavity (outputs B and C). The radiation from such a laser can be shifted from about 1.55 μ m to other wavelengths through the generation of dispersive waves (blueshift) or Raman shift (redshift) [13,14]. After amplification, these can be used to generate a supercontinuum in a nonlinear fiber [15], to be used as a pump for nonlinear conversion [16].

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ULTRA-STABLE COMPACT AND TRANSPORTABLE LASER FOR THE GROUND TESTS OF THE LISA PAYLOAD

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Abstract

The LISA (Light Interferometer Space Antenna) mission aims to detect gravitational waves in the 0.1mHz to 1Hz range, with a strain sensitivity $\Delta L/L\approx 10-21$. With the Time Delay Interferometry, this translates to a light source with a frequency stability $\Delta f/f\approx 0.5*10-13\tau-1/2$ or a noise level under 30Hz/ \sqrt{Hz} . The nominal solution for the light source is a 1064nm Nd:YAG laser locked on an ultra-stable cavity which has proven itself with the Grace Follow On mission. Another solution, compact, monolithic and that does not require realignments is needed for the assembly, integration, verification, and testing (AIVT) of the mission payload. We propose a pair of Nd:YAG lasers phased locked on each other, with the master phased locked on a reference laser, as shown in Figure 1. The reference is a Telecom laser locked by its third harmonic on a reference iodine vapor, using a monolithic spectroscopy Doppler-free setup. The generation of the third harmonic signal used is shown in Figure 2. This setup is based on previous works made at the SYRTE, which used a 1542nm frequency tripled diode laser locked on a 514nm hyperfine transition of the iodine[1]. It has proven to have a frequency stability below the LISA requirements. We use in a simple manner the second harmonic of the master Nd:YAG laser to transfer the frequency stability from the third harmonic of the reference laser[2].



Fig. 1: Full setup to be delivered to the CNES for the AIVT of the LISA mission. THG: Third Harmonic Generation. SHG: Second Harmonic Generation.



Fig. 2: Principle of the Third Harmonic Generation.

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Introduction

Silicon tetrafluoride (SiF₄) is interesting from both a practical and theoretical point of views. It is used in electronics and semiconductor industry, as well as for silicon cleaning and etching. This molecule is formed during volcanic activity [1] and, as this gas is highly toxic, releasing extremely poisonous hydrogen fluoride (HF) upon contact with hot water and acids, it is necessary to be able to detect this compound in the atmosphere with high accuracy. Thus, a better knowledge of spectroscopic parameters is needed for this molecule in order to derive accurate concentrations. From the theoretical point of view, the SiF₄ molecule is a spherical top molecule (STM), and, along with other molecules, is a prototype in the study of many more complex molecules. The particular features of STM, which were initially seen as difficulties to be removed, became the motivation that led to original modelling methods applicable to a wide range of spectroscopic problems.

Theoretical Background

As already mentioned in one of the previous works [2], devoted to this molecule, silicon tetrafluoride is a tetrahedral spherical top molecule with T_d point symmetry group and possesses four normal modes of vibration: v_1 (A_1 symmetry, 800.7 cm⁻¹), v_2 (E symmetry, 264.2 cm⁻¹), v_3 and v_4 (F_2 symmetry, 1031.5 and 388.4 cm⁻¹, respectively). Due to the high symmetry of the molecule, we use the tensorial formalism and group theory methods developed in the Dijon group [3]. Different aspects of this formalism application to the XY₄ (T_d –symmetry) molecules were discussed in the spectroscopic literature many times. For this reason, only a brief theoretical basis of our present study is given in this section.

As we know from general vibrational-rotational theory (see for example [3-4]), the Hamiltonian for polyatomic molecules can be reduced to such a free Hamiltonian, in a broader sense or a set of effective mechanisms. In our case, when the molecule has high symmetry, the general equation can then be rewritten in a symmetrized form:

$$H^{\nu i b. -rot.} = \sum_{\nu \gamma, \nu' \gamma'} \sum_{n \Gamma} \left[(|\nu \gamma\rangle \otimes \langle \nu' \gamma'|)^{n\Gamma} \otimes H^{n\Gamma}_{\nu \gamma, \nu' \gamma'} \right]^{A_1} = \sum_{\nu \gamma, \nu' \gamma'} \sum_{n \Gamma} \sum_{\Omega K} \left[(|\nu \gamma\rangle \otimes \langle \nu' \gamma'|)^{n\Gamma} \otimes R^{\Omega(K, n\Gamma)} \right]^{A_1} Y^{\Omega(K, n\Gamma)}_{\nu \gamma, \nu' \gamma'}, \tag{1}$$

where $|\upsilon\gamma\rangle$ is symmetrized oscillatory function; γ are types of function symmetry; $R^{\Omega(K,n\Gamma)}$ is symmetrized rotational operator, and Ω is the degree of rotation operators $J_{\alpha}(\alpha = x, y, z)$ for each operator R; K is the rank of this operator; Γ is symmetry in a point symmetry group T_d , and n marks out the different operators $R^{\Omega(K,n\Gamma)}$, having the same meaning Ω , K and Γ . The symbol \otimes denotes the tensor product, and $Y_{\nu\gamma,\nu'\gamma'}^{\Omega(K,n\Gamma)}$ values include spectroscopic parameters of different types (for example, the Fermi-type interactions and Coriolis–type interactions). The rotational operators $R^{\Omega(K,n\Gamma)}$, symmetrized in the group T_d , are defined as follows:

$$R^{\Omega(K,n\Gamma)} = \sum_{m}^{(K)} G^{m}_{n\Gamma\sigma} R^{\Omega(K)}_{m}, \qquad (2)$$

where the operators $R^{\Omega(K,n\Gamma)}$ are so-called irreducible rotational operators symmetrized with respect to a complete orthogonal group.

Analysis on Spectra

Our investigation includes four combination bands, namely v_1+v_3 , v_1+v_4 , v_2+v_3 and v_2+v_4 . For this we used new spectra recorded on the AILES Beamline of the SOLEIL Synchrotron facility. The data were obtained using a cryogenic long path cell regulated at 163 K temperature along the entire optical path, set up to 93 m.

At the initial stage of solving the inverse spectroscopic problem the values of the fundamental band parameters from [5] have been taken as the reference values of the effective Hamiltonian constants. For each band, between 1100 and more than 2900 lines could be assigned for *J* values higher than 55 (up to 82 for v_1+v_3) and this leads to a determination of accurate molecular parameters with root mean square deviations for line positions of a few 10⁻⁴ cm⁻¹. In the case of the v_1+v_3 band, the ²⁹SiF₄ and ³⁰SiF₄ isotopologues could also be assigned and fitted (Fig. 1). These results will allow the calculation of hot bands like $v_3+v_2-v_2$, etc., in the regions of strong atmospheric absorption.



Fig. 1: Overview of the $v_1 + v_3$ spectrum, compared to the simulation for all isotopologues. The insert details a part of the Q branch region.

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Off-axis integrated cavity output spectroscopy enhanced Faraday rotation approach for measurements of total OH reactivity

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Abstract

OH radical is known as a major atmospheric oxidant playing a central role in the degradation of trace gases and pollutants in the atmosphere [1]. Measurement of total OH reactivity is crucial for understanding of the atmospheric oxidation capacity. In this paper, we report on the development of an optical instrument for interference-free measurement of OH radicals in laboratory based on a combination of off-axis integrated cavity output spectroscopy (OA-ICOS) and Faraday Rotation Spectroscopy (FRS) operating at 2.8 μ m (OA-ICOS-FRS). OH radical concentrations in the range of 10^{12} molecule.cm⁻³ were generated by continuous microwave discharge of water vapor at low pressure and monitored by the OA-ICOS-FRS instrument, providing a limit of detection of ~ 10^{10} molecule.cm⁻³ within an integration time of 20 s. The performance of the system was evaluated by the reaction of OH with CH₄. The rate coefficient $k_{OH-CH4}=(4.2\pm0.4)\times10^{-15}$ cm³.molecule⁻¹.s⁻¹ was obtained by measuring the decay time of the OA-ICOS-FRS signal during the reaction time and is in good agreement with values reported in the literature. The developed instrument provides a suitable analytical tool for study of total OH reactivity in simulation chamber [2,3].

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The C_2H_2 molecule with its two isomers acetylene (HCCH) and vinylidene (H₂CC) is one of the simplest systems for studying isomeric reactions involving hydrogen. In the past decades, their neutral, cationic and anionic species have been subject to theoretical and experimental investigations.

For the anion, the state with lowest total energy has the vinylidene structure, H_2CC^- , and a vertical electron affinity of about 0.5 eV. This state lies 1.5 eV above the lowest neutral level of the acetylene structure, opening up the principal possibility that isomerization linked with electron emission could intrinsically limit the lifetime of the vinylidene anion.

Indeed, an experiment at a room-temperature storage ring indicated a finite intrinsic lifetime of about 110 s [1]. This experiment compared the ion beam decays of H_2CC^- and a lighter reference ion for which an isomerization decay path cannot exist. Both beam lifetimes $(1/k \sim 10 \text{ s})$ were limited by residual-gas collisions and the small difference of the decay rates was ascribed to the intrinsic H_2CC^- lifetime.

To re-address this topic with a state-of-the-art experimental technique, we employed the electrostatic Cryogenic Storage Ring (CSR) at the Max-Planck-Institut für Kernphysik in Heidelberg [2] for measuring the ground-state H_2CC^- lifetime.

CSR provides a cryogenic environment with strongly suppressed blackbody radiation and extremely low residual gas density, allowing to store and observe fast ion beams over time scales on the order of an hour. The measured rest-gas induced neutralization rates indicated that even these long lifetimes are not limited by residual gas collisions. Hence, the storage-ring induced loss rates should be largely independent of the ion beam composition in our experiment.

We used photodetachment to monitor the decays of simultaneously stored H_2CC^- and CN^- ion beams. Here, CN^- served as a stable reference ion with nearly identical mass-to-charge ratio. Comparing the two decays at storage times up to 3000 s allowed us to cancel a large part of the storagering induced losses. Also, by using the novel isochronous mass spectrometry method [3] we were able to prove that no other contaminant ions could significantly affect the observed lifetimes.

We present preliminary results which suggest that the intrinsic lifetime of the ground-state of H_2CC^- is several 10³ s, i.e., at least an order of magnitude longer than assumed previously.

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Abstract

The study of cooling dynamics and ground state properties of molecular ions is one of many research goals at the Cryogenic Storage Ring (CSR) at the Max-Planck-Institut für Kernphysik in Heidelberg. The CSR is a fully electrostatic storage ring, which can be cooled down to a few kelvin and reaches residual gas densities down to 100 cm⁻³ [1]. Thus, the ring provides a unique research environment enabling the study of gas-phase ion species in a very low radiation field and almost free of collisional background.

Here we present investigations of the carbon-based molecule C_4O , which is predicted to be observable in interstellar clouds [2]. Its detection requires a detailed knowledge of the anion's vibronic structure. Past studies of this molecule have left open questions about its geometry as well as its electron affinity. A previous measurement of photon absorption properties of C_4O in a neon matrix revealed multiple absorption resonances attributed to vibronic transitions [3]. For our measurement internally hot C_4O ions were produced in a sputter source and injected into the CSR. They were probed with different photon energies, using a pulsed OPO laser at various storage times to monitor the evolution of their internal excitations. Neutral and charged fragments were measured in coincidence by two detectors.

The results include resonant fragmentation ($C_4O^{-} + hv \rightarrow C_3^{-} + CO$) in the photon energy region of about 21300 cm⁻¹ to 29000 cm⁻¹. The resonance curves exhibit changes in shape and height attributed to cooling dynamics of the anions inside the CSR. One feature is attributed to the radiative cooling of a vibrational hot band. Furthermore, the possible onset of the electron detachment channel is visible around 29 000 cm⁻¹. We will present our experimental results together with a detailed theoretical investigation of the observed features. In particular, the molecule's geometry and vibronic structure were calculated, revealing that both initial and final electronic state of the observed transitions suffer from a Renner-Teller interaction.



Fig. 1: Coincidence events for the process: $C_4O^- + hv \rightarrow C_3^- + CO$ as a function of photon energy for different storage times in the energy photon region 22400 cm⁻¹ to 25000 cm⁻¹.

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Laser spectroscopy of CdAr van der Waals complex: a shape of the double – well lowest – lying Rydberg state

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Abstract

It has long been known that the $E^{3}\Sigma_{1}^{+}(6^{3}S_{1})$, the lowest Rydberg state potential of CdAr van der Waals complex possesses a double-well structure (Fig 1a) [1]. However, until now, only the inner well (E_{in}) has been fully characterized [2], whereas parameters of the shallow outer well (E_{out}) and the potential barrier (E_b) were only estimated [3] or calculated [4], respectively.

In this study, we present experimentally determined shape of the $E^{3}\Sigma_{1}^{+}$ - state potential barrier and the outer well bond length. In the experiment, CdAr complexes are cooled in a supersonic expansion beam to their lowest ground-state vibrational levels and then excited from the ground state in optical-optical double resonance (OODR) process (Fig. 1a). Next, LIF excitation spectra of the $E^{3}\Sigma_{1}^{+} \leftarrow B^{3}\Sigma_{1}^{+}(5^{3}P_{1})$ (v'') transitions consisting of both vibrational bound \leftarrow bound (for v'' = 1-4) and free \leftarrow bound (for v'' = 0-4) parts are recorded (Fig. 1b). Having had the intermediate $B^{3}\Sigma_{1}^{+}$ -state potential well-characterized, the information on the outer well bond length was obtained from the former, whereas the potential barrier shape was modelled from the latter.

In conjunction with our previous determination of the shape of the $E^{3}\Sigma^{+}_{1in}$ - state potential using inverted perturbation approach (IPA) method [3], a consistent and reliable potential energy curve (PEC) of the whole $E^{3}\Sigma^{+}_{1}(6^{3}S_{1})$ state in CdAr complex was derived experimentally for the first time.



Fig. 1: a) PECs and transitions used in the experiment with OODR scheme. b) Example bound \leftarrow bound (red) and free \leftarrow bound (blue) spectra of the $B^{3}\Sigma_{1}^{+} \leftarrow X^{1}\Sigma_{0^{+}}(5^{1}S_{0})$ (on the right) and $E^{3}\Sigma_{1}^{+}$ out $\leftarrow B^{3}\Sigma_{1}^{+}$ (on the left) transitions.

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Microwave Spectroscopic and Quantum Chemical Investigations of 2,5-Dimethylfluorobenzene

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Abstract

A phenomenon in molecular physics is the large amplitude motion of methyl groups in isolated molecules. The internal rotation of methyl groups can be used to detect molecular structures.^[1] The surrounding steric and electronic environment of the methyl group affects the methyl torsional barrier. A pulsed molecular jet Fourier transform microwave spectrometer in the frequency range 2 GHz to 26.5 GHz were used to study the organic molecule 2,5-dimethylfluorobenzene. The internal rotations of two inequivalent methyl groups with relatively low torsional barriers cause all rotational transitions to split into quartets, resulting in separations of hundreds of megahertz in the microwave spectrum. Spectral analysis and modeling of the observed splittings using the programs *XIAM* ^[2] and *BELGI-C_s-2tops* ^[3] allow us to access the values of the torsional barriers. The experimental results were compared with those calculated from quantum chemistry.

Acknowledgments

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Optical frequency comb in mid-infrared for laser spectroscopy application

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Abstract

Optical frequency combs are ideal laser sources for molecular spectroscopy, with their broad optical spectrum, high-brightness, and possible wavelength tunability [1]. Detection of most molecules requires a source that covers the mid-infrared spectral range, where strong fundamental vibrational transitions are present [2]. In this region, there is a lack of direct and simultaneously broadband laser sources. The most common solution is to use nonlinear optical processes to convert the radiation from near-IR to mid-IR. For this purpose, optical parametric oscillators (OPOs) or difference frequency generation (DFG) are widely used.

The DFG process is based on the interaction of two input beams (pump and signal beam) in a material with high nonlinearity, resulting in the generation of a third beam (idler). The idler frequency equals the difference between the two input beams' frequencies. The DFG approach does not require a cavity (in contrast to OPOs) and has a passive cancellation of the carrier-envelope offset frequency (f_{CEO}), making it an easy-to-implement system that does not need f_{CEO} stabilization. Broadband detection schemes compatible with mid-IR comb sources include, e.g. Fourier-transform spectroscopy [3] or Vernier cavity filtering [4].



Fig. 1: (a) The setup for difference frequency generation (HWP – half-wave plate; PBS – polarizing beam splitter, HNLF – highly nonlinear fiber). (b) The optical spectra of the frequency comb in the mid-IR generated through the DFG process for different polling periods of the crystal, together with the average output power (black stars).

The heart of the whole setup, pictured in Fig. 1(a), is a polarization-maintaining (PM), modelocked ytterbium-doped fiber laser, which pulses are then amplified in the gain-managed nonlinear fiber amplifier [5]. The central wavelength of the pulse is 1078 nm, with a width of 67 nm. The pulse duration is 51 fs, and the average power equals 2.85 W, which corresponds to the pulse energy of 20.7 nJ and peak power of 406 kW.

After amplification, the signal was divided into two parts, the "pump" arm and the "signal" arm. In the "signal" arm, a nonlinear process called soliton self-frequency shift (SSFS) in a highly nonlinear fiber (HNLF) was used to redshift the wavelength of the pulse. In the "pump" arm, a delay line was placed to equalize the optical path in both arms. The pulses from both arms were combined with a dichroic mirror and focused into a periodically poled lithium niobate (PLLN) crystal. As a result of the DFG process, a coherent mid-IR idler was generated. The generated spectra for different polling periods are pictured in Fig. 1(b).

The presented setup allows obtaining a spectrum in the range of 3.5-5 μ m with a maximum average power of 19.5 mW for the central wavelength of 4010 nm. The generated mid-IR optical frequency comb source is inherently f_{ceo}-free and can be used in laser-based gas sensors requiring stable carrier-envelope offset.

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Hyperspectral analysis of the contaminants on the surface of Ganymede

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Abstract

Ganymede, one of the moons of Jupiter and the largest in the Solar System, presents a surface characterized by a complex tectonic activity. The surface of the satellite is covered by two types of terrains, the dark and the bright ones. The dark terrains are the older one. They are covered by a mixture of ice-silicate minerals that possibly came from a past cryovolcanism associated with an extrusion of material through fissures and fractures. Dark terrains are locally dislocated by wedge-shaped areas of bright terrain. The emplacement of these bright terrains could be related to extensional deformation and extrusion of cryovolcanism in extensional context, similar to terrestrial rifts on Earth. The bright terrains, composed by silicate-free ice, are shaped by linear topographical depressions called grooves. The water lava flooded and down faulted the ancient dark terrain causing a resurfaced and tectonically deformed bright terrain so called chaotic terrains. The density of impact craters is less than in the dark terrain indicating they are younger.

Spectral data from the Near Infrared Mapping Spectrometer (NIMS) instrument onboard the Galileo mission show the existence of hydrated salty material on bright terrains. The origin of these hydrated salts could be associated with the internal geodynamic activity of Ganymede. The water ice at the surface of bright terrains results from the fusion of the ice shell or from the ocean that exists under this shell. Water lave migrated through the ice shell to the surface along fractures and faults visible in the bright terrain. Some of the hydrated salt minerals detected are $MgSO_4$ and Na_2SO_4 . Those minerals are detected in chaotic terrains. Water ice detections are concentrated in the polar regions. The NIMS data and the ground-based spectrums also show evidence of non-water ice material different from hydrated salts. The composition of this material is not clear.

Here we present an analysis of the recent hyperspectral IR data that have been acquired on Ganymede by Juno mission. The digital spectral data were obtained at the cartography and imaging sciences node of the Planetary Data System (PDS). We used the bands of the image mosaics from the JIRAM experiment onboard the Juno mission, which covers the region in the near infrared, between 2.0 μ m and 5.0 μ m.

The resolution of these data is good enough to map differentially bright and dark terrains. A general map has been drawn from the spectral dataset. This map has been compared to the map of the repartition of bright and dark terrains. In a second time, the IR spectra have been processed in order to find a possible signal of hydrated salts. A map of the possible occurrences of these salts is compared to the distribution of bright and dark terrains. Finally, a specific study has been realized on the largest impact craters of bright and dark terrains in order to evaluate the differences in ice composition between these two kinds of salts.

The spectral analysis was realized using the ISIS software. We performed an evaluation of the quality of the data, applying the radiometric and geometric corrections for detecting any absorption bands. Then we performed the estimation of the PO spectrums and the treatment for detecting the physical parameters, obtaining the classification of the spectral profiles. Later, the extracted spectral profiles were compared with spectral libraries to evaluate the nature of element or molecule responsible for the absorption band.

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Spectroscopic characterization of the metastable $a^3\Pi$ state and of singlet-triplet doorway states of aluminum monofluoride

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Abstract

Aluminum monofluoride (AlF) possesses highly favorable properties for laser cooling, both via the $A^{1}\Pi$ and $a^{3}\Pi$ states [1]. The spin-forbidden $a^{3}\Pi \leftarrow X^{1}\Sigma^{+}$ transition around 367 nm has a recoil limit in the micro Kelvin range. We here report on the spectroscopic characterization of the metastable $a^{3}\Pi$ state of AlF, includung its lifetime measurement [2]. All experiments are carried out using a jet-cooled, pulsed molecular beam and various multi-resonance ionization schemes for ion detection or fluorescence detection.

Determining efficient pathways between the singlet and the triplet manifold of electronic states will be advantageous for future experiments at ultralow temperatures. The lowest rotational levels of the $A^{1}\Pi$, v = 6 and $b^{3}\Sigma^{+}$, v = 5 states of AIF are nearly iso-energetic and interact via spin-orbit coupling [3]. These levels thus have a strongly mixed spin-character and provide a singlet-triplet doorway. We present a hyperfine resolved spectroscopic study of the $A^{1}\Pi$, $v = 6 // b^{3}\Sigma^{+}$, v = 5 perturbed system. From a fit to the observed energies of the hyperfine levels, the fine and hyperfine structure parameters of the coupled states, their relative energies as well as the spin-orbit interaction parameter are determined. The radiative lifetimes of selected hyperfine levels are experimentally determined using time-delayed ionization, Lamb dip spectroscopy and accurate measurements of the transition lineshapes. The measured lifetimes range between 2 and 200 ns, determined by the degree of singlet-triplet mixing for each level.



Figure (1): Overview excitation spectra to the lowest rotational levels of the perturbed $A^{1}\Pi$, $v = 6 //b^{3}\Sigma^{+}$, v = 5 system, recorded via (1+1') REMPI. The spectra originate from single rotational levels in the $a^{3}\Pi$, v = 5 state at energy E_{a} and that are indicated on the right. The spectra are plotted such that the energy level structure in the excited state, shown as grey bars near the top and bottom, can be directly recognized.

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Palm-sized optical sensor of methane based on a mini-multi-pass cell coupling to a quartz tuning fork used as thermal detector

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Abstract

In this work, we report a palm-sized optical sensor based on tunable diode laser absorption spectroscopy (TDLAS). A quartz tuning fork (QTF) was employed as a thermal detector [1] working together with a mini-multi-pass cell (mini-MPC) having a compact dimension of 78 mm × 40 mm × 40 mm [2]. A 1.65 μ m near-infrared distributed feedback (DFB) laser was coupled to this compact gas detection module (GDM) for methane (CH₄) detection [3]. A minimum detection limit (MDL) of 52 ppb was achieved in an integration time of 300 μ s, corresponding to a normalized noise equivalent absorption coefficient (NNEA) of 2.1 × 10⁻⁸ cm⁻¹·W/Hz^{1/2}. A seven-day continuous monitoring of atmospheric CH₄ concentration was implemented to verify the sensor's long-term stability.

Experimental details including theoretical simulation and application demonstration will be discussed and presented.

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Development, test and validation of a new instrument for in-situ isotope analysis

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Abstract

The measurement of the isotopic composition of seawater is a powerful tool to gather information about the conditions of formation, evolution and transport of water as well as seawater salinity and temperature measurement1. Indeed, because physicochemical processes prefer certain isotopologues, the isotopic composition is characteristic of water masses, containing information on their formation condition and their evolution^{2,3}.

Currently, the understanding of the phenomena of melting and isotopy of water in the oceans is quite low, due in particular to the low spatial and temporal resolution of the measurements obtained by discrete sampling of measurements to then analyze the samples in the laboratory.

Here, we present the result of the development of a new in-situ Membrane Inlet Laser Spectroscopy (MILS), figure 1, including its characteristics and the important elements of its performance.



Figure 1: Photography of the instrument. On the top the casing of the tested instrument waterproof to 3000m depth and on the bottom the sensor.

The instrument is currently undergoing optimization, testing and validation in the laboratory. Measurements provided by the instrument, visible on figure 2, are at this point to an accuracy of 0.2‰ for δD and $\delta^{18}O$, with a measurement taken every 4 minutes.



Figure 2: Long term referenced isotopic measurement on miliQ water for 17hours

Its geometry, presented in the figure 3, allows to deploy it from vessels, through boreholes into the ice shelves, and to be integrated in autonomous underwater vehicles (AUVs). The instrument will run on batteries, with an autonomy of ~12h.



The sensor will now be used in the field, notably on campaigns in lakes and in Antarctica on a borehole, to be validate in a first step and to provide data.

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Millimeter-wave emission spectroscopy of radical species

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Abstract

Radical species are often intermediates in interstellar or atmospheric chemical reactions. The relative instability and short lifetime of radical species complicate their laboratory study. At Lille, we developed a jet-cooled instrument coupled with a millimeter-wave emission spectrometer^[1] to study the rotational spectroscopy of radical species. The radicals are produced via discharge chemistry, and immediately stabilized in a supersonic expansion. During this expansion, radicals are rotationally cooled to about 10 K to allow spectroscopy measurements. The emission spectrometer offers a detection method more sensitive than traditional absorption spectroscopy. We present the configuration of the spectrometer, and preliminary result of a successful detection of the CH_2CN radical.

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