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Résumés

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Table des matières

Session 1

chairman : Michaël Rey

Exploring excited state potential energy profile and luminescence properties of uranyl-based complexes by TRLFS and ab initio method

Valérie Vallet[1*], Hanna Oher[1,2], Florent Réal[1], Thomas Vercouter[2], André Severo Pereira Gomes[1], Richard E. Wilson[3]

[1] *Université Lille, CNRS, UMR8523-PhLAM- Physique des Lasers Atomes et Molécules, F-59000 Lille, valerie.vallet@univ-lille.fr*
[2] *DEN-Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France*
[3] *Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne Illinois USA*

Uranyl complexes have been the subject of many research works for fundamental chemistry of actinides, environmental issues, or nuclear fuel cycle processes. The formation of various uranyl complexes, with organic and inorganic ligands in solution must be characterized for a better understanding of U(VI) speciation. As uranyl-ligand interactions and the symmetry of the complexes affect the electronic structure of U(VI) and thus its luminescence properties, time-resolved laser induced fluorescence spectroscopy (TRLFS) is one of the major techniques to characterize U(VI) complexes, with high sensitivity and selectivity. However, most of the relevant systems have complex chemical composition in solution and the identification of each species from spectroscopic data is challenging.

In our study, the synergy between TRLFS and *ab initio*-based interpretation appears as a promising route for complexation data. Luminescence spectra of uranyl complexes in solution show in general a narrow energetical range about 6000 cm^{-1} and we can identify a single electronic transition between the initial and target states with the vibrationally resolved band [1]. The main challenge consists in exploiting a computationally cheap and effective theoretical approach, in a relativistic context, to characterize the main spectral parameters of the ground and luminescent states of symmetrical uranyl compounds (*i.e.* $UO_2Cl_4^{2-}$, $UO_2F_5^{3-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(NO_3)L_2$) with different organic or inorganic counter ions after the photo-excitation. We will illustrate that TD-DFT with the CAM-B3LYP functional is able to provide accurate excitation/emission energies for these systems, together with accurate vibronic progressions allowing the assignment of experimental data.

As a benchmark system serving the purpose of assessing the accuracy of our theoretical protocol, the uranyl tetrachloride $UO_2Cl_4^{2-}$ was selected because of the extensive amount of structural and spectroscopic data available [2]. A good agreement was found between ours and previously obtained theoretical data (structural parameters, orbitals nature, excitation energies) [3]; the final luminescence spectrum is in remarkable agreement with our TRLFS measurements [4]. We will also quantify the effects of organic or inorganic counterions [5, 6], along with that of first-sphere ligands that might perturb the uranyl(VI) moiety.

This work showcases how one can predict vibrationally resolved spectra to assign the recorded TRLFS data, and shed light on the relationship between the uranyl coordination and its luminescence properties.

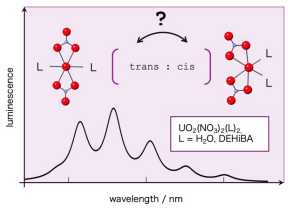

Figure 1. Vibronic spectra of cis and trans-$UO_2(NO_3)_2L_2$

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* correspondant : valerie.vallet@univ-lille.fr

Spectroscopic study of intermolecular interactions between mannose and receptor models

Ander Camiruaga[1], Gildas Goldsztejn[1], Pierre Çarçabal[1*]

[1] *Institut des Sciences Moléculaires d'Orsay, ISMO, UMR8214, Université Paris-Saclay, CNRS, Bat.520, F-91405 Orsay cedex, France*

Carbohydrates (CBH) represent one of the most important families of biomolecules. Beyond their best-known function of energy source in living systems, they act as mediators of molecular recognition processes, carrying molecular information in the so-called "sugar code". Carbohydrate-protein interactions [1,2] are crucial for the development of new drugs addressing selectively their receptors. [3] Among the many possible biomedical applications, one example is the addition of CBHs to photosensitizers (PS) used in PhotoDynamic Therapy (PDT), [4] a highly promising approach for cancer treatment. Monitoring the global interaction between PSs and MRs containing artificial membranes provides key information on affinity and selectivity. However, a precise description of the structural basis of Mannose-MR interplay critically lacks to design PSs with improved selectivity.

To fill this gap, we study the structure of complexes of mannose with phenylalanine (Phe) and alanine (Ala) peptides, with or without a controlled number of water molecules, by means of a combination of mass-resolved conformer selective vibrational spectroscopy and computational methods. Using laser desorption, molecules and aggregates are isolated and formed in a supersonic expansion. The non-covalent interactions that govern the molecular assemblies are characterized by comparing the experimental results with DFT calculations at B3LYP-ED=GD3/cc-pVTZ level. Results obtained will shed light into the multiple interaction preferences of CBH-peptide complexes, specially the complexes formed with few water molecules, which may highlight the role of water in molecular recognition processes in an unprecedented manner, in the isolated phase.

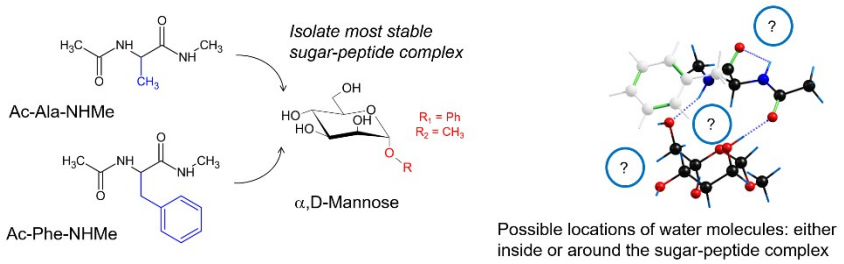

Figure 1 : Scheme of the model system between capped Ala and Phe peptides with α,D-Mannose.

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* correspondant : pierre.carcabal@universite-paris-saclay.fr

Activités de spectroscopie TeraHertz large-bande de gaz et d'aérosols au laboratoire IEMN en collaboration avec le PC2A, le LOA et le LPCA

Jeyan Bichon[1,2], Denis Petitprez[2], Hervé Herbin[3], Arnaud Cuisset[4], Francis Hindle[4], Gaël Mouret[4],Karine Deboudt[4], J.-F. Lampin[1], Romain Peretti[1], Sophie Eliet[1]

[1]Institut d'Electronique, de Microélectronique et Nanotechnologie, Villeneuve d'Ascq
[2]Laboratoire de PhysicoChimie des Processus de Combustion et de l'Atmosphère, Villeneuve d'Ascq,
[3]Laboratoire d'Optique Atmosphérique, Villeneuve d'Ascq,
[4]Laboratoire de PhysicoChimie de l'Atmosphère, Dunkerque

L'institut d'Electronique, Micro-électronique et Nanotechnologies (IEMN) est au coeur d'un tissu régional de laboratoires ayant développé une expertise dans la spectroscopie haute résolution rotationnelle de gaz (LPCA) ainsi qu' en spectroscopie UV-Vis-Infrarouge d'aérosols (PC2A/LOA)
L'IEMN est aujourd'hui à l'initiative de projets de recherche collaboratifs en apportant son expertise complémentaire en spectroscopie TeraHertz (THz) large-bande (200 GHz-5 THz) en domaine temporel (THz-TDS) et traitement de ce signal riche en information.

Concernant l'activité « gaz », à titre d'exemple, la méthode de super-résolution développée à l'IEMN permet une résolution spectrale de la centaine voire quelques dizaines de MHz, dépassant ainsi la limite de résolution annoncée de l'appareil (1,2 GHz). Les premiers travaux réalisés et publiés [1] sur l'ammoniac ont amené à un autre sujet de collaboration qui est l'étude spectroscopique d'halogénures de méthyle et le développement d'un banc pour atteindre des seuils de détection pertinent (de l'ordre du ppb au ppt).

Concernant l'activité « aérosols », nous développons actuellement un banc de remise en suspension de particules couplé à une cellule de spectroscopie THz afin de déterminer les indices complexes de réfraction (ICR) d'aérosols (indices réels et imaginaires) dont les bases de données sont très lacunaires encore dans ce domaine spectral. Pourtant, la connaissance des ICR d'aérosols est cruciale pour les communautés des climatologues, météorologues et sédimentologues.
Notre but est d'obtenir des jeux d'ICR dans des conditions opératoires similaires et sur les mêmes échantillons sur la gamme spectrale la plus large possible (collaboration avec le PC2A et le LOA), allant ainsi de l'UV jusqu'au THz. Les aérosols ciblés (billes de silice, carbonate de calcium, poussières désertiques) ont été caractérisées morphologiquement et chimiquement [2] par SEM-EDX (collaboration avec le LPCA). Ces informations seront très précieuses pour ensuite établir un lien entre propriétés optiques et physico-chimiques de ces particules.

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Laser-Induced Breakdown Spectroscopy for atmospheric monitoring of selected fine and ultrafine particles

O. Sublemontier, M. Briant and C. Alvarez-Ilamas, Université Paris-Saclay, CEA, CNRS, NIMBE, 91191, Gif sur Yvette, France

Air quality monitoring is a major challenge for this decade. One of the most important and difficult issues concerns the monitoring of fine particles (1 µm or less), and in particular ultrafine particles (100 nm or less). In mid-2018, ANSES published a report recommending strengthening the monitoring of ultrafine particles, classified as priority pollutants in the air [1]. In addition, access to the number concentration of fine and ultrafine particles of a given elementary composition is crucial for the following reasons:

- Ultrafine particles typically make up less than 1% of the mass of aerosols, but more than 80% of the total number of particles in the atmosphere.
- Ultrafine particles remain suspended in the air for a very long time, unlike micrometric particles.
- The health risks due to ultrafine particles by inhalation are high and linked to their chemical composition since they penetrate the respiratory system and can pass into the blood.

Here, we propose to discuss a method that should makes it possible to obtain the number and mass concentrations, in real time and *in situ*, of particles of a given elementary composition, without limitation in the type of particle. The size range considered is from few tens of nm to 1000 nm, covering as much as possible the domain of fine and ultrafine particles [2, 3].

The process is based on Laser-Induced Breakdown Spectroscopy (LIBS) applied to aerosols. It differs from previous works [4] by an interaction taking place under vacuum between a focused high-speed pulsed laser and a jet of particles produced by an aerodynamic lens system (SLA) [5]. The interaction with the laser therefore takes place only with the particulate phase without interaction with the gaseous phase, and continuously. The SLA makes it possible to produce a very fine and very dense jet of particles under vacuum while avoiding contamination by particle deposition of the optical elements. This deposit is indeed a major limitation of the online analysis of aerosols by optical technique.

The advantages of the presented technique compared to conventional ones at ambient pressure are:

- Zero background noise from the surrounding gas plasma.
- Highly increased sensitivity thanks to SLA concentration effect.
- Detection of individual particles, allowing counting, connected to the number concentration of particles in the air.
- More efficient detection of elements emitting in the far UV, even down to VUV.

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Session 2

chairman : Guillaume Dhont

High resolution rotational spectroscopy of large amplitude motions and molecular structures

Ha Vinh Lam Nguyen*

Univ Paris Est Creteil, Université Paris Cité, CNRS, LISA, Créteil, France

An enormous number of investigations using molecular jet based Fourier transform microwave spectroscopy has come up since this technique was established almost a century ago and has become more and more popular in the last decade. The complexity of molecules studied by this method also increased dramatically, and still shows a great potential in the future towards even more complex systems with applications in diverse research fields. With the capability to observe the spectra of heavier and larger molecules, microwave spectroscopy is emphasizing and consolidating its key role in yielding precise information on various physical and chemical objectives.

The effects of intramolecular dynamics cause tunneling splittings on the rotational energy levels. The two prototypes of such Large Amplitude Motions (LAMs) are methyl group internal rotation and inversion tunneling involving a double minimum potential. These LAMs sometimes complicate the spectra that much that their assignments were inhibited. New theoretical tools involving correct Hamiltonians have to be developed to reproduce the experimental spectra.

Density functional theory and ab initio calculations implemented in programs such as GAUSSIAN or GAMESS are commonly used today in the spectroscopic community to predict the molecular equilibrium structures, the conformational and tautomeric preferences from the potential energy surfaces, electric field gradients, etc., and to calculate trial values of the related spectroscopic parameters, including barriers for different types of LAMs.

The talk will give an overview on how high resolution spectroscopy in the microwave frequency domain helps to advance the field of LAM beside the classic topic on structure determination.

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* correspondant : lam.nguyen@lisa.ipsl.fr

Understanding the atmosphere of hot Jupiter exoplanets: high resolution spectroscopy of ethylene in the 1.6 µm spectral region

S. Perot[1], L. Rutkowski[1*], S. Kassi[2] and R. Georges[1*]

[1]*IPR (Institut de Physique de Rennes), Université Rennes 1, CNRS, France*
[2]*LIPhy (Laboratoire Interdisciplinaire de Physique), Université Grenoble-Alpes, CNRS, France*

The hot Jupiter exoplanets are giant gas planets orbiting very closely to their star, leading to external temperatures up to 3000 kelvins. Methane [1] and acetylene [2] were already detected in such environments, and the presence of other small hydrocarbons is expected. The recent launch of the James Webb Space Telescope (JWST) and the upcoming Ariel mission will allow a better understanding of their atmospheric composition using infrared spectrometry [3]. Interpretation of these observations will require accurate knowledge of the absorption fingerprint of the expected species. In the case of ethylene (C_2H_4), unambiguous spectral assignment in the near infrared is not available beyond 3500 cm^{-1} [4].

We focus on providing accurate assignments of the ethylene cold transitions. We use a cavity ring-down spectrometer to probe the cold gas in the 1.65-1.68 nm spectral range. The low temperature is obtained by expanding the gas contained in a high-pressure reservoir into a low-pressure chamber through an 80 mm long and 100 µm wide slit. This process enables a simplification of the absorption spectrum by reducing the number of excited transitions and by narrowing the linewidths. Figure 1 shows the cold spectrum (red markers) that was obtained by using 20 slm of Ar buffer gas, 1 slm of C_2H_4 initially at room temperature. The measured line widths were used to estimate the sample temperature to 13 K. Unambiguous assignment of the observed lines will later be performed using the two-temperature method [5]. Hence, we repeated the experiment at 24 K, by using 20 slm of Ar buffer gas, 3 slm of C_2H_4 preheated at 160°C prior to the expansion. The resulting spectrum is shown in black: 'hot' transitions have emerged and the discrepancy between the intensities of the two cold transitions is inversed. The produced assignment will be later compared to the TheoReTS simulations [6], which will provide ethylene line lists at temperatures relevant to the hot Jupiters.

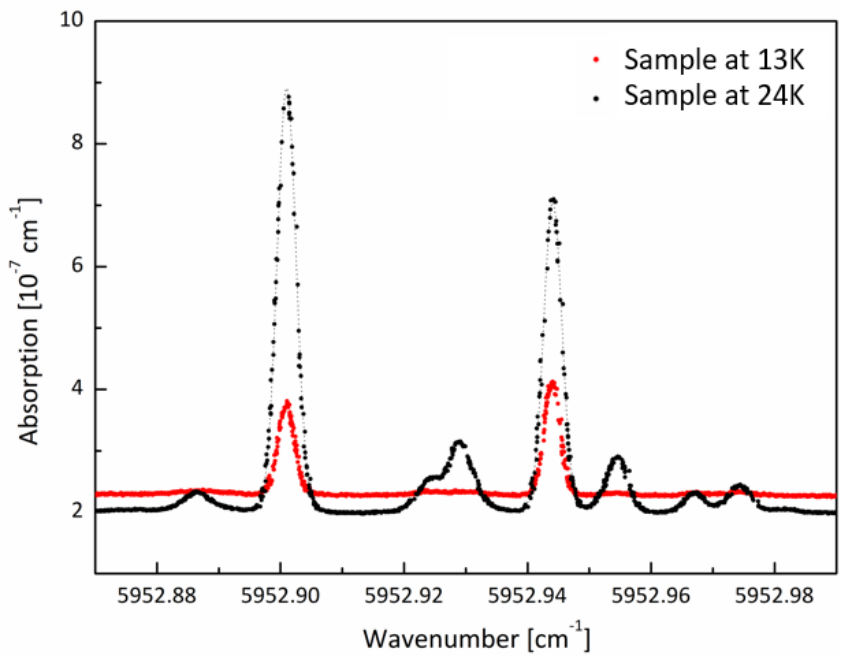

Figure 1: Recorded spectra of C_2H_4 at different temperatures: 13K (red) and 24K (black), emphasizing the appearance of absorption lines belonging to hot bands when the gas is heated.

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* correspondants : lucile.rutkowski@univ-rennes1.fr, robert.georges@univ-rennes1.fr

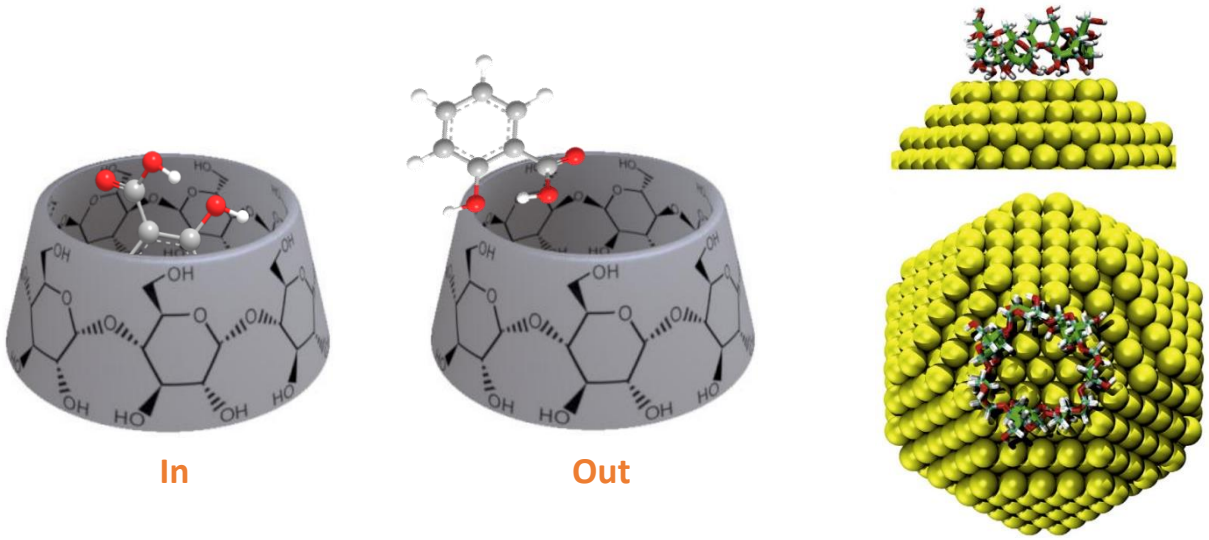
Host-guest complexes between β-cyclodextrins and small drugs for SERS detection in drinking water

G. Berden[1], J. Oomens[1], D. Scuderi[2], A. Beydoun[3], C. Desfrançois[3], F. Lecomte[3], B. Manil[3], N. Nieuwjaer[3]

[1] *HFML – FELIX, Radboud University , Toernooiveld 7c, 6525 ED Nijmegen , Nederland*
[2] *Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, 91405 Orsay Cedex, France*
[3] *Laboratoire de Physique des Lasers, CNRS, Université Sorbonne Paris Nord, 93430 Villetaneuse, France*

β-CycloDextrin (β-CD) is a macrocyclic oligosaccharide composed of seven D-glucopyranoside units linked in α-(1,4) bonds. β-CD has a truncated cone tri-dimensional structure. Its central cavity is hydrophobic, allowing low-polarity molecules to be encapsulate partially or entirely by host-guest interaction, meanwhile the external part is hydrophilic because of the presence of 21 hydroxyl groups making β-CD soluble in water. This host-guest type relationship can modify the physical, chemical or biological characteristics of the guest molecule, and applications are found in practically all sectors of industry. One of these applications consists in functionalizing silver nanoparticles with β-CD-SH in order to develop a Surface-Enhanced Raman Scattering (SERS) sensor to detect pollutants such as PAHs [1]: the β-CD cavity traps PAHs near the metallic surface where the large increase in Raman cross-section is induced. Such a SERS sensor could be considered for the detection of traces of small drugs (salicylic acid, paracetamol) in drinking water. That is why we have started to study host-guest complexes between salicylic acid or paracetamol with β-CD.

The advent of soft ionization techniques has allowed for extensive examination of cyclodextrin complexes by mean of mass spectrometry, and structural information on β-CD complexes have recently been provided by IRMPD and IM spectroscopy [2] or also action-FRET [3]. Our goal is to probe in the gas phase the relative position of the non-covalently bound subunits in two systems: complexes between salicylic acid and β-CD and complexes between paracetamol and β-CD. These structures are obtained by combining IRMPD spectroscopy experiments and quantum calculations for simulating IR spectra on mass-selected ions. Comparison with studies in the condensed phase will give information on the possible conversion of inclusion complexes to nonspecific complexes (and vice versa) and on the importance of relative interactions for the formation of the complexes.



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Calcul de l'absorption induite par collision de CH_4 + CO_2 dans l'infrarouge lointain

Wissam Fakhardji[1*], Christian Boulet[2], Ha Tran[1], Jean-Michel Hartmann[1]

[1] *Laboratoire de Météorologie Dynamique/IPSL, CNRS, Ecole polytechnique, Institut polytechnique de Paris, Sorbonne Université, Ecole normale supérieure, PSL Research University, F-91120 Palaiseau, France*
[2] *Institut de Sciences Moléculaires d'Orsay, CNRS, Université Paris-Saclay, Orsay F-9140*

L'effet de serre dans l'atmopshère primordial de Mars, nécessaire à la stabilité de l'eau liquide à sa surface, peut être expliqué par la contribution de l'absorption induite par collision (CIA) des pairs CH_4+CO_2 (and H_2 CO_2) dans l'infrarouge lointain [1]. Le besoin de ces spectres de CIA ont motivé un premier travail expérimental [2] réalisé à température ambiante, suivi d'un second [3] complété par des calculs semi-empiriques pour différentes températures, nécessaires pour les sciences planétaires. Ces calculs réalisés avec « l'approximation isotropique » négligent l'influence de l'anisotropie du potentiel. Dans ce travail, nous avons calculés les spectres de CIA en utilisant la méthode de la dymanique moléculaire classique utilisant un potentiel ab initio [4] et une expression du dipole à long portée [5]. Le point clé de cette approche est de calculer la fonction d'autocorrelation du dipole induit (ACF) donnée par,

$$ACF(t-t_0)=\sum_{i=CH_4}\sum_{j=CO_2}\overrightarrow{\mu_{i,j}}(t_0)\overrightarrow{\mu_{i,j}}(t) \quad \text{pour} \quad t\geq t_0$$

avec t_0 étant l'origine du temps choisi pour le début de la simulation, $\overrightarrow{\mu_{i,j}}$ désignant le dipole induit entre la pair CH_4 – CO_2 dénotés par les indices respectifs i et j. Le coefficient d'absorption esy obtenu pour chaque valeur de la fréquence angulaire ω ($\omega=2\pi c\sigma$ avec σ the nombre d'onde exprimé en cm^{-1}) avec la formule,

$$\alpha(\omega)=A\frac{4\pi}{3hc}f_D(\omega)\omega[1-\mathrm{e}^{-h\omega/2\pi k_b T}]\frac{1}{V}C(\omega)$$

avec $V=N/d$ the volume associé au nombre de molecules N et à la densité d . A est un facteur de conversion défini par $A=(ea_0)^2/4\pi\epsilon_0$ avec e la charge d'un électron, a_0 le rayon de Bohr et ϵ_0 la permittivité du vide. $C(\omega)$ est la partie réelle de la transformée de Fourier comme suit,

$$C(\omega)=\Re\{\frac{1}{\pi}\int_0^{t_{max}-t_0}ACF(t)\mathrm{e}^{-i\omega t}dt\}=\frac{1}{\pi}\int_0^{t_{max}-t_0}\cos(\omega t)ACF(t)dt$$

avec t_{max} la durée de la simulation. Le facteur de déssymétrization $f_D(\omega)$ est utilisé pour assurer la condition d'équilibre détaillé. Différentes procedures sont disponibles dans la litérature (non décrites ici) ont été testées. Une comparison avec les données expérimentales montrent un bon accord à T=300K ce qui nous permet de valider notre approche. Une étude sur l'anisotropie du potentiel a montré qu'elle a effet important sur le niveau du coefficient d'absorption. Ce résultat démontre que la partie anisotropique du potentiel doit être prise en compte pour une descrption précise de la CIA pour CH_4+CO_2 et supposément pour des systèmes similaires. De plus, les spectres à T=100K, 200K, 400k et 500K ont été calculés indépendament de tout ajustement emprique, constituant de nouvelles données pour des applications en sciences planétaires.

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Session 3

chairman : Sébastien Zamith

Collisions réactives entre ions et molécules à basse température : apports des écoulements supersoniques uniformes

Ludovic Biennier, Ahmad Mortada, Sophie Carles, Abdessamad Benidar, Sandor Demes, François Lique

Institut de Physique de Rennes, Univ. Rennes 1, UMR CNRS 6251

Une des questions majeures en astrophysique moléculaire est de comprendre comment le cycle de la matière entre les différentes phases conduit à un accroissement de la complexité moléculaire. La physico-chimie en phase gazeuse et les processus de surface rivalisent pour décrocher le premier rôle. Un des enjeux est notamment de déterminer la nature et l'abondance des molécules observées ou supposées présentes dans une grande variété d'environnements astrophysiques, des nuages interstellaires, des régions de formation d'étoiles, aux atmosphères planétaires. Parmi les mécanismes clés gouvernant la physico-chimie en phase gazeuse de ces objets, on trouve de nombreux processus ioniques

L'élucidation des mécanismes des réactions élémentaires sous-jacentes, en particulier aux faibles énergies de collision, fournit des informations cruciales pour la modélisation de la chimie de ces environnements. Malgré des efforts de longue haleine, la cinétique et la nature des produits de nombreuses réactions clés en phase gazeuse restent mal connues aux températures pertinentes.

Dans notre laboratoire, nous avons mis au point une méthode originale combinant la technique CRESU pour générer des écoulements supersoniques uniformes, une source sélective d'ions, et la spectrométrie de masse pour étudier les collisions réactives entre ions moléculaires et espèces neutres à basse température [1]. Les derniers développements instrumentaux visant à explorer la réactivité des ions froids seront présentés. Nos résultats semblent mettre en évidence une dépendance en température des voies de sortie de nombreuses réactions chimiques stimulant ainsi les calculs théoriques et conduisant à la révision des modèles photochimiques.

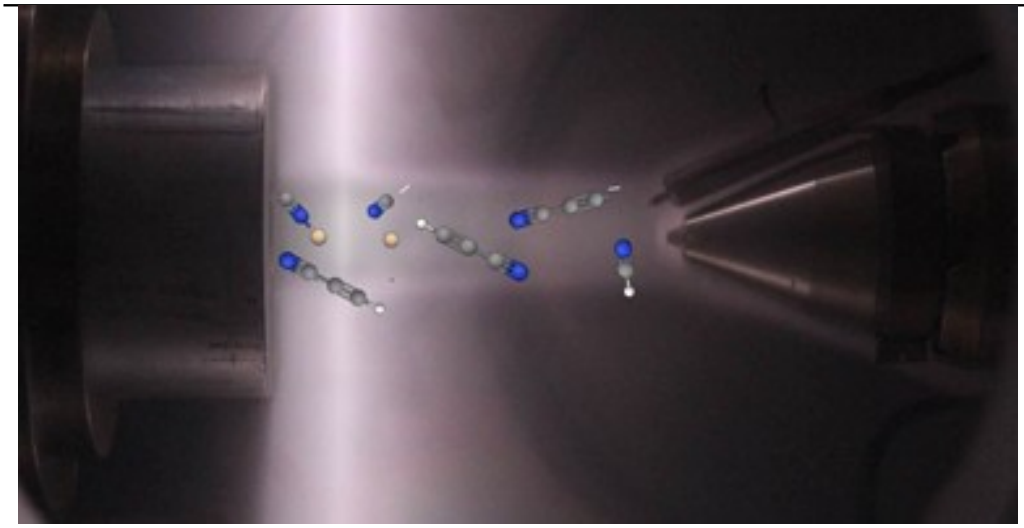

Figure 1 : Les processus ioniques se produisant dans l'écoulement supersonique uniforme sont sondés par un spectromètre de masse mobile.

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New (TD-)DFT-based methodology for describing the electron attachment

G. Thiam[1], F. Rabilloud[1]

[1]*Université de Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, France,*
franck.rabilloud@univ-lyon1.fr

The interaction of low-energy electron collisions with molecules may lead to temporary anions via resonant processes. While experimental measurements, e.g. electron transmission spectroscopy or dissociation electron attachment spectroscopy, are efficient to characterize the temporary anions, simulating the electron attachment (most often in a metastable excited state) is still very challenging.

A complete theoretical characterization of the temporary anion should describe the electron attachment, the relaxation of electronic and vibrational degrees of freedom, and possible fragmentation processes. However, limitations coming from the difficulty to treat the electron correlation in an anionic system, the need to combine continuum and discrete states, and the high number of degrees of freedom, make the numerical calculation very cumbersome. The most popular computational methods for describing temporary anions [1], such as the R-matrix [2], the so-called empirical correlation method [3], the Schwinger multichannel method [4], or the stabilization method [5], may provide valuable results, but they rely on either cumbersome calculations or empirical parameters.

Here, we will show that DFT and TDDFT calculations are now able to describe the attachment of an extra electron, whether it is located in a valence state [6] or in a long-range state [7]. We will present an efficient approach to predict the resonance energies of the electron attachment using a TDDFT calculation and two different atomic basis sets [6]: a large basis set to compute the vertical electron affinity, and a smaller one to calculate the excitation energy of the anion. Doing so, one computes the relevant resonant attachment energies of the electron without intruder states from the continuum discretized due to the finite size of the simulation box. We will also show that DFT can describe dipole-bound or multipole-bound anionic states, where the electron lies at a long range, provided that a correct asymptotic exchange and correlation potential is used.

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Rotational study of atmospheric volatile organic compounds using the new CP-FTMW spectrometer of Lille

Elias M. Neeman[1*], Noureddin Osseiran[1], Manuel Goubet[1], Pascal Dréan[1], Thérèse R. Huet[1]

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

The introduction of the CP-FTMW technique by Pate and co-workers has revolutionized the rotational spectroscopy field providing rapid acquisition of broadband spectra [1]. The design of a newly constructed chirped-pulse Fourier transform microwave spectrometer CP-FTMW covering the range of 6-18 GHz will be presented. In particular, the chirped pulse (6-18 GHz, 4 µs) is generated by a fast-arbitrary waveform generator (AWG, Keysight M8195A 65 GSa/s). Free Induction Decays (FID) are detected and collected on a recent generation of a fast oscilloscope (Keysight DSOZ634A 160 GSa/s). The high speed of the oscilloscope allows to achieve a high spectral resolution (FWHM better than 40 kHz) by recording the FID during 80 µs. Up to three pulsed nozzles can be used simultaneously [2]. The CP-FTMW spectrometer is currently used to study volatile organic molecules of atmospheric interest. The results of this work will be discussed in detail.

Hervé Damart and Gauthier Dekyndt are gratefully acknowledged for their technical assistance.

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* correspondant : elias.neeman@univ-lille.fr

Methyl iodide with the perturbers of atmospheric interest: line-broadening coefficients and their temperature dependence

Larisa Troitsyna[1]*, Anna Dudaryonok[2], Nina Lavrentieva[2], Nikolai Filippov[3], Jeanna Buldyreva[4]

[1] GSM, UMR CNRS 7331 Université de Reims Champagne Ardenne (URCA), *France*

[3]Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS, *Russia*

[4]Laboratory of Molecular Spectroscopy, Faculty of Physics, Saint-Petersburg State University, *Russia*

[4]Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, *France*

As modern radiative transfer and climate change models aim to account for minor atmospheric compounds, the interest in the characteristics of those gases is growing. Though the concentration of methyl iodide in the terrestrial atmosphere is small, it is the potential source of reactive iodine that can sorb to dust particles and aerosols or react with ozone. Moreover, CH_3I participates in marine cloud formation, influencing the terrestrial radiative budget. Changes in climate (especially increase of the seawater temperature) have an impact on the rate of production of this gas in the oceans. To monitor the concentrations of atmospheric methyl iodide satellite observations can be applied, as the ν_6 fundamental of CH_3I falls in the 11µm transparency window [1]. For this reason the line-broadening parameters for this band and their temperature dependencies are required.

The present study is devoted to the calculations of methyl iodide self-, nitrogen-, oxygen- and air-broadening in the wide range of rotational quantum numbers ($0 \leq J \leq 70$ and $K \leq 20$) traditionally required for databases for all six sub-branches of the ν_6 band. First, the line-broadening coefficients are computed at room temperature (296K) by a semi-classical [2] and a semi-empirical [3] methods and the results are compared between themselves and with available experimental data. Next, the coefficients are obtained in a wider temperature range (200-400K) and their temperature dependence is analyzed.

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Session 4

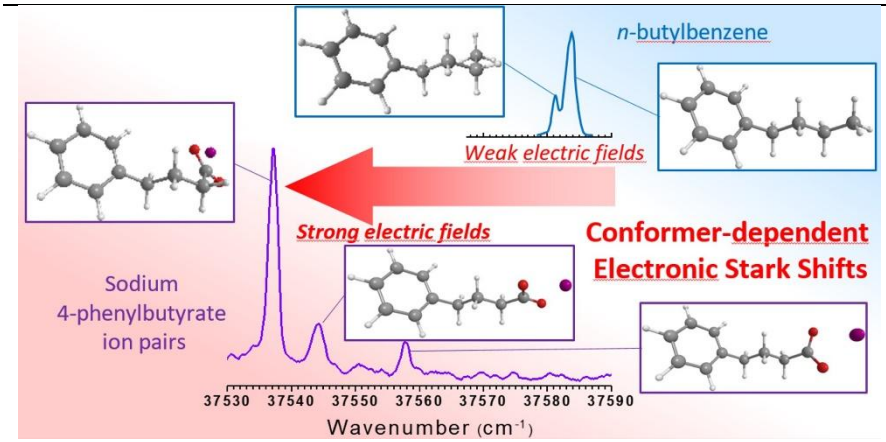
chairman : Valérie Brenner

Analyse conformationnelle par spectroscopie laser UV : l'apport décisif de l'étude théorique des effets Stark induits par l'environnement du chromophore

Eric Gloaguen*

Université Paris-Saclay, CEA, CNRS, Laboratoire Interactions Dynamiques et Lasers, Gif-sur-Yvette, France

L'étude de paires d'ions moléculaires isolées en phase gazeuse a révélé une corrélation entre leur spectroscopie électronique et le champ électrique généré par l'environnement moléculaire autour du chromophore UV [1]. L'approche théorique, basée sur un calcul de champ électrique à l'état fondamental, a permis de caractériser des effets Stark au sein de ces systèmes, en reproduisant les déplacements spectraux avec une précision de l'ordre du cm^{-1}. Cette nouvelle interface entre spectroscopie UV et chimie quantique a ensuite été utilisée pour l'analyse conformationnelle de systèmes flexibles, et s'est avérée particulièrement utile et complémentaire des autres diagnostics s'appuyant sur la spectroscopie IR ou la spectrométrie de masse [2]. Particulièrement adaptée aux systèmes où le chromophore est lié à des groupements polaires, cette approche repose sur des calculs suffisamment légers pour être appliqués à de grands systèmes afin de faciliter l'interprétation de leur spectroscopie UV, et plus généralement leur étude structurale.



La corrélation entre les transitions électroniques et les champs électriques calculés permet d'attribuer précisément les structures moléculaires et d'interpréter quantitativement les spectres UV à l'échelle du cm^{-1} [2].

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* correspondant : eric.gloaguen@cnrs.fr

Novel methodology for systematically constructing global effective *ab initio*-based models: towards a change of paradigm in high-resolution molecular spectra analysis?

Michaël Rey[1*]

[1] *GSMA, UMR CNRS, Université de Reims Champagne-Ardenne, Reims, France*

The current needs require knowledge of increasingly complex molecular systems over wide wavenumber and temperature ranges. The empirical effective Hamiltonians have greatly contributed to the "golden age" of the high-resolution molecular spectroscopy but they are beginning to reach their limits for the study of complex polyads. A change of paradigm in high-resolution spectra analysis could be needed.

A novel methodology is presented [1] for the construction of global effective rotation-vibration spectroscopic models from potential energy and transition moment *ab initio* surfaces. Non-empirical effective Hamiltonians are obtained *via* the block-diagonalization of selected variationally-computed eigenvector matrices. For the first time, the derivation of non-empirical effective transition moment operators is also carried out in a systematic way. This general approach turns out to be a clear alternative to the rather involved Van Vleck perturbation method. Symmetry is exploited at all stages to translate first-principles calculations into a set of spectroscopic parameters to be further refined on experiment. We demonstrate on H_2CO, PH_3, CH_4, C_2H_4 and SF_6 that the proposed effective model can provide crucial information within a very short time compared to more traditional spectroscopic models (*few hours, days or weeks against few months, years or decades*) if, for a given molecule, the *ab initio* surfaces are available. 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.

[1] M. Rey, *(2022) Submitted*

* correspondant : michael.rey@univ-reims.fr

Development of photoacoustic sensor for the measurement of peroxy radicals and ozone production in the atmosphere

Ghoufrane Abichou[1,2], Sébastien Dusanter[2], Alexandre Tomas[2], Tong N. Ba[1], Markus W. Sigrist[3], Weidong Chen[1]

[1]*Laboratoire de Physicochimie de l'Atmosphère/ Université du Littoral Côte d'Opale-59140 Dunkerque, France*

[2] *IMT Nord Europe, Institut Mines-Télécom, Univ. Lille, Center for Energy and Environment, 59000 Lille, France*

[3]*Laser Spectroscopy and Sensing Laboratory, Institute for Quantum Electronics, ETH Zurich, Switzerland*

Key words: Metrology, atmosphere, peroxy radicals, ozone, climate change

Peroxy radicals are key atmospheric species sustaining the oxidative capacity of the atmosphere through their propagation to the hydroxyl radical (OH), the most important daytime oxidant, and the formation of oxygenated byproducts that can further photolyze to produce more radicals [1]. In the troposphere, peroxy radicals convert NO into NO_2, whose subsequent photolysis leads to the formation of tropospheric ozone, a major species of air pollution, both in terms of health and climate [2]. Given the photochemical nature of ozone, the design of mitigation strategies for this pollutant involves the use of predictive atmospheric chemistry models. However, these models are at the whim of the embedded chemical and physical processes and emission inventories, and it is therefore essential, in an area where socio-economic stakes are considerable, to develop alternative strategies.

The work proposed in this project involves the development of an integrated instrument, allowing simultaneous measurements of peroxy radicals and nitrogen monoxide (NO) in ambient air. Computing the NO-to-NO_2 conversion rate from these measurements allows assessing the rate of ground-level ozone formation, which provides useful information on (i) the contribution of local photochemistry to ozone levels observed at a monitoring site and (ii) the chemical regime of ozone formation at this site, which in turn will help public authorities in the management of pollution peaks. This instrument includes a combination of (i) a chemical amplifier (CA) that converts peroxy radicals into NO_2 [3] and a 2-channel photoacoustic spectrometer to measure the resulting NO_2, and (ii) a NO analyzer.

We report here the development of the first part of this integrated instrument, which consists of a photoacoustic spectrometer (PAS) operating at 450 nm. To characterize its performance, calibration experiments and side-by-side measurements of NO_2 have been performed with a commercial NO_x analyzer. The 1-σ minimum detectable mixing ratio was evaluated to be 0.5 ppb at a time resolution of 1 s. This minimum detectable can be reduced to 0.2 ppb using a longer integration time of 1 min. Experimental details and preliminary results will be presented and discussed.

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The hydration of polycyclic aromatic compounds: the case of naphthaldehyde

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

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

Polycyclic aromatic hydrocarbons (PAHs) and their oxygenated products (oxi-PAH) are considered as important pollutants of the Earth's atmosphere since they are emitted by the combustion of fuels.[1] The study of their intermolecular interactions is essential to understand the formation of their aerosols. In this work, we have studied at molecular level the interactions present in the hydration of the oxi-PAH, α- and β-naphthaldehyde. This study has been performed using a supersonic jet Fourier transform microwave (FTMW) spectrometer in the 4-15 GHz range, with the support of theoretical calculations. Both isolated α- and β-naphthaldehyde species could present two possible structures: *cis,* the most stable one for α, and *trans* for β.[2] Our calculations show that there are three low energy monohydrates predicted for each conformer, *cis*/*trans*, in a range of 1500 cm^{-1}. Experimentally, one conformer has been observed in gas phase for α and two for β, corresponding to the most stable structures. All species are stabilized by intermolecular H-bonds between the water molecule and the aldehyde group of naphthaldehyde: for the first case, the oxygen of the aldehyde acts as proton acceptor and the aldehyde hydrogen as proton donor; for the second case, the oxygen of the aldehyde acts as proton acceptor and one of the ring hydrogens as a proton donor.[3]

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

Session 5

chairman : Wutharath Chin

Spectroscopy of sugars

Physical chemistry answers to analytical chemistry questions

Isabelle Compagnon[1*]

[1] *Institut Lumière Matière, Université Claude Bernard Lyon 1-CNRS, Villeurbanne, France*

La spectroscopie IRMPD (InfraRed Multiple Photon Dissociation) est une technique de spectroscopie vibrationnelle d'ion qui combine un schéma spectroscopique d'action IR relativement frugal à des technologies des spectrométrie de masse avancées, allant initialement du couplage d'une source ESI (electrospray) avec un piège de Paul dans les années 2005 ; jusqu'au couplage à des workflows analytiques élaborés, tels que nous les réalisons aujourd'hui.

Ce schéma spectroscopique a d'abord été très apprécié dans la communauté de Physico Chimie pour sa capacité mettre en phase gazeuse des ions moléculaire de taille et de complexité croissante, voire même de contrôler leur micro-environnement, tout en donnant accès à une gamme et une résolution spectrales pertinentes dans le contexte de l'étude conformationelle de biomolécules. Ces 15 dernières années ont vu une littérature abondante d'analyse IRMPD d'ions biomoléculaires adossés aux développements les plus récents de la Chimie Quantique, ou les challengeant. [1]

Dans un deuxième temps, l'IRMPD est aussi apparu comme un outil puissant pour distinguer des molécules isomérique. Cette propriété s'est avérée un « game changer » en glycomique (la branche de la Chimie Analytique traitant de la famille des sucres) car les sucres présentent pratiquement toutes les combinaisons de symétries possibles, ce qui rend les méthodes de spectrométrie de masse insuffisante à leur identification. Dans ce contexte, l'ajout d'une dimension spectroscopique s'est révélé déterminant pour identifier des isomères de sucres et pour développer la méthode de séquençage générique de cette classe de biomolécules, basée sur l'analyse IRMPD de fragments MS/MS. [2]

Sur la base de ces concepts, le potentiel de la spectroscopie IRMPD pour la Chimie analytique s'est considérablement développé.J'en présenterai une application très récente : le projet GEPHIR dont l'objectif est d'identifier des défauts de glycosylation présents à la surface de protéines du système immunitaire chez des patients présentant un terrain génétique favorable à des maladies auto-immunes, telle que l'arthrite rhumatoide ou Crohn, afin de proposer un diagnostic précoce de ces maladies. [3]

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[3] projet financé par l'ANR
* correspondant : isabelle.compagnon@univ-lyon1.fr

Extracting vibrational anharmonicities from short driven molecular dynamics trajectories

Loïse Attal[(a)], Cyril Falvo[(a),(b)], Romain Maupin[(a)], Florent Calvo[(b)] and Pascal Parneix[(a)]

(a) Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405, Orsay, France
(b) University Grenoble Alpes, CNRS, LiPhy, 38000 Grenoble, France

Anharmonicities of the potential energy surface provide a wealth of information about the vibrational dynamics, especially mode coupling and energy transfer, within a polyatomic system. In this contribution we show how *driven* molecular dynamics (DMD) trajectories, as initially suggested by Bowman and coworkers [1] to extract the harmonic vibrational frequencies in large systems, can be extended to determine anharmonicity properties under very short times of a few hundreds of vibrational periods, using two exciting fields at, and slightly off-resonance.

The DMD trajectory is described by numerically solving the Hamiltonian, which includes a quadratic harmonic contribution, an anharmonic contribution, and an out-of-equilibrium interaction with a time varying external field at frequency Ω.

Detailed analyses on generic quartic potential energy surfaces and applications to various model systems are presented, giving good agreement with perturbation theory. Application to a realistic molecule, cubane (C_8H_8), modelled with a tight-binding quantum force field, further indicates how the method can be applied in practical cases [2] (see Fig. 1).

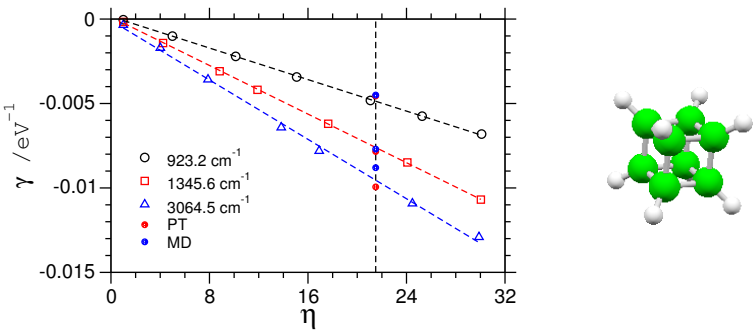

Figure 1: Effective anharmonicity coefficient γ_{DMD} obtained from DMD simulations as a function of the relative excess energy η for the three IR active modes of the cubane molecule. The true value of γ is obtained at the position of the vertical dashed line and compared with pertubation theory (PT) and MD simulations.

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PIRENEA and PIRENEA 2: studying photon-PAHs interactions in relevant astrophysical conditions

A. Marciniak[1,2,†], A. Bonnamy[1], S. Zamith[2], L. Nogues[1], O. Coeur-Joly[1], D. Murat[1], P. Moretto-Capelle[2], J.-M. L'Hermite[2], G. Mulas[3] and C. Joblin[1]

[1] *IRAP, Université de Toulouse, CNRS, CNES, Toulouse, France*
[2] *LCAR/IRSAMC, Université de Toulouse, CNRS, 118 Route de Narbonne, F-31062 Toulouse, France*
[3] *INAF – Osservatorio Astronomico di Cagliari, Via della Scienza 5, I-09047 Selargius (CA), Italy*

[†] Correspondence to : `marciniak@irsamc.ups-tlse.fr`, `https://www.lcar.ups-tlse.fr/marciniak/`

About 10% to 20% of the carbon in the universe is contained in polycyclic aromatic hydrocarbon (PAH) molecules which can be found in the gas phase of various interstellar environments. Studying their interaction with UV and VUV photons is of high interest in astrophysics as it permits to better understand the physical and chemical evolution of photodissociation regions (PDRs) associated with star forming regions. In particular, this interaction induces the well-known aromatic infrared bands (AIB) emission [1] but other mechanisms such as fragmentation [2] can be involved.

In this context, laboratory astrophysics experiments are needed to study photoinduced mechanisms in these carbonaceous species. PIRENEA (standing for Piège à Ions pour la Recherche et l'Etude de Nouvelles Espèces Astrochimiques) and PIRENEA 2 (the 2nd generation of PIRENEA) are two setups developed in Toulouse which are specifically dedicated to the study of such processes. These setups allow us (i) to produce molecular species of interest in astrochemistry, (ii) to isolate and trap them for minutes in a cold ($\leq$ 30 K) and collisionless environment ($\leq 10^{-11}$ mbar), (iii) to make them interact with photons at different energies from IR to VUV and (iv) to follow and study the fragmentation of the trapped species thanks to non-destructive very high resolution FT mass spectrometry. In this work, we present (1) the results of a recent study performed with PIRENEA on the VUV photodissociation of aliphatic PAH derivatives [3] and (2) a challenging project which will be performed with PIRENEA 2 and aims to investigate photon-gas-cluster interactions [4].

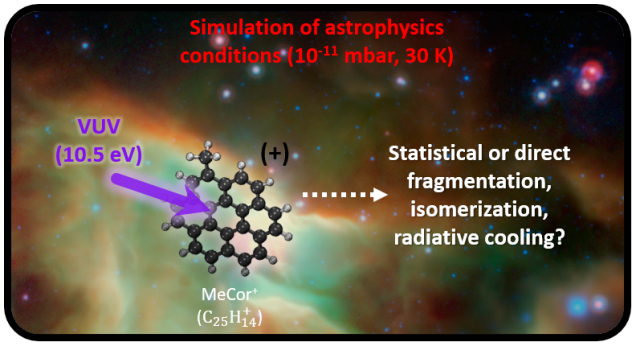

Figure 1: Scheme of principle of studies performed with PIRENEA or PIRENEA 2.

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Session 6

chairman : Aude Simon

Construction, Destruction and High-resolution Spectroscopic Characterization of Fragile Molecular Edifices

Clément Lauzin[1*]

[1] *Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium*

In this talk, I will present results concerning H_2O-X van der Waals complexes, where X are atmospheric constituents (N_2, CO_2, O_2). These complexes are studied (and destroyed) in the mid- and near-infrared using various experimental instruments. The spectroscopic characterization is performed above the dissociation threshold through the excitation in the range of the single and double OH/OD stretches. H_2O-CO_2 and H_2O-N_2 will be used to illustrate how spectral signature recorded at high-resolution can be used to retrieve detailed information on the coupling with the dissociation continuum and the tunneling dynamics of molecular complexes. I will also present our efforts to study the same complex in the 3OD stretching region and our efforts to study larger molecular edifices, extending our work towards higher molecular complexity but also reactivity.

Photo-isomérisation sélective de l'acide salicylique

Julien Berthomier[1,2], Wutharath Chin[1], Rasa Platakyte[3], Justinas Ceponkus[3], Claudine Crépin[1]

[1] *ISMO, UMR8214, Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, 91405, Orsay Cedex*
[2] *obvioTec AG, Garstligweg 8, 8634 Hombrechtikon, Suisse*
[3] *Department of General Physics and Spectroscopy, Vilnius University, Lituania*

L'acide salicylique, un précurseur dans la synthèse de l'aspirine, est une molécule qui présente plusieurs isomères : la forme E (la plus stable), la forme R et la forme H ont été observées [1]. Notre objectif est de caractériser et comprendre la formation par irradiation UV de ses différents isomères, en les piégeant dans un solide d'argon. On a ainsi observé des émissions de phosphorescence et de fluorescence grâce à un laser accordable. En mettant en évidence les corrélations entre ces émissions et les spectres d'absorption infrarouge et UV, on a pu attribuer une fluorescence entre 360 et 450nm à la forme E (τ<9ns) et des émissions de phosphorescences aux formes R et H (τ>1,5s) (cf. Figure 1). Nous avons également montré qu'il était possible de convertir un isomère en un autre en irradiant l'échantillon à des longueurs d'ondes spécifiques.

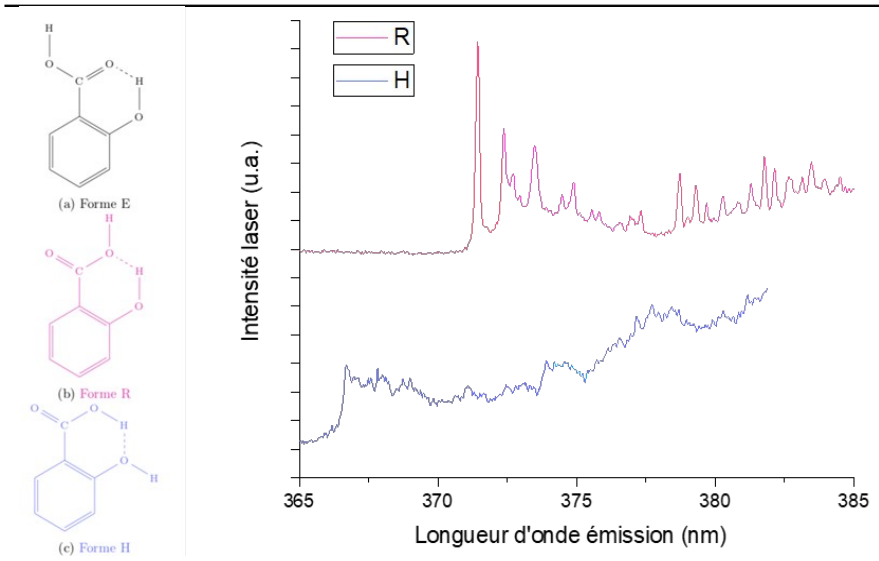

Figure 1 :

À gauche, les différents isomères de l'acide salicylique observés.

À droite, l'émission de phosphorescence de la forme R (excitation à 315,5nm) – haut - et l'émission de phosphorescence de la forme H (excitation à 295,3nm) – bas -.

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* correspondant : julienberthomier5@gmail.com

Water-corannulene clusters embedded in a rare gas matrix: structures, energetics and IR spectra

Héloïse Leboucher[1], Aude Simon[1], Joëlle Mascetti[2], Jennifer A. Noble[3]
[1] Laboratoire de Chimie et Physique Quantiques (LCPQ), Fédération FeRMI, UMR5626, Université de Toulouse [UT3] & CNRS, University Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France
[2] Institut des Sciences Moléculaires (ISM), Université de Bordeaux, UMR5255, CNRS, 351 Cours de la Libération, CEDEX, 33405 Talence, France
[3] Laboratoire Physique des Interactions Ioniques et Moléculaires (PIIM), UMR7345, CNRS, Aix-Marseille Université, 13013 Marseille, France

Polycyclic aromatic hydrocarbons (PAHs) have multiple research interests, in particular in environnemental science and in astrochemistry. Indeed, unidentified aromatic IR bands have been observed in the interstellar medium (ISM) for almost forty years and are attributed to a PAH population [1]. In the denser and colder regions of the ISM, it is believed that PAHs could condense on the ice mantle covering the surface of nanograins [2] and interact with some water molecules located at the surface of the ice. It is therefore of interest to study the interactions of PAHs with water molecules and clusters and their spectroscopic signatures in low temperature and pressure conditions. In this context, we present joint experimental and theoretical studies on the interactions of corannulene $C_{20}H_{10}$, a non-planar PAH, with small water clusters, using the same approach as for coronene $C_{24}H_{12}$, a planar PAH [1].

Briefly, the structures and energetics of the most stable isomers of $(C_{20}H_{10})(H_2O)_{1-3}$ in an argon matrix (see Fig.1) were obtained by local optimisation of finite-size clusters with the electronic structure computed using the mixed density-functional based tight-binding and force field scheme [3]. The low temperature anharmonic effects were investigated by means of all-atoms on-the-fly Born-Oppenheimer molecular dynamics simulations and anharmonic IR spectra were derived. The computed shifts of the modes induced by the interaction were compared to experimental FTIR spectroscopy data. Interestingly, theoretical results show that for 2 and 3 water molecules, π isomers are favored in the case of corannulene [4]. The comparison between experiments and theory demonstrates in particular the formation in the matrix of the most stable isomer of $(C_{20}H_{10})(H_2O)_3$ where the water trimer is trapped inside the corannulene bowl (see Fig.2). On the opposite, we showed in our previous work that for complexes of water with planar PAHs such as coronene, the formation of σ isomers is favored in the same conditions [1]. Interestingly, these isomers react with water under UV irradiation, whereas corannulene does not. This illustrates the dependence of photoreactivity on the relative orientation of the different monomers [4]. The electronic excited states of these complexes are currently under investigation.

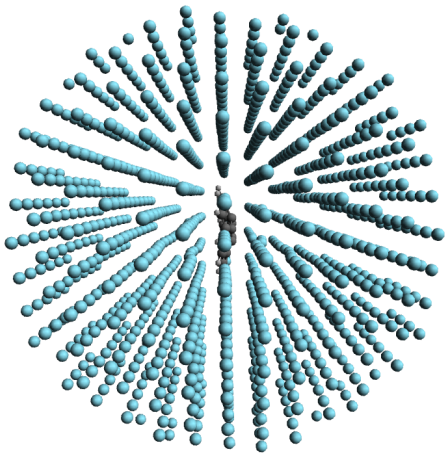

Figure 1: Argon matrix with the corannulene in the center

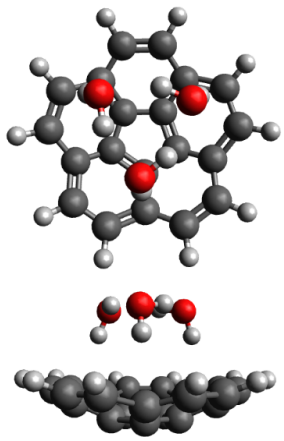

Figure 2: Top and side views of the most stable isomer of $(C_{20}H_{10})(H_2O)_3$

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Session 7

chairman : Ha Tran

Some unusual aspects in the absorption spectrum of the first greenhouse gas

A. Campargue [1], S. Kassi [1], D Mondelain, S. Vasilchenko[2], S. Mikhailenko [2]

[1] *Univ. Grenoble Alpes, CNRS, LIPhy, Grenoble, France*
[2] *Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, RAS, Tomsk, Russia*

Our knowledge of the absorption spectrum of water vapour is insufficient for a number of atmospheric applications. In this talk, we will show that cavity-enhanced absorption spectroscopy (in particular cavity ring down spectroscopy - CRDS) provides an ideal tool to investigate several aspects of the water vapor spectroscopy: weak lines, line parameters [1], Lamb dips, minor isotopologues, electric-quadrupole transitions [2] and self- and foreign-continuum absorption [3].

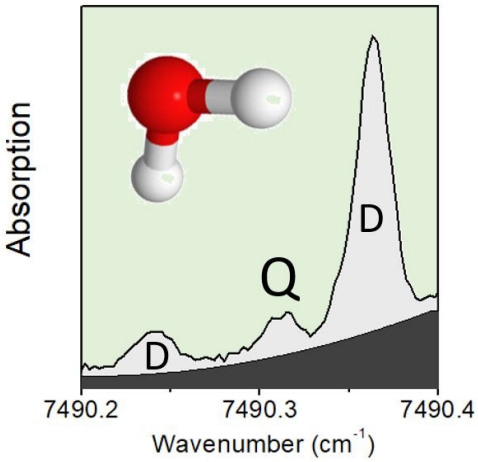

Figure 1 : First detection of electric quadrupole lines (Q) in the high sensitivity absorption spectrum of water vapor recorded by cavity ring down spectroscopy [2].

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* alain.campargue@univ-grenoble-alpes.fr

Laser moléculaire à NH_3 pour la spectroscopie hétérodyne THz

Marie-Hélène Mammez[1*], Dominique Mammez[1], Thomas Hearne[3], Olivier Pirali[3,4], Marie-Aline Martin-Drumel[3], Zach Buchanan[3,5], Guillaume Ducournau[2], Sophie Eliet[2], Francis Hindle[1], Stefano Barbieri[2], Pascale Roy[4], Gaël Mouret[1], Jean-François Lampin[2]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère (LPCA), Université du Littoral Côte d'Opale, Avenue Schumann F-59140 Dunkerque*
[2] *Institut d'Electronique Microélectronique et Nanotechnologie (IEMN), CNRS UMR 8520, Université de Lille, Avenue Poincaré F-59652 Villeneuve d'Ascq Cedex, France*
[3] *Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay, France*
[4] *SOLEIL synchrotron, AILES beamline, l'Orme des Merisiers, Saint-Aubin, F-91190 Gif-sur-Yvette, France*
[5] *Department of Chemistry, University of California, Davis, One Shields Ave, Davis, CA 95616, United States*

La gamme de fréquence térahertz (THz) est conventionnellement située à la jonction des micro-ondes et des ondes infrarouges, soit entre 100 GHz et 10 THz (*i.e.* 3-333 cm^{-1} ou 3000-30 µm). Malgré l'intérêt croissant de nombreux groupes de recherche pour cette région du spectre électro-magnétique [1], il reste difficile de produire un rayonnement THz continu qui soit à la fois largement accordable et puissant. Par exemple, les chaînes de multiplication de fréquence sont limitées en puissance au-delà de 1 THz ; tandis que les lasers à cascade quantique (QCL) requièrent un refroidissement cryogénique pour une fréquence émise supérieure à 2 THz et présentent une faible gamme d'accord. Les premières générations de lasers moléculaires THz produisaient un rayonnement puissant à température ambiante, mais le nombre de fréquences accessibles était restreint du fait des méthodes employées pour générer l'inversion de population (soit par décharge, soit par pompage par un laser à CO_2) [2]. Nous présenterons une nouvelle génération de laser moléculaire THz à pompage optique par QCL qui permet une émission continue, puissante, et largement accordable par pas discrets. Le milieu amplificateur est constitué d'ammoniac (NH3) [3] et 36 transitions lasers ont été obtenues expérimentalement entre 0,7 et 5,5 THz. D'autres molécules ont également été utilisées [5] pour générer un rayonnement à des fréquences inférieures à 1,3 THz. Le choix de la fréquence THz émise est basé sur une figure de mérite, le facteur de gain moléculaire, qui quantifie le « potentiel lasant » de chaque paire de transitions pompe/laser [4].

Ce prototype laser a été mis œuvre en tant qu'oscillateur local dans un spectromètre hétérodyne [6]. Celui-ci est développé dans le cadre du projet HEROES pour le synchrotron SOLEIL, en tant que futur outil d'analyse haute résolution de la ligne AILES. Nous présenterons les spectres hétérodynes haute résolution obtenus pour le méthanol entre 1 et 3,4 THz.

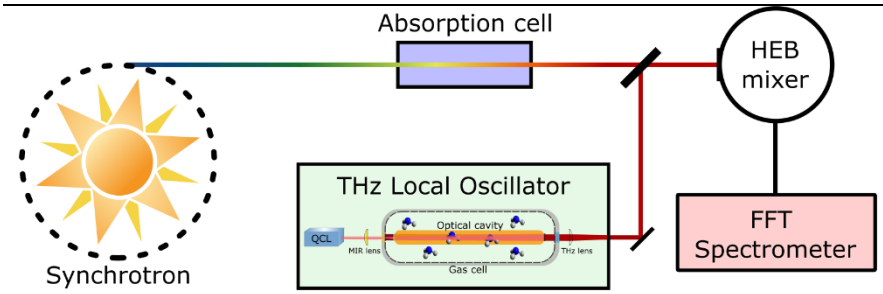

Figure 1 : Schéma de principe du spectromètre hétérodyne THz. Le rayonnement synchrotron est partiellement absorbé par le gaz d'intérêt, avant d'être mélangé avec la radiation du laser moléculaire via un bolomètre à électron chaud (HEB). Le spectre hétérodyne est enregistré à l'aide d'un spectromètre à transformée de Fourier rapide.

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* correspondant : mmammez@univ-littoral.fr

Interactions of atmospheric pollutants with water: 4-methyl-2-nitrophenol and its water complex studied by microwave spectroscopy and quantum chemistry

Eléonore Antonelli[1], Isabelle Kleiner[1], Ha Vinh Lam Nguyen[1] and Maria Eugenia Sanz[2]

[1] *CNRS UMR 7583, Université Paris-Est Créteil, Université Paris Cité, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France*

[2] *Department of Chemistry, King's College London, London, United Kingdom*

The microwave spectrum of 4-methyl-2-nitrophenol was measured by a molecular jet chirped-pulse Fourier transform microwave (FTMW) spectrometer working in the frequency range from 2 to 8 GHz an a resonator FTMW spectrometer from 2 to 26 GHz. Quantum chemical calculations were performed at the B3LYP-D3BJ/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory to obtain optimized molecular geometries. Large tunneling splittings arising from the low barrier to internal rotation of the methyl group. Hyperfine structures of the rotational effects, resulting of the quadrupole effect of the nitrogen were observed. The splittings were analyzed and fitted using the *XIAM* and the *BELGI-C_s-hyperfine* codes to measurement accuracy. The deduced V_3 potential value of 100 cm^{-1} is in reasonable agreement with the values predicted by quantum chemistry.

Microwave spectra of dinitrotoluene isomers: a new step towards the detection of explosive vapors

Mhamad Chrayteh[1*], Pascal Dréan[2], Manuel Goubet[2], Anthony Roucou[1], Arnaud Cuisset[1*]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*
[2] *Physique des Lasers Atomes et Molécules, PhLAM, UMR8523, Université de Lille, CNRS, F-59000 Lille, France*

The spectroscopic characterization of explosives taggants, like nitrotoluenes (NT) used for the TNT detection, is a research subject of growing interest. Recently, the spectroscopic studies of the three NT isomers in the microwave and millimeter-wave ranges were reported [1,2]. We present the gas-phase rotational spectroscopic study of weakly volatile dinitrotoluenes (DNT) isomers. The pure rotational spectrum of, 2,4-DNT and 2,6-DNT was recorded in microwave range (2-20 GHz) using a Fabry-Perot Fourier-transform microwave (FP-FTMW) technique coupled to a pulsed supersonic jet. The spectral analysis was supported by quantum chemical calculations carried out at the B98/cc-pvtz and MP2/cc-pvtz levels of theory. The spectra of DNT were complicated by the presence of two ^{14}N nucleus giving rise to congested hyperfine structures. The methyl group internal rotation barriers were calculated at the B98/cc-pvtz level of theory to be V_3=563 cm^{-1} and V_3= 696 cm^{-1} for 2,4- and 2,6-DNT, respectively. Although no splitting due to internal rotation was observed for 2,6-DNT, several splittings were observed for 2,4-DNT and their analysis in under progress. The semi-rigid and the nuclear quadrupole couplings descriptions obtained from the spectral analysis are presented. An anisotropic internal rotation of the coupled $-CH_3$ and $-NO_2$ torsional motions, as already mentioned for 2-NT [1], will be discussed for 2,4-DNT.

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* correspondant : mhamad.chrayteh@univ-littoral.fr; cuisset@univ-littoral.fr

Conférence grand public

L'odyssée d'une bulle de champagne

Gérard Liger-Belair[1*]

[1] Equipe Effervescence & Champagne, GSMA (UMR CNRS 7331)
Université de Reims Champagne-Ardenne, France

En moyenne, ce sont près de dix bouchons de champagne qui sautent chaque seconde à l'échelle du globe ! Et ce chiffre explose bien entendu le jour de la Saint Sylvestre. Depuis quelques années maintenant, le champagne et les vins effervescents au sens large connaissent un essor sans précédent. La valse des bulles dans une flûte n'est pas étrangère à cet incroyable engouement. L'effervescence qui agite votre verre engendre une kyrielle de phénomènes d'une complexité insoupçonnée, qui met en éveil tous vos sens. Je vous propose une vue d'ensemble des phénomènes qui accompagnent une dégustation de champagne, depuis le débouchage de la bouteille [1], jusqu'à l'éclatement d'une bulle, en passant par le rôle essentiel du verre en dégustation [2]. Profondément inscrite dans l'imaginaire collectif, la bulle de champagne devient prétexte à une flânerie scientifique qui vous entraînera dans le monde fascinant des gaz dissous, des changements de phase et des fluides en mouvement. Nous montrerons aussi en quoi ces travaux sur l'effervescence dépassent le cadre d'une simple flûte de champagne, pour trouver des analogies et des applications possibles dans des domaines très inattendus (à la surface des océans, et même jusqu'aux confins du système solaire). Vous allez découvrir la valse des bulles comme vous ne l'avez encore jamais vue. Bon voyage au cœur de l'effervescence !

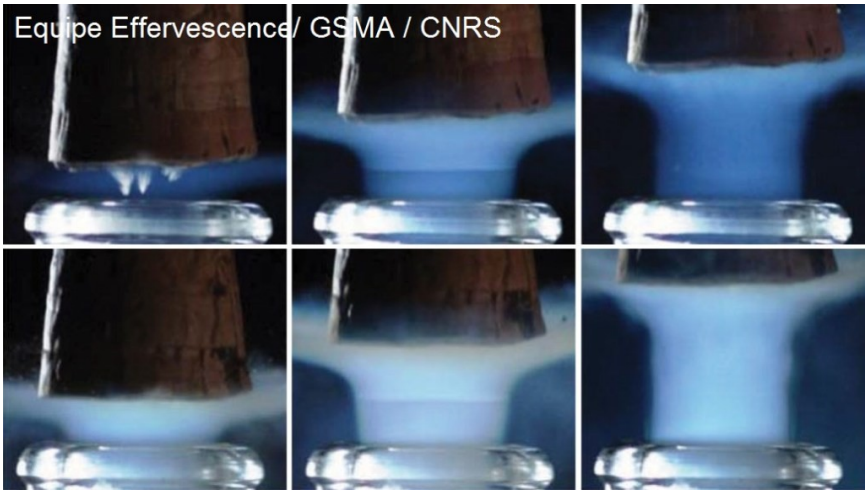

Figure 1 : Lorsque le bouchon saute, dans certaines conditions de température et de pression, le gaz carbonique sous pression dans le goulot d'une bouteille de champagne se transforme en cristaux de glace carbonique (mis en évidence ici par imagerie haute-vitesse). Dans le sillage du bouchon qui saute, on distingue même une onde de choc transversale, caractéristique des écoulements supersoniques.

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* correspondant : gerard.liger-belair@univ-reims.fr

Session 8

chairman : Marc Briant

Multiscale modeling approaches for the protein-solid interface

Sophie Sacquin-Mora[1*]

[1] *Laboratoire de Biochimie Théorique, CNRS UPR9080*
Institut de Biologie-Physico Chimique, Paris

The adsorption of proteins on solid surfaces remains a complex but central issue in the biomaterials field, which requires us to understand this process at the atomic level. In particular, designing efficient devices using immobilized proteins requires us to grasp details of the protein-solid interface, such as the adsorbed enzyme orientation, the stability of the adsorption and its consequences on the protein function [1]. Such information can be obtained using molecular modeling approaches on different scales, either with classical all-atom Molecular Dynamics simulations, or with coarse-grain calculations based on Elastic Network Models [2]. Applications on [NiFe]-hydrogenases (which catalyze hydrogen oxidation) [3-4] and copper-billirubin oxidase (which catalyzes oxygen reduction) [5] show how simulations give us insight on factors determining enzymes orientation on the electrode surfaces, and how the adsorption on a solid surface can impact proteins structure, dynamics and mechanical properties, and therefore their catalytic activity. Furthermore, simulations on β-glucosidase A (a central enzyme for cellulose degradation) adsorbed on bare and SAM-functionalized gold surfaces highlight how one must find an acceptable stability-activity trade-off when working with immobilized enzymes [6].

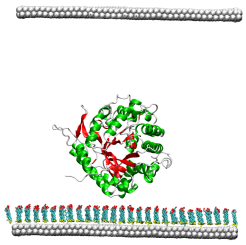

Figure 1 : Adsorption of the enzyme β-glucosidase A on a gold surface functionalized with SAMs

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* correspondant : sacquin@ibpc.fr

Mapping the electronic transitions of protonation sites in peptides using NEXAMS

J. Leroux[(a,b,e)1], A. Kotobi[(a)], K. Schubert[(a)], C. Mahecha[(f)], F. Trinter[(c)], I. Unger[(d)], J.-C. Poully[(e)], L. Schwob[(a)] and S. Bari [(a,b)]

[(a)] *Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany*
[(b)] *Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands*
[(c)] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*
[(d)] *Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden*
[(e)] *Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, CIMAP, Caen, France*
[(f)] *Hamburg University of Technology, Institute of Polymers and Composites, Hamburg, Germany*

Proton transfer is a fundamental charge transfer process in Chemistry, and it is particularly important for biological molecules, since they usually contain basic groups (DNA, peptides, proteins…). Therefore, in order to study charge dynamics in isolated biomolecules, it is crucial to determine the initial location of protons. Although it is now well established that protonation occurs primarily at nitrogens of the most basic side chains (arginine, histidine, lysine) of protonated peptides, in the absence of such group or in the case of multi-fold protonated species, the N-terminus and the peptide backbone oxygens can compete for the proton(s). This is for instance the case in protonated Ac-Ala, as IR multiphoton dissociation (IRMPD) coupled to quantum-chemical calculations has demonstrated.[1] This methodology has been extensively used for the determination of protonation sites but also geometrical structure of biomolecules in the gas phase.[2] However, the fragmentation yield falls rapidly with the number of atoms in the molecule, since IRMPD is a statistical process. Thus, there is a need for other methods able to determine the protonation sites of large systems.

In this context, near-edge X-ray absorption mass spectrometry (NEXAMS) is a promising technique as it provides a local probe into the atomic environment. NEXAMS is based on the electronic excitations of core electrons to unoccupied molecular orbitals and thus captures the electronic and geometric structure of a system under investigation. For instance, through photoabsorption around the nitrogen K-edge, it is possible to distinguish between the secondary and primary amine groups of proline and glycine, respectively.[3] In order to map the electronic transitions of the different protonation sites in peptides, we studied, experimentally and theoretically, the following tailored peptides: Gly-Gly-Gly-Gly-Xxx where Xxx is the basic residue Arginine, Histidine or Lysine (i.e. the singly-protonated peptides contain a protonated side chain and a non-protonated N-terminus), Pro-Gly-Gly-Gly-Gly and Gly-Gly-Gly-Gly-Gly (protonation on N-terminus), Ac-Gly-Gly-Gly-Gly-Gly (backbone protonation) and Gly-Gly-Gly (controversial protonation site)[4],[5].
The NEXAMS experiments have been carried out at the P04 soft X-ray beamline of the PETRA III synchrotron (DESY, Hamburg, Germany) using our home-built tandem mass spectrometer and at the UE52_PGM Ion trap endstation of the BESSY II synchrotron (HZB, Berlin, Germany). The analysis was supported by calculations of the electronic transitions of the most stable conformers obtained with a REMD (Replica Exchange Molecular Dynamics) method. Results obtained on the custom-made peptides at the nitrogen K-edge will be presented.

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1 juliette.leroux@desy.de

QUANTUM CHEMICAL INVESTIGATION OF INTRAMOLECULAR HYDROGEN BONDS IN OXYGENATED AROMATIC MOLECULES: INFLUENCE OF RING SIZE, DONOR/ACCEPTOR GROUPS AND SUBSTITUTANTS

Jonas Bruckhuisen[1*], Cecilia Gomez Pech[1], Valérie Vallet[2], Malgorzata Olejniczak[3], Arnaud Cuisset[1], Manuel Goubet[2], and Guillaume Dhont[1]

[1]Université du Littoral Côte d'Opale, UR4493, LPCA, Laboratoire de Physico-Chimie de l'Atmosphère, 59140 Dunkerque, France
[2]Université de Lille, CNRS, UMR8523, PhLAM, Physique des Lasers Atomes et Molécules, 59000 Lille, France
[3]University of Warsaw, Centre of New Technologies, 02-097 Warsaw, Poland

Hydrogen bonds (HBs) are important for a broad range of applications and play a fundamental role in structural chemistry and biology. HB interactions, dynamics and their directionality are discussed for almost one century and there is still a need for further experiments and theoretical investigations to fully encompass this complex interaction. Especially the experimental investigation of weak intramolecular HBs of isolated molecules in the gas phase remains challenging. Quantum chemical tools are needed to support high resolution THz and IR spectroscopies which can reveal the influence of intramolecular HBs on the rovibrational dynamics[1]. In this work we focus on intramolecular HBs of oxygenated aromatic molecules. They are investigated through a combination of quantum theory of atoms in molecules QTAIM[2], non-covalent interactions NCI[3], natural bond orbitals NBO[4], and topological data analysis TDA[5]. We studied the influence of the substitutants, of the donor or acceptor groups and of the number of atoms included in the ring formed by the HB. We relate our findings with recent rovibrational measurements in catechol (1,2-dihydroxybenzene) and guaiacol. We provide an overview of the problems arising while studying weak intramolecular HBs stabilizing oxygenated aromatic compounds and we discuss the performance of the different quantum chemical tools.

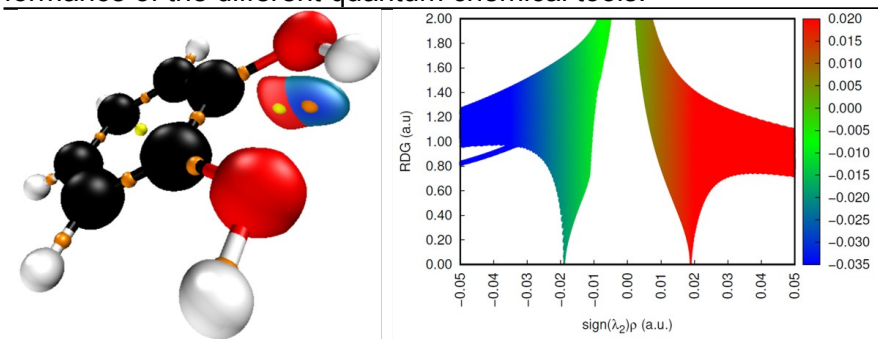

Figure 1: left: bond critical points (orange dots) and ring critical point (yellow dot) of the electron density of catechol; right: NCI analysis of intramolecular HB in catechol. Level of theory: CCSD/VDZ, reduced density gradient isovalue =0.5.

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* correspondant : jonas.bruckhuisen@univ-littoral.fr

UV spectroscopy of highly aliphatic naphthalene derivatives and perspectives as new carrier for the interstellar bump.

J. Fréreux[1], Z. Jia[2], M. Godard[2], E. Dartois[2], T. Pino[2]

[1] : Institute of Condensed Matter and Nanosciences (ICMN), UC Louvain, Chemin du Cyclotron 2, bte L7.01.07, 1348 Louvain-la-Neuve, Belgium

[2] : Institut des Sciences Moléculaires d'Orsay (ISMO) - UMR 8214, Université Paris-Saclay, Rue André Rivière, bte 520, 91405 Orsay cedex, France

The UV bump is a large absorption feature observed in the interstellar medium (ISM). This signature shows a fixed position at 217.5 nm but large variation on its FWHM can be observed (8000 cm^{-1} to 11 000 cm^{-1}) [1]. The interstellar bump is widely assigned to aromatic carbons transitions $\pi^* \leftarrow \pi$ but the exact shape of the carriers remains under discussion. In the Nanograins experimental setup at ISMO laboratory [2], a stationary combustion process stabilized at low-pressure by a McKenna burner allows us to produce a large variety of aromatic species, especially Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives. UV electronic transitions and mass of the produced molecules can be recorded through Resonance Enhanced MultiPhoton Ionisation (REMPI) spectroscopy which is done in the extraction chamber of our homemade Time of Flight Mass Spectrometer (ToF-MS).

Results are focused on a large mass distribution starting from mass 128 u up to 394 u with 14 u step. Most species from this distribution exhibit a common electronic transition profile centered at 220 nm with FWHM of 1400 cm^{-1}. This mass distribution is assigned to naphthalene derivatives with heavy aliphatic carbons substitutions and the electronic profile is assigned $\pi^* \leftarrow \pi$ transition from naphthalene aromatic cycles. Except the narrower FWHM, the common electronic transition profile shows a good comparison to the mean extinction of the interstellar bump feature. With supports from previous studies in the literature, these new results allow us to propose a new family of carrier for the bump interstellar feature.

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Session 9

chairman : Manuel Goubet

Mesure expérimentales des effets électroniques de ligands dans les complexes organométalliques

Héloïse Dossmann*

Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France

En catalyse organométallique, les ligands sont connus pour jouer un rôle essentiel dans l'orientation de la réactivité du centre métallique grâce à leurs propriétés électroniques et stériques. Une description précise de ces effets peut ainsi être nécessaire pour permettre une mise au point très fine des chemins de réactions catalytiques. Pour décrire ces effets, le modèle de Dewar-Chatt-Duncanson (DCD) est généralement le plus utilisé et décompose en termes d'effet donneur σ et accepteur π l'interaction du ligand avec le métal [1]. Plusieurs méthodes expérimentales et théoriques se sont employées à mesurer ces effets afin de pouvoir classer les ligands en fonction de leur capacité à enrichir le centre métallique mais peuvent parfois présenter des limitations en termes de sensibilité et concernant le type de systèmes auxquelles elles peuvent s'appliquer.

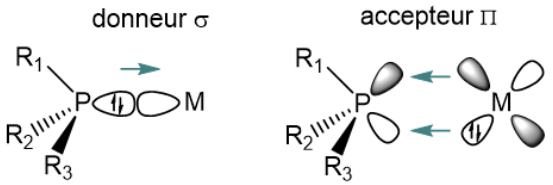

Schéma 1. Interaction métal-ligand (phosphine) décrite par le modèle DCD.

Notre équipe s'intéresse ainsi depuis plusieurs années au développement de méthodologies expérimentales afin d'accéder à de nouveaux descripteurs des effets électroniques de ligands dans des complexes organométalliques ([2]-[4]). Les approches utilisées se basent sur la spectrométrie de masse et les techniques d'activation d'ions (CID (collision-induced dissociation), HCD (higher-collision dissociation), BIRD (blackbody infrared radiative dissociation),..) ainsi que sur la spectroscopie de photoélectrons sélectionnée en masse accessible au centre synchrotron SOLEIL. Des calculs complémentaires de structures électroniques et descriptives de liaison par analyse de décomposition en énergie aident à l'interprétation des résultats. Ces méthodes seront présentées et illustrées par des résultats obtenus sur des complexes d'or, de molybdène et de fer.

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* *heloise.dossmann@sorbonne-universite.fr*

Modelling prebiotic molecules trapped in interstellar ice.

New DFTB/MM (QM/MM) Hybrid Method and Real Time – TD-DFTB in deMonNano : implementation and first applications.

Maysá Yusef Buey[1], Tzonka Mineva[2],Mathias Rapacioli[1]

[1] Lab. Chim. Phys. Quant (LCPQ), Univ. Paul Sabatier, CNRS, Toulouse, France
[2] ICGM, Univ. Montpellier, CNRS/ENSCM, Montpellier, France.

Formation, distribution and behavior of complex organic molecules (COM's) in space is an important subject of research to the better understanding of the initial condition for the appearance of life on Earth. Furthermore, the study of high energy chemical processes in the interstellar medium (cosmic radiation's effect) and in solar system (solar wind's effect), is been of high interest [1].

The aim of this work is to study astrophysical molecules trapped in interstellar ice systems under the effect of high energy radiation. These ices are characterized by being large systems, with large number of atoms.

QM/MM hybrid method has become a very popular tool for molecular systems' simulations with a large number of atoms, appearing as a good compromise between accuracy and computational costs. We report the implementation of QM/MM hybrid method [2] in the deMonNano software, using the Density Functional based Tight Binding (DFTB) [3,4], an approximated DFT scheme, combined with Molecular Mechanic (MM) approach, namely Force Fields (FF) of class 1, such as OPLS-AA and AMBER-families of FFs. A complete implementation was performed using the QM/MM additive coupling scheme [5].

In addition, the investigation of high energy chemical processes requires the explicit simulation of the electronic dynamics beyond the Born Oppenheimer approximation [6].
As first step towards such dynamics, we will report the implementation of Real Time TD-DFTB in deMonNano, consisting in solving the Time-Dependent Schrödinger equation within the DFTB [7], where the electronic density matrix is propagated along time.

We report a brief introduction to new DFTB/MM and RT-TD-DFTB implementations as well as the first applications on glycine prebiotic molecule trapped in an interstellar ice. PAH and hydantoin interstellar systems will be a matter of future studies.

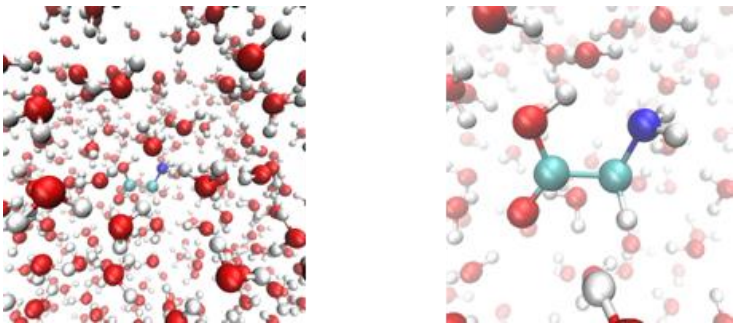

Figure 1 : Glycine molecule trapped in an interstellar ice.

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* correspondant : myusef@irsamc.ups-tlse.fr

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

Haoyue Sun, Isabelle Kleiner, Martin Schwell, Ha Vinh Lam Nguyen

Université Paris Cité, Univ Paris Est Créteil, CNRS, LISA, Paris, France

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.

* correspondant : hsun@lisa.ipsl.fr

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Session 10

chairman : Céline Toubin

Gas hydrates: naturally occurring water-gas assemblies

Arnaud Desmedt[1],
Charlène Guimpier[1], Art-Clarie Constant Agnissan[1,2], Cyrielle Métais[1,3,4], Claire Petuya[1], Ludovic Martin-Gondre[4], Jacques Ollivier[3], Françoise Damay[5], Vivian Nassif[3], Thomas Hansen[3], Livio Ruffine[2]

[1] *Groupe Spectroscopie Moléculaire, ISM UMR5255 CNRS – Univ. Bordeaux*
[2] *IFREMER, Brest*
[3] *Institut Laue Langevin, Grenoble*
[4] *UTINAM UMR6213 CNRS – Univ Franche-Comté*
[5] *Laboratoire Léon Brillouin, UMR12 CNRS – CEA, Saclay*

The natural occurrence of large quantities of gas hydrates in deep oceans, permafrost and plausibly in planets or comets of the solar system, is certainly at the origin of numerous developments and researches on gas hydrates in fields ranging from physical-chemistry, geosciences or astrophysics to chemical engineering and innovative technologies [1,2]. Gas hydrates are ice-like systems made of water molecules forming nano-cages stabilized by the encapsulation of foreign molecules. At a fundamental level, the understanding of their physical-chemistry properties (trapped-gas selectivity, kinetics formation mechanism, influence of sedimentary matrices, etc.) is of prime importance to track the evolution of the abundances of species taking part in the compositions of hydrate-bearing deposits not only on Earth, but also potentially on extraterrestrial bodies. The understanding of their molecular interactions plays a key role, requiring multi-scale approaches and the combination of advanced experimental and theoretical approaches. The presentation will review recent physico-chemical results (e.g. metastability [3,4,5], molecular selectivity [6,7], formation kinetics [8,9], etc.) relevant in gas hydrates sciences and associated challenges in areas such as geosciences and astrophysics, through the investigated guest species (CO, N_2, CO_2, CH_4, etc.) and through the investigations of gas hydrate/sediment surrogates mimicking their natural environments.

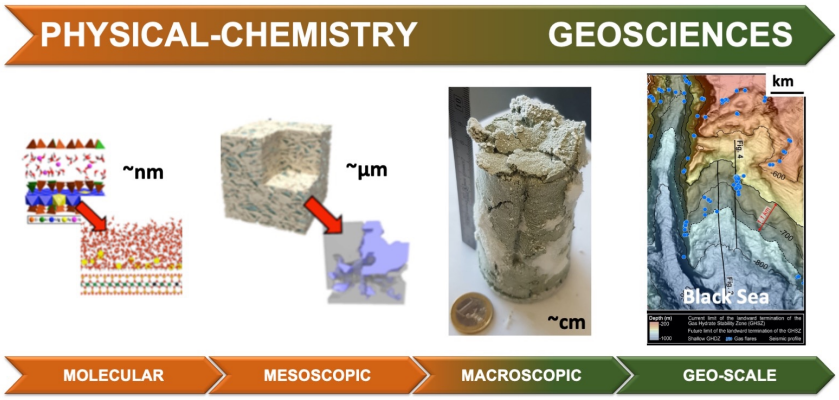

Illustration of the multi-scale investigations required for understanding the formation of gas hydrate in natural environment on Earth.

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* correspondant : arnaud.desmedt@cnrs.fr

Molecular dynamics investigation of the influence of surfactants on halogens propensity at the air-water interface

R. Abouhaidar[1*], C. Toubin[1], D. Duflot[1]

[1]*Laboratoire de Physique des Lasers, Atomes et Molécules (PhLAM, UMR 8523 CNRS), Université de Lille. Lille, F-59000, France*

In the atmospheric environment, both organic and inorganic compounds are present and have a strong influence on the chemical composition of the troposphere. On the other side, the ocean surface water and sea mist spray are enriched with surface active organic compounds, which may have a significant effect on the distribution of halide ions at the interface [1,2]. For instance, the abundance of bromide (Br^-) ions at the interface is implicated in halogen activation processes relevant for the ozone budget in the troposphere [3]. In this context, we evaluate the surface affinity of cationic hexylammonium, neutral hexylamine, and anionic propylsulfate at the air/liquid interface, and the effect of these ionic surfactants on the abundance of bromide at interfaces. Inspired by liquid X-ray Photoelectron Spectroscopy (XPS) experiments, we conducted Molecular Dynamics (MD) simulations and we were able to speculate about the distribution of these species between bulk and surface area in aqueous systems. Here, the results are in good agreement with the experimental ones, which clearly advocate that those organic molecules dislike the bulk and prefer to reside near the free surface; indicating the effect of salting. In contrast, both solutions containing hexylammonium and hexylamine show an enhancement of the surfactant bromide concentration while the propylsulfate solution do not alter the bromide concentration. In parallel, the same results were observed in the presence of NaCl. These results demonstrate that molecular level properties bring valuable insights on the interfacial behavior of organic and inorganic species on water films, that can be transposed to aerosol particles.

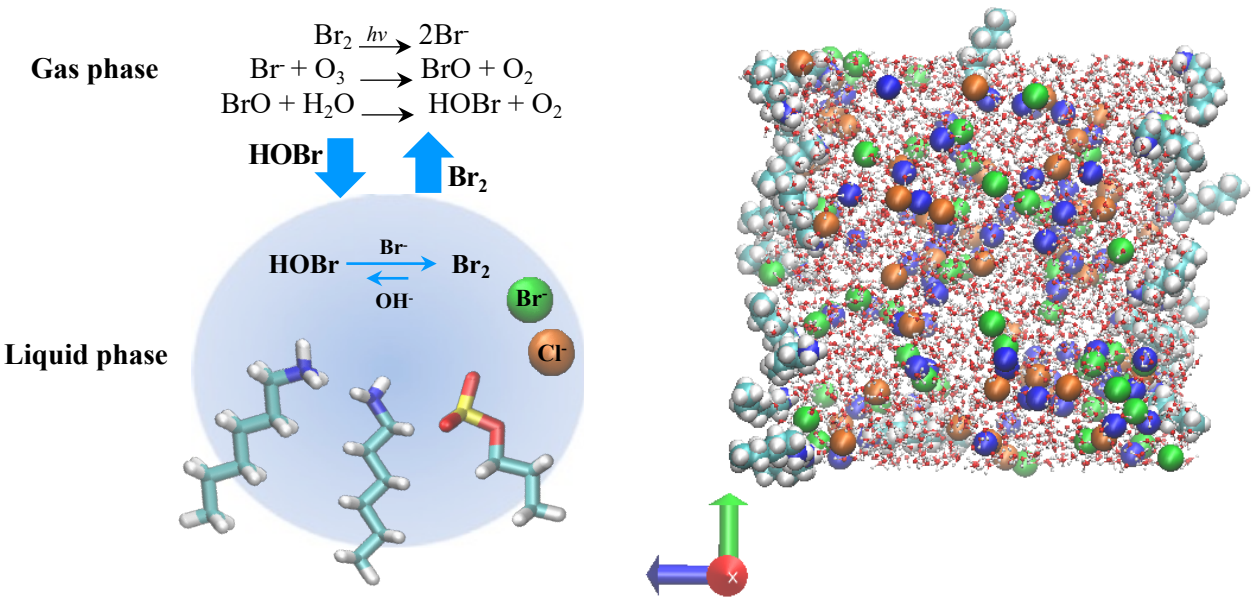

Figure 1: (a) The influence of surfactants on halogen propensity at the air-water interface. (b) Molecular view of a hexylammonium bromide with NaCl aqueous solution. Color code for the ions: Br^-: green, Cl^-: orange, and Na^+: blue.

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*corresponding author : rawan.abouhaidar@univ-lille.fr

Measuring the difference in collisional excitation of He with HCN and HNC through low temperature pressure broadening measurements

Brian M Hays[1,2*], Divita Gupta[1], Theo Guillaume[1], Omar Abdelkader Khedaoui[1], Ilsa R. Cooke[1], Franck Thibault[1], François Lique[1], and Ian R. Sims[1]

[1] Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes
[2] IMCN, NAPS, Université catholique de Louvain, 1348 Louvain-la Neuve, Belgique

The abundance ratio of HCN and its unstable isomer HNC are commonly observed throughout the interstellar medium, but strangely HNC can be found to be more abundant in very cold environments. Recent scattering calculations have indicated that collisional excitation with common interstellar species, He or H_2, is very different between the two isomers despite the many similarities between HCN and HNC. We sought to measure the difference in collisional interaction with He using the chirped pulse in uniform flow technique. The two isomers were produced using pulsed laser photolysis within cold uniform flows of He and probed using a chirped pulse Fourier transform millimeter wave spectrometer operating ~90 GHz. Through fitting the free induction decay of HCN and HNC directly to obtain the T_2 decay time, we find that HCN and HNC have different pressure broadening cross sections with He between 10 – 70 K. These results are compared to high level *ab initio* calculations, showing good agreement over the measured temperature range. The results of these experiments and implications for observations in interstellar medium will be discussed.

Session 11

chairman : Pierre Carçabal

High-resolution terahertz spectroscopy of atmospheric compounds

Anthony Roucou[1*], Gaël Mouret[1], Francis Hindle[1], Guillaume Dhont[1], Robin Bocquet[1], Arnaud Cuisset[1]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère (LPCA), Université du Littoral Côte d'Opale (ULCO), France*

High-resolution gas phase terahertz (THz) spectroscopy of atmospheric compounds consists in measuring and analyzing molecular transitions between rotational energy levels within an electronic state and one or more vibrational states using light sources from the centimeter range to the far infrared (0.1-6 THz). In addition to provide accurate information on the structure and molecular dynamics, it allows to provide line lists of observed transitions in laboratory with a high degree of precision in order to feed the databases and guide atmospheric and astrophysical observations using telescopes or onboard instruments.

The sensitivity and frequency accuracy of THz techniques are currently showing progress for the study of heavy molecules or molecules in low concentration. Various THz techniques recently developped at the LPCA [1-5] applicated to the study of atmospheric compounds will be presented, in particular for the study of volatile organic compounds identified as secondary organic aerosols precursors in atmospheric simulation chambers (CHARME, LPCA-ONE) [6-9]. The ability of THz spectroscopy to study and monitor explosive taggants will be also discussed [10,11].

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* correspondant : anthony.roucou@univ-littoral.fr

JET-COOLED MID-INFRARED LASER SPECTROSCOPY OF CENTROSYMMETRIC TWO-RING PAHS

Sathapana CHAWANANON[1*],Pierre ASSELIN[1], Manuel GOUBET[2], Olivier PIRALI[3]

[1] CNRS, De la Molécule aux Nano-Objets: Réactivité,Interactions, Spectroscopies, MONARIS, Sorbonne Université, PARIS, France
[2] UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille,France
[3]Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France.

The recent detection of cyano naphthalenes within TMC-1 using radioastronomy[a] provided the first unambiguous confirmation of the interstellar PAH's hypothesis. In the mid-infrared (IR) domain, the James Webb Space Telescope launch opens exciting perspectives to collect information about polycyclic aromatic compounds. In this context, high resolution (HR) IR studies' enabling to resolve the rotational structure of vibrational bands of large aromatic species mainly used synchrotron-based Fourier Transform (FT) spectroscopy coupled to room temperature long path cells but the spectral analysis of such recordings remains very challenging. Nowadays, few set-ups combining HR IR spectroscopy with the supersonic jet technique were developed to target low volatile PAH compounds[b].

A recently implemented tunable mid-IR quantum cascade laser spectrometer coupled to a pulsed supersonic jet (SPIRALES set-up) allows recording the rotationally resolved spectra of large molecules at low temperatures. We report the jet-cooled rovibrational IR study of three centrosymmetric two-ring PAH molecules: naphthalene, 1,5-naphthyridine, and biphenyl in both regions of in-plane ring C-H bending and C-C ring stretching vibrations, enabling to extract of reliable spectroscopic parameters both in-ground and excited vibrational states. Comparison between experiment and quantum chemistry calculations give confidence in the predictive power of corrected calculated rotational parameters. Last, experimental inertial defects of naphthalene and 1,5-naphthyridine complemented by similar two-ring and larger species agree well with an extended Oka's empirical formula for estimating the inertial defects of aromatic ring compounds.

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Etude de la vanilline protonée/déprotonée en phase gazeuse

Alejandro Gutiérrez-Quintanilla[1], Christophe Jouvet[1], Alicia Infantino[2], Isabelle Compagnon[2], Jennifer Noble[1]

[1] *Laboratoire de Physique des Interactions Ioniques et Moléculaires, Aix-Marseille Université, Marseille, France*
[2] *Institut Lumière Matière, Université Claude Bernard Lyon 1, Lyon, France*

Les processus de protonation et déprotonation dans les dérivés de systèmes aromatiques sont jouent un rôle important dans différents domaines de la chimie, notamment en biochimie. La « compétition » entre différents centres pour accepter ou donner un proton dépend des plusieurs paramètres qui impliquent notamment des effets de la densité électronique. On dit que différents tautomères peuvent être formés. Au même temps, la photophysique du système dépendra du tautomère présent. La vanilline est un système modèle où trois groupements fonctionnels avec des caractéristiques différentes sont présents (cf. Figure 1). Dans ce travail, on s'est intéressé d'abord à déterminer, en utilisant différentes techniques laser d'action (IRMPD, et UVPD en piège à ion cryogénique), les tautomères protonés et déprotonés formés dans la vanilline à partir d'une source éléctrospray. Les résultats montrent que le site de protonation observé se trouve sur l'oxygène du C=O, tandis que le site de déprotonation est au contraire sur l'oxygène du groupe OH [1]. L'analyse de résultats a permis également de déterminer sans ambiguïté le conformère produit dans les conditions expérimentales utilisées. Ces résultats sont en accord avec l'ordre de stabilité prédit par les calculs théoriques au niveau de la DFT. De plus, pour la forme protonée, les calculs théoriques et l'expérience indiquent une spectroscopique similaire à celle du benzaldéhyde (benzène avec groupe HC=O) protoné quant à l'absorption électronique, mettant en évidence l'influence importante du groupement HC=O sur la photophysique du système. En revanche, la photophysique de la éspece déprotonée anionique est comparé avec celle du phénol déprotonée. Certains défis trouvés dans l'analyse de l'espèce déprotonée (p.ex. l'interprétation du spectre IRMPD) seront également discuté.

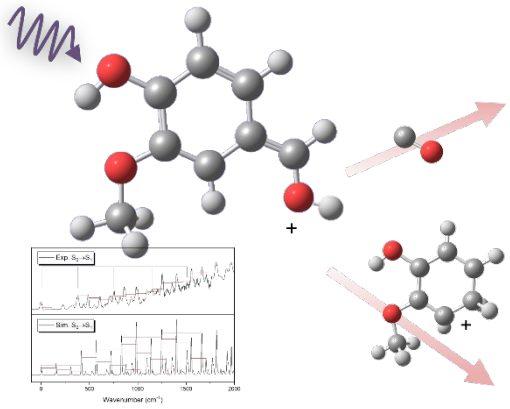

Figure 1 : Structure observé de la vanilline protonée, avec l'un des voies de photofragmentation observés lors des excitations électroniques. C gris, O rouge, H blanc.

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Poster Session

Measurements of Line Intensities and self-broadening coefficients in the ν_2, ν_5 and $\nu_3+\nu_6$ Bands of Methyl Iodide

O. Ben Fathallah[1,2*], F. Hmida[1,2], A. Boughdiri[1,2], L. Manceron[3], M. Rotger[2] and H. Aroui[1]

[1]*Laboratoire de Spectroscopie et Dynamique Moléculaire, Université de Tunis, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av Taha Hussein, 1008 Tunis, Tunisia.*
[2]*GSMA, UMR CNRS 7331, Université de Reims Champagne Ardenne, Moulin de la Housse B.P. 1039, F-51687 Reims Cedex 2, France.*
[3]*Synchrotron Soleil Ligne AILES, BP 48, 91192 Cedex Gif-sur-Yvette, France and MONARIS, UMR 8233 CNRS-UPMC, case 49, 4 place Jussieu, 75252 Cedex Paris, France.*

Halogenated hydrocarbons have been recognized as important species in atmospheric studies. Among these halocarbons, methyl iodide (CH_3I) is the most abundant iodine-containing compound, emitted primarily by the oceans [1]. It is likely to play an important role in the budget of tropospheric ozone, through production of iodine by photolysis.

All these reasons give a great interest to measure spectroscopic parameters of this molecule.

In this work, we present measurements of absolute intensities and self-broadening coefficients of ro-vibrational lines in the ν_2, ν_5 and $\nu_3+\nu_6$ bands of CH_3I (1280 - 1600 cm^{-1}).

The spectra were recorded with a high-resolution Fourier transform spectrometer at T = 297.6 K in the spectral region from 1280 to 1600 cm^{-1}.
To retrieve line parameters, a multi-pressure fitting technique using a Voigt profile was used to fit a series of five spectra at pressures ranging; from 1.15 to 9.98 mbar of about 1326, 900 and 225 transitions for the ν_2, ν_5 and $\nu_3+\nu_6$ bands respectively, with $2 \leq J \leq 70$ and $0 \leq K \leq 13$.
The rotational dependencies of line intensities were analyzed and used to derive the transition dipole moments squared for each line. The analysis of these moments using the theoretical model of Watson [2], allows us to derive a consistent set of line intensity parameters such as vibrational transition moments, band intensities as well as Herman-Wallis coefficients for each band. The results were compared with previous works.

The average accuracies have been estimated to be about 5 % for the three studied bands of the CH_3I line intensities.

The rotational dependencies of self-broadening coefficients have been clearly observed and modeled using the Starikov empirical model [3]. The average accuracies have been estimated to be about 5 % for the ν_2 band and 7 % for the other two bands.

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Correspondant: *Ons.ben.fathallah.1994@gmail.com
*Ons.ben-fathallah@univ-reims.fr

Utilization of a THz ultra-sensitive spectrometer for trace gas detection

Coralie Elmaleh[1*], Fabien Simon[1], Arnaud Cuisset[1], Francis Hindle[1], and Gaël Mouret[1]

[1] *Université du Littoral Côte d'Opale, UR 4493, LPCA, Laboratoire de Physico-Chimie de l'Atmosphère, F-59140 Dunkerque, France*

Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring-Down Spectroscopy (CRDS) are well established as very sensitive methods for the measurements in the infrared domain of gas phase compounds at trace level from their rovibrational signatures [1, 2]. The recent successful development of a THz Fabry-Perot spectrometer [3] shows that such techniques can be applied to the THz and submillimeter wavelength allowing the rotational transitions of light polar compounds to be probed.

We will report the first THz-CRDS measurements, performed with a cavity composed of a low-loss corrugated waveguide with high reflectivity photonic mirrors. A finesse of 3500 was obtained around 620 GHz, providing an effective path length of one kilometer. The figure 1 shows the absorption of a 640 ppb calibrated mixture of HCN demonstrating a limit of detection (LOD) around 10 ppb, confirmed by the detection of the minor isotopologue $H^{13}CN$ in natural abundance of 1%.

In addition, we will also demonstrate the possibility to resolve hyperfine structure using cavity enhanced spectroscopy. High-resolution sub-Doppler saturated-absorption Lamb dips were measured at pressures of no more than 6µbar on rovibrational lines of C_2H_5OH in the submillimeter-wave region from 550 to 600 GHz (Fig. 2).

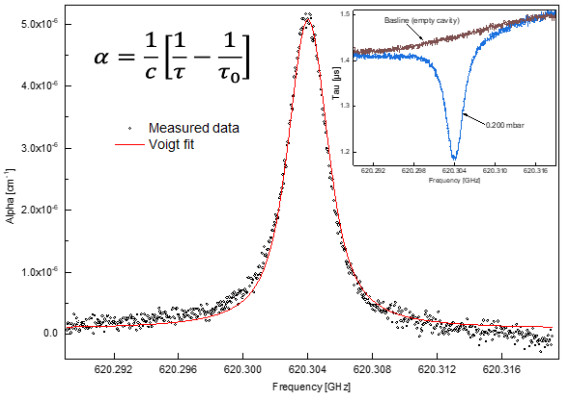

Figure 1 : HCN (J=7-6), 620,3040952 GHz, 301,3µbar

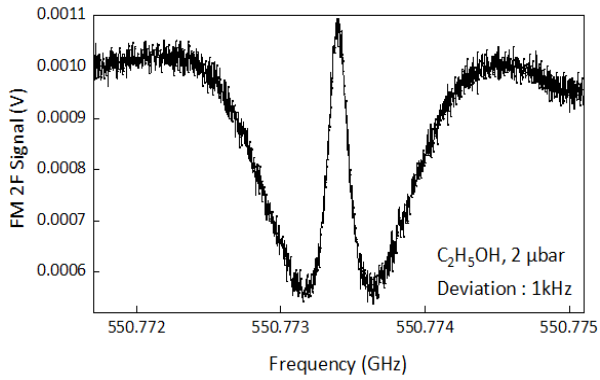

Figure 2 : Lamb dip with C_2H_5OH (J=4-3), 550.7734062 GHz, 2µbar

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* correspondant : coralie.elmaleh@univ-littoral.fr

Is neutral C_{60} molecule a carrier of the diffuse interstellar bands?

J. Lecomte[1], L. Rutkowski[1], S. Kassi[2], S. Chakraborty[1], A. Benidar[1], L. Biennier[1], R. Georges[1]

[1]*Dpt. Physique Moléculaire, Institut de Physique de Rennes, CNRS/Université Rennes 1, France*
[2]*LAME, Lab. Interdisciplinaire de Physique, CNRS/Université Grenoble-Alpes, France*

The diffuse interstellar bands (DIBs) are unassigned absorption features that were first observed in the interstellar medium (ISM) by Marie Lea Heger in 1922 [1]. Nowadays, more than six hundred absorption bands have been detected in the ISM, both in the visible and in the near-infrared (NIR) spectral ranges, but only a few have been firmly assigned to an identified species. In 2015, Campbell *et al.* assigned unambiguously two DIBs to C_{60}^+ in the NIR [2]. Additionally, the fundamental vibrational emission bands of neutral C_{60} and C_{70} have been detected in a planetary nebulae by Cami *et al.* [3]. Therefore, the question arises whether these neutral molecules are also carrier candidates?

Spectroscopy of C_{60} in the gas phase has proven to be extremely challenging [4,5]. Practically, C_{60} comes in a solid sample that needs sublimation at 1000 K to reach the gas phase. The produced C_{60} molecules have consequently a large number of vibrational modes thermally excited. Given that C_{60} has 174 normal modes of vibration, its vibrational partition function quickly increases with temperature. This depletes the population of the ground vibrational state to the benefit of a multitude of excited levels. However, DIBs are unlikely to be assigned to hot bands but rather to cold ones, and their investigation requires efficient cooling of the high-temperature C_{60} vapour.

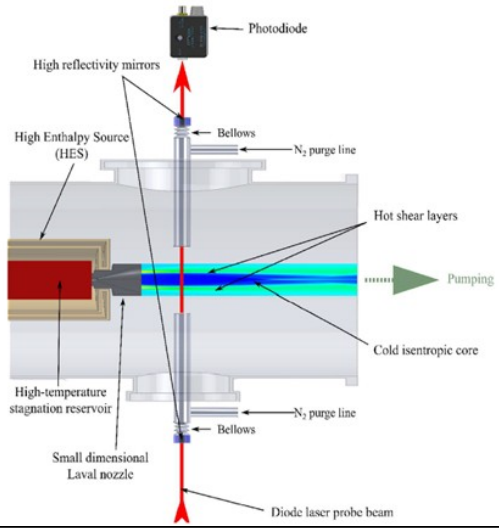

Figure 1: Laval Nozzle supersonic jet coupled with CRDS technique [6].

The FULLDIBS ANR funded project aims at combining gas jet cooling with a transverse cavity ring-down spectrometer (CRDS) (Fig. 1). The supersonic adiabatic expansion will be used to cool down the preheated C_{60} sample to a few tens of kelvins. The gas will be expanded through a Laval nozzle, yielding a number of molecular collisions four orders of magnitude larger than with a slit free-jet [4]. This is expected to enable an efficient vibrational relaxation which is of capital importance for cold bands detection. The cold gas will be generated at low densities (~10^{11} cm^{-3}) and the absorption path will be limited to a few cm by the transverse dimension of the Laval nozzle. Sensitivity high enough will be achieved by CRDS, which relies on a Fabry-Perot cavity trapping the light of a laser diode in the expansion chamber, therefore leading to an absorption path length of several hundred meters.

We will first focus on the fundamental band of C_{60} at 8.5 microns, which was already observed at low temperatures [5], before investigating the absorption bands in the NIR [7].

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Intensités et coefficients d'élargissement par la pression de raies de CH_3Br observées dans le domaine THz

Wilfried Tchana Betnga,[1,2 *] Francis Hindle,[1] Arnaud Cuisset,[1]
Fridolin Kwabia Tchana,[2] Jean Vander Auwera[3]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*
[2] *Laboratoire Interuniversitaire des Systèmes Atmosphériques, Université Paris Cite et Université Paris-Est Créteil, Créteil, France*
[3] *Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), C.P. 160/09, Université Libre de Bruxelles, B-1050 Brussels, Belgium*

Le bromure de méthyle (CH_3Br) présent dans l'atmosphère terrestre est d'origine naturelle et anthropique. Ses sources connues comprennent la production naturelle des océans (mais il se peut qu'ils en absorbent aussi) [1] et la combustion de la biomasse [2]. Le bromure de méthyle a également pour origine les additifs bromés contenus dans l'essence et est produit industriellement car utilisé pour la stérilisation des sols en agriculture [3]. CH_3Br est par ailleurs un gaz à effet de serre et contribue majoritairement au budget global du brome atmosphérique, directement impliqué dans la destruction catalytique de l'ozone. Du point de vue spectroscopique, CH_3Br a fait l'objet de plusieurs études, en particulier dans le domaine infrarouge, ayant résulté en paramètres spectroscopiques pour les isotopologues $CH_3{}^{79}Br$ et $CH_3{}^{81}Br$ [4-6].

Dans le cadre de ce travail, nous avons utilisé un spectromètre THz [7] pour enregistrer en AM et FM les spectres de rotation pure de CH_3Br en phase gazeuse, auto-perturbé et perturbé par N_2 et O_2. Les spectres en FM présentent une structure hyperfine. Une première analyse des spectres en AM a été effectuée, utilisant une méthode d'ajustement mono-spectre, pour extraire les paramètres de raies (intensités et coefficients d'élargissement). Par exemple, les valeurs du coefficient d'auto-élargissement mesurées dans la gamme de 70 à 110 GHz de la transition R(3,2) de $CH_3{}^{79}Br$ et $CH_3{}^{81}Br$ sont respectivement égales à 0.2602 (95) et 0.3688 (111) cm^{-1}/atm. Elles sont en accord avec les valeurs mesurées dans le domaine IR, respectivement égales à 0.2601 et 0.3610 cm^{-1}/atm [4]. L'analyse en cours des spectres en FM utilise une méthode d'analyse multi-spectres. L'ensemble des résultats obtenus seront présentés et discutés.

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* Correspondant : wtchana@lisa.ipsl.fr

Molecules probed with a slow chirped-pulse excitation: analytical model of the free-induction-decay signal

Guillaume Dhont[1*], Daniele Fontanari[1], Cédric Bray[1], Gaël Mouret[1], Arnaud Cuisset[1], Francis Hindle[1], Robin Bocquet[1], Kevin Hickson[2]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*
[2] *Institut des Sciences Moléculaires, Université de Bordeaux, Talence, France*

A chirped pulse experiment is a powerful means to rapidly obtain an high-resolution spectrum of molecules on a large frequency band. The theoretical paper from McGurk et al. [1] is the main reference paper to describe the polarization induced by fast chirped pulses generated with microwave sources.

We built a chirped pulse spectrometer operating at 200 GHz for astrophysical applications [2]. It works in the millimeter domain with slower chirped pulses. In such a situation, the paper of McGurk *et al.* does not capture all the physics involved in the polarization step. In particular, the intensity of a molecular transition is dependent on its temporal position inside the chirped pulse, as discovered by Abeysekera *et al.* [3].

A theoretical study of the polarization of molecules subjected to a slow chirped pulse is presented for three typical cases: the cell, the uniform flow and the molecular beam. Analytical expressions are proposed alongside the numerical solution and are used in the expression of the free induction decay signal. We test the analytical expression on the rotational emission spectra of OCS molecules. In the thermalized case, a relation between the pulse duration, the line position in the chirped pulse, and the signal amplitude is proposed to correct the line intensities [4].

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* correspondant : guillaume.dhont@univ-littoral.fr

Kinetics and thermodynamics insights in conformational relaxation from trap and release tandem-IMS measurements

Aurélien Le Fèvre,[1] Benjamin Tassignon,[2] Clothilde Comby-Zerbino,[3] Julien De Winter,[2] Pascal Gerbaux,[2] and Fabien Chirot[3]*

[1] *Institut des Sciences Analytiques, UMR5280 Université de Lyon, Université Claude Bernard Lyon 1, CNRS*
[2] *Organic Synthesis and Mass Spectrometry Laboratory, Interdisciplinary Center for Mass Spectrometry (CISMa), University of Mons, Mons, Belgium*
[3] *Institut Lumière Matière, UMR5306 Université de Lyon, Université Claude Bernard Lyon 1, CNRS Villeurbanne, France*

A classical route to the characterization of reaction kinetics and to the characterization of transition states consists in temperature dependent kinetics measurements. The evolution of reaction rates as a function of temperature can then be exploited to derive the relative enthalpy and entropy of the transition state. This procedure was largely exploited in the gas phase, especially to investigate ion fragmentation kinetics in thermalized ion traps. We recently demonstrated that this procedure can also be applied to characterize isomerization processes, based on tandem-IMS measurements, yielding detailed in sight in the conformational landscape of the investigated system.

We used a homemade dual-drift tube instruments in which IMS selected ions can be stored for a controlled duration at a controlled temperature before analysis by IMS-MS. The temperature of the ion trap can be controlled from room temperature to 250°C and processes with half-lives ranging from few milliseconds to several seconds can be investigated.[1]

Our trap and release procedure was applied to different classes of molecular species, displaying different types of conformational changes, ranging from “simple” cis-trans isomerization to large scale structural reorganization. The Eyring plot derived from such measurements as a function of temperature for a small azobenzene derivative is shown in Figure 1. We discuss the type of information that can be derived from such measurements as a function of the complexity of the system, of the number of conformational states involved, and on their relative stability. We also compare our results to more classical collision-induced isomerization experiments (often denoted collision induced unfolding, or CIU, in the case of proteins).

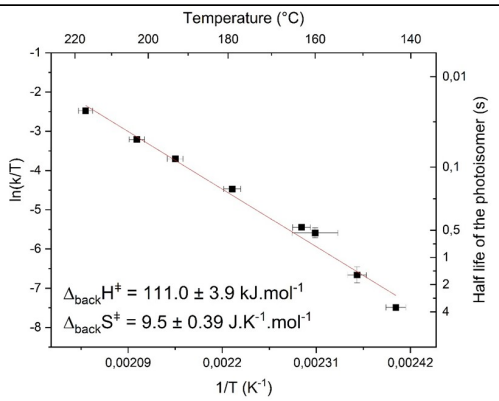

Figure 1 : Eyring’s plot for the back isomerization of an azobenzene derivative..

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* correspondant : fabien.chirot@univ-lyon1.fr

Millimeter-wave Fabry-Perot resonator for the detection of semi-volatile organic vapors

Fabien Simon*, Mhamad Chrayteh, Coralie Elmaleh, Francis Hindle, Gaël Mouret, Arnaud Cuisset

Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France

Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring-Down Spectroscopy (CRDS) are well established for sensitive infrared measurements of gas phase compounds at trace level using their rovibrational signatures.[1,2] The recent successful development of a THz Fabry-Perot spectrometer shows that such techniques may be employed at THz and submillimeter frequencies [3] to probe the rotational transitions of light polar compounds. Here we report on the development of a new millimeter resonator based on a low-loss corrugated waveguide (internal diameter 31,75 mm), with highly reflective photonic mirrors, obtaining a finesse above 3500 around 150 GHz. Cavity length is controlled thanks to one moving mirror mounted on a piezo stick-slip linear stage in the nanometer resolution range. With an effective path length of one kilometer, a significant sensitivity has been evaluated by the measurement of line intensities lower than 10^{-26} cm^{-1}/(molecule/cm^2). First spectroscopy measurements have been carried out with nitromethane, a degradation product of TNT. This spectrometer will be used to detect semi-volatile organic vapors at trace level which could not be envisaged with a conventional detection technique.[4,5]

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Acknowledgment: This work received financial support from the French Agence Nationale de la Recherche via funding of the project Millimeter-wave Explosive Taggant vapors Investigations using Spectral taxonomy (METIS) under contract number ANR-20-ASTR-0016-03.
* correspondant : fabien.simon@univ-littoral.fr

Collision induced dissociation of mixed water pyrene clusters

Arya Nair[1,2*], Sebastien Zamith[1], Christine Joblin[2], Alexandre Marciniak[1], Jean Marc L'Hermite[1]

[1]*LCAR, IRSAMC; Université de Toulouse; UPS; CNRS; F-31062 Toulouse, France*
[2]*IRAP, Université de Toulouse; UPS; CNRS; CNES; F-31028 Toulouse, France*

In photodissociation regions (PDRs) associated with star formation, the matter composed of gas and tiny dust particles is in strong interaction with the ultraviolet (UV) radiation from young stars. From previous infrared space missions such as the Spitzer telescope, we have observed the destruction of very small carbonaceous grains and the production of polycyclic aromatic hydrocarbons (PAHs) at the edge of these PDRs [1]. These carbonaceous nanograins come from the inner part of interstellar clouds where models predict a transition from gaseous to icy water [2]. Furthermore, clusters of PAHs are proposed as models for carbonaceous nanograins [3]. In order to get insight into the interaction of water with these carbonaceous nanograins we are performing experiments on water-PAH cluster complexes.

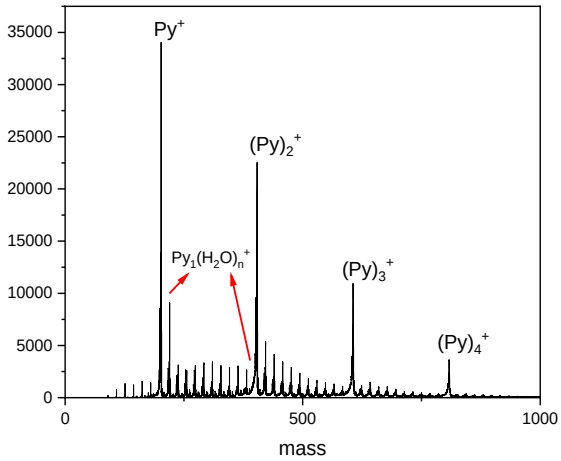

Figure 1: Mass spectrum of water pyrene clusters

In this work, we produce pyrene-water clusters in a gas aggregation source which was developed at LCAR [4]. Mixed water pyrene cluster ions are produced in the source prior to thermalization at 25K. An example of the produced species is presented in Figure 1. In the present conditions, clusters containing up to 28 water molecules and 4 pyrene molecules can be observed. Protonated species dominate the mass spectrum. We also observe contributions from dehydrogenated pyrene molecules. In order to study these species, we perform mass selection and vary the kinetic energy of the ions before they undergo collisions with inert gases (helium, neon). The products resulting from collision induced dissociation (CID) are analyzed by time-of-fight mass spectrometry.

CID cross sections when plotted as a function of the collision energy can give us access to the threshold for dissociation. Measurements were performed for complexes made of one pyrene molecule (non-dehydrogenated and dehydrogenated) and 1 to 5 water molecules. For the water pyrene clusters, we observe sequential water losses as the dominant channel. For clusters with dehydrogenated pyrene, hydroxypyrene is found to be the stable fragment.

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*correspondant : arya.nair@irsamc.ups-tlse.fr

Complex refractive index determination of PTFE, TPX and polypropylene windows for TeraHertz broadband spectroscopy

J. Bichon[1,2*], A. Pillet[1], A. Sklia[1,3], D. Petitprez[2], R. Peretti[1], S. Eliet[1]

[1] *Univ. Lille, CNRS, Centrale Lille, Univ. Polytechnique Hauts-de-France, UMR 8520 - IEMN, F-59000 Lille, France*
[2] *Univ. Lille, CNRS, UMR 8522 - PC2A - Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France*
[3] *3ENS Paris-Saclay, 91190 Gif-sur-Yvette, France*

Polymers are valuable materials in research for their exceptional properties such as durability and resistance. They are, for instance, widely used in optical assemblies as lenses or windows due to their transparency in the visible and TeraHertz range (THz). However, only few studies have calculated their complex refractive indices (CRI) and data from 3 to 10 THz is almost non-existent.

Broadband spectroscopy in the THz is of paramount importance in the study of aerosols and/or gases to understand current issues such as climate change or disease diagnosis [1]. Nonetheless, the analytical equipment needs windows with opto-mechanical requirements (e.g. withstand pressure, avoid degassing and maximize transmission). In this regard, three low-loss polymer candidates, i.e. polytetrafluoroethylene (PTFE – 2.5 mm thick), polymethylpentene (TPX – 2 mm) and polypropylene (PP – 50 microns), are analyzed with a TeraHertz Time Domain Spectrometer (THz-TDS). In comparison with other techniques, THz-TDS has the advantage of measuring the time-dependent amplitude E(t) and hence simultaneously acquiring the amplitude and the phase. The real and imaginary parts of their CRI are then extracted from the time-traces using the Fit@TDS software [2].

The CRI of PTFE from 0.2 to 3.3 THz is introduced in the figures below (fig.1). Our results demonstrate a broad absorption band of small oscillator strength characteristic of low-loss polymers. The figures show a Lorentz-shaped resonant absorption around 1 THz with a linewidth of 0.42 THz above a broad Boltzmann-shaped band of higher frequency.

During the conference, indices up to 5 THz will be presented for each polymer. Additionally, an overview of the dielectric, optical and mechanical properties of the three materials will be provided to enable proper comparison and benchmark of the windows.

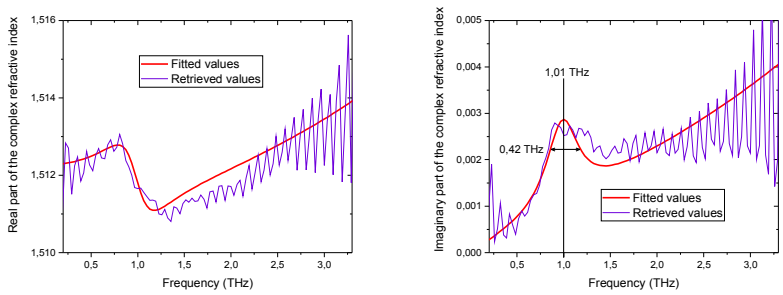

Figure 1 : The real and imaginary parts of CRI for 2.5 mm thick PTFE from 0.2 to 3.3 THz.

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* correspondant : jeyan.bichon@iemn.fr

Toward ab initio model potential for rare gas atoms and closed-shell molecules

Erwan Hochard[1*], Benoit Gervais[2], Julie Douady[3]

[1] *Faculté de physique - CIMAP, Université de Caen, Caen, France*
[2] *CIMAP, Centre de recherche sur les Ions, les Matériaux et la photonique, Caen, France*
[3] *Faculté de physique - CIMAP, Université de Caen, Caen, France*

Electric dipole moment (EDM) are sensitive probes for new physics beyond the Standard Model of particle physics. In the framework of EDMMA project led by Aimé Cotton laboratory in Orsay, we propose to investigate the EDM for Cs atoms embedded in a solid matrix of inert gas or molecular hydrogen, by means of hyperfine spectroscopy analysis. Those matrices offer unprecedented sample sizes while preserving some characteristics of an atomic physics experiment. As the EDM might be quite sensitive to the atomic trapping sites in the matrix, we investigate the trapping and its spectroscopic signature by numerical simulation. For this purpose, our first goal is to develop new 0- electron pseudo-potential for the noble gases similar to the ab initio model potential (AIMP) developed by Huzinaga, Seijo and Barandiaran [1]. Our model takes into account explicitly the direct Coulomb interaction, the static exchange, the Pauli repulsion and the polarisation effect without any parameter fitting. It is supplemented by a non-local corrective potential, which takes into account the correlation effects, adjusted on phase shifts obtained from electron scattering. We expect our approach to provide more transferable core polarisation pseudo-potentials (CPP) and to allow us to obtain reliable parametrisation for Kr and Xe. In the same way, we obtain 1-electron AIMP for alkali cores. Such an approach allows us to model accurately the spin-orbit coupling for the heaviest alkali, Rb or Cs. Moreover, our approach allows us to developed pseudo-potential for molecules, like H2 for example, which could be used for para-hydrogen matrices. We shall present our first results for alkali-rare gas dimer, which is the first benchmark of the developed model potentials. Our model potential results will be compared to ab initio calculation and experimental vibrational spectroscopy experiments.

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* correspondant : erwan.hochard@ensicaen.fr

High resolution rovibrational spectroscopy of jet-cooled PAH nitrogen derivatives

Pierre Asselin[1*], Sathapana Chawananon[1], Augustin Léger[2]

[1]*Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, Paris, F-75005 France*
[2]*Université Gustave Eiffel, 5 Bd Descartes, 77454 Champs-sur –Marne, France*

Polycyclic Aromatic Hydrocarbons (PAH) molecules, together with their numerous derivatives, in particular nitrogen ones (e.g. PANHs), have long been proposed as carriers of the so-called Aromatic Infrared bands observed in a large variety of astrophysical objects between 3 and 20 µm. The recent detections of benzonitrile [1) and cyano-naphthalenes [2] provided the first unambiguous confirmations of the interstellar PAHs hypothesis as well as the launch of the James Webb Space Telescope will open in near future exciting perspectives. In this context, new laboratory measurements, performed at high spectral resolution in the mid-infrared (IR) range, are mandatory to optimize the next exploitation of astronomical observations.

A tunable mid-IR quantum cascade laser (QCL) spectrometer coupled to a pulsed supersonic jet (SPIRALES set-up) recently implemented within the MONARIS laboratory allows recording the rotationally resolved spectra of large heavy molecules at low rovibrational temperatures.[3]

We report here the rovibrational jet-cooled study of a series of two-heterocycles PANHs with one (quinoline, isoquinoline) or two (quinazoline, quinoxaline) N-bearings in the region of characteristic in plane C-H bending and C-C (or C-N) ring stretching vibrations. Our first objective is to provide accurate excited state molecular parameters for such derivatives in support of astronomical observations. As well, an intriguing question arises in relation with previous centimeter, millimeter-wave and far-IR range studies about quinoline and isoquinoline of which c-type Coriolis interaction and Fermi resonances were evidenced between the lowest frequency out-of-plane vibrations.[4,5] Spectral investigations in the mid-IR range of higher frequency fundamental vibrations aim to determine if such perturbations could occur also within a- or b-type transitions of these low symmetry (C_s) PANHs.

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*corresponding author : pierre.asselin@upmc.fr

Broadband quartz enhanced infrared photodetector for tunable diode laser spectroscopy

Tingting Wei[1,2,3*], Andrea Zifarelli[2,4], Stefano Dello Russo[2,4], Hongpeng Wu[2,3], Giansergio Menduni[4,5], Pietro Patimisco[4], Angelo Sampaolo[4], Vincenzo Spagnolo[2,4], Lei Dong[2,3], Weidong Chen[1]

[1] *Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque 59140, France*
[2] *State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China*
[3] *Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China*
[4] *PolySense Lab-Dipartimento Interateneo di Fisica, University and Politecnico of Bari, Via Amendola 173, 70126 Bari, Italy*
[5] *Photonics Research Group, Department of Electrical and Information Engineering, Politecnico di Bari, 70126 Bari, Italy*

Infrared laser technology over the last decades has led to an increasing demand for optical metrology with high sensitivity and wide operative spectral range for spectroscopic applications [1-2]. In this work, we report on the innovative investigation of a custom quartz tuning fork (QTF) used as a sensitive and broadband infrared photodetector for absorption spectroscopy [3]. The photodetection process is based on light impacting on the tuning fork and creating a local temperature increase that generates a strain field. This light-induced, thermoelastic conversion produces an electrical signal proportional to the absorbed light intensity due to quartz piezoelectricity. A finite-element-method analysis was used to relate the energy release with the induced thermal distribution. To efficiently exploit the photo-induced thermoelastic effects in the low-absorbance spectral region of quartz, chromium/gold layers, acting as opaque surface, have been deposited on the quartz surface. To demonstrate the flat response as photodetectors, a custom tuning fork, having a fundamental resonance frequency of 9.78 kHz and quality factor of 11 500 at atmospheric pressure, was employed as photodetector in tunable diode laser absorption spectroscopy. Its performance has been tested using five different lasers with emission wavelengths in the 1.65–10.34 μm range. A spectrally flat responsivity of ~2.2 kV/W was demonstrated, corresponding to a noise-equivalent power of 1.5 nW/Hz$^{1/2}$, without employing any thermoelectrical cooling systems. Finally, a heterodyne detection scheme was implemented to retrieve the resonance properties of the QTF together with the gas concentration [4].

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

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* correspondant : waitingonce@163.com

Tropospheric reactivity with NO3 radicals of biomass burning emitted compounds, the methylated-furans: rate coefficients and mechanistic pathways in the gas- and aerosol phases

Fatima AL ALI[1,2], Cécile COEUR[1], Nicolas HOUZEL[1], Manolis ROMANIAS[2], Alexandre TOMAS[2]

[1] *Laboratoire de physico-chimie de l'atmosphère, Université du Littoral Côte d'Opale*
[2] *IMT Nord Europe, Institut Mines-Télécom, Univ. Lille, Centre Energie et Environnement, 59000 Lille, France*

Biomass burning events emits a wide variety of gases and particulate matter (PM) into the atmosphere, which inevitably affects both climate and air quality [1]. Quite recently furan compounds have been identified as an important family emitted during fires [2]. Methylated furan compounds are the first generation compounds of this family and their reaction with the nighttime oxidant NO_3 is poorly understood in literature. This work aims at studying the rate coefficients and the mechanism of nitrate radical (NO_3) reaction with 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran and 2,3,5-trimethylfuran. The experiments were done in CHARME atmospheric simulation chamber in LPCA-Dunkerque and the reaction compounds were monitored using different spectrometric (PTR-MS, GC-MS, LC-MS) and spectroscopic (FTIR) techniques. Rate coefficients were measured and as a result the atmospheric lifetimes τ (NO_3) for these compounds upon reaction with NO_3 radical ranged between (0.5-55) mins respectively. Qualitative and quantitative product analysis were performed, both in the gas- and aerosol-phases. The two major initiation pathways for these reactions are identified as either nitrate addition to the ring or hydrogen abstraction from a methyl group substituted to the ring. As a result, these reactions lead to the formation of large number of oxygenated primary and secondary products as well as secondary organic aerosols.

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Multipass enhanced QEPAS (quartz-enhanced photoacoustic spectroscopy)

Ruyue Cui[1,2*], Lei Dong[2], Hongpeng Wu[2], Weidong Chen[1]

[1] *Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque 59140, France*

[2] *State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China*

Laser-based spectroscopy approaches, such as tunable diode laser absorption spectroscopy (TDLAS) [1] and quartz-enhanced photoacoustic spectroscopy (QEPAS) [2], have been widely used for trace gas detection, leading to the advent of reliable and robust gas sensors. Among them, QEPAS is an attractive approach characterized by high cost-effectiveness, high sensitivity and small footprint, due to the use of a high Q-factor, low-cost quartz tuning fork (QTF) [3] as acoustic detector [4]. In a traditional single-pass QEPAS, the modulated laser beam is focused at the QTF gap and only one acoustic source is generated between the QTF prongs. In the present work, multiple sound-source excitation has been applied to quartz-enhanced photoacoustic spectroscopy (MSSE-QEPAS) by using a multi-pass cell (MPC) based on a single-line spot pattern [5]. The single-line spot pattern MPC is designed to make laser beam passing through the QTF 60 times to produce 60 acoustic sources between the QTF prongs. The setup is shown in Fig. 1. A signal gain factor of ~ 20 was achieved in the developed MSSE-QEPAS setup with respect to the conventional single-pass QEPAS. A theoretical model is proposed to modeling the MSSE-QEPAS approach. Highly sensitive QEPAS sensors based on MSSE-QEPAS described in this paper represents high opportunities for applications in atmospheric monitoring, industry process control and medical diagnostics.

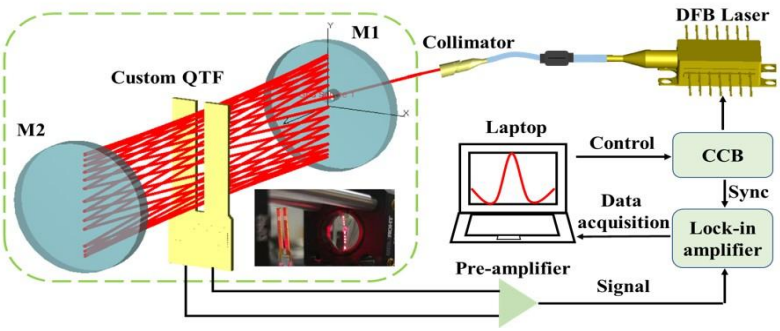

Figure 1. MSSE-QEPAS system configuration. Red lines: laser beams between two identical spherical mirrors M1 and M2; QTF: quartz tuning fork; CCB: control circuit board. Inset: Photograph of the single-line spot pattern on the M1 surface and the QTF.

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* correspondant : cuiruyue1993@163.com

Optical monitoring of OH radicals using Faraday rotation measurement enhanced by off-axis integrated cavity output spectroscopy at 2.8 μm

Minh-Nhut NGO[1*], Tong NGUYEN-BA[1], Weixiong ZHAO[2], Weidong CHEN[1*]

[1] *Laboratoire de Physico-Chimie de l'atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*

[2] *Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, China*

Playing a crucial role in the degradation of trace gases and pollutants in atmosphere, OH radical is a key species determining the atmospheric oxidation capacity [1]. We report on the development of a compact optical instrument for interference-free measurement of OH radicals based on Faraday rotation spectroscopy (FRS) [2] coupled to off-axis integrated cavity output spectroscopy (OA-ICOS) operating at 2.8 μm. Production of OH radicals (of concentration in the order of 10^{12} molecule.cm^{-3}) was well-controlled through microwave discharge of water vapor at low pressure. With a long path length enhancement (366 m), OA-ICOS method was used for determination of OH concentration. OA-ICOS was coupled to a balanced detection-Faraday rotation measurement approach (OA-ICOS-FRS) to enhance the sensitivity of OH monitoring. A 1σ detection limit of ~9.3×10^{9} cm^{-3} was obtained for an averaging time of 20 s, which is 7 times better than that obtained by the OA-ICOS approach alone. The OA-ICOS-FRS approach exhibits the specific advantage of interference-free of close-by (non-paramagnetic) water vapor absorption. According to an Allan variance analysis, the OA-ICOS-FRS approach operates in a white-noise dominated regime and its signal-to-noise ratio could be further improved through data averaging.

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* correspondant : minh-nhut.ngo@univ.littoral.fr
weidong.chen@univ-littoral.fr

Rotational spectroscopy of reactive species for interstellar discovery

Thomas S Hearne[1*], Olivia Chitarra[1], Olivier Pirali[1], Marie-Aline Martin-Drumel[1]

[1] *Institut de Sciences Moléculaires d'Orsay, Université Paris-Saclay, Orsay, France*

Molecular species with a dipole moment produce a unique rotational spectrum that is isomer, conformer, and isotopologue specific. The rotational spectra of molecules thus can be used as a fingerprint to help identify them in remote media such as the interstellar medium. Furthermore, this spectral signature can be used to infer the physical properties of a system, such as its structure or the dynamics of any internal motion. In our group, we are continuously developing a range of spectroscopic techniques spanning from the microwave to the terahertz spectral regions for the characterisation of the rotation spectrum of molecules found, or likely to be found, in outer space. In this way, we hope to enable new interstellar detections of species playing a role in interstellar chemistry.

The experimental work is centred on two complementary spectrometers: a frequency multiplication-based absorption spectrometer employing lock-in detection of a frequency-modulated signal (75-900 GHz), and a chirped pulse spectrometer (75 – 110 GHz). The two spectrometers can be coupled with single or dual-pass samples cells for the study of stable species, or a range of radical production techniques for the study of reactive species. Currently, we are producing reactive species through either a radiofrequency discharge, and/or fluorine abstraction. These methods produce rich spectra, containing the rotational signatures of a range of interesting species. Experimental manipulation can help identify these species. For example, the modulation of a magnetic field (either through a second lock-in demodulation scheme of a pulsed electromagnet in the case of the absorption spectroscopy, or manual addition of a permanent magnet for chirped-pulse spectroscopy) is used to discriminate between open-shell species and stable reaction products. An example of a previous application of these techniques is the characterisation of the spectrum of the CH_2OH radical from 140 to 330 GHz [1]. To help with the identification of new species, we are implementing post-processing tools to help rapidly identify interesting spectral features. Finally, we are building a new pulsed-jet experiment that will be able to produce radical species cooled to below 10 K, for the sensitive detection of particular rotational transitions relevant to cold molecular clouds. In my talk, I will be discussing these methods and our latest results on reactive systems and their analysis.

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Theoretical studies of photodesorption of molecular interstellar ices

Samuel DEL FRÉ[1*], Alejandro Rivero[1], Céline Toubin[1], Denis Duflot[1], Maurice Monnerville[1]

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

In the coldest parts (~10K) of the interstellar medium (ISM), most of the molecular species except H_2 accrete onto dust grains leading to the formation of chemically rich physisorbed molecular ice mantles, referred to as molecular ices. However, surprisingly large abundances of gas phase molecules are also observed in these cold regions. Due to the cold temperature, the existence of these gaseous species is naturally suggested to be the result of non-thermal desorption processes at the ice surfaces. One of these processes is the desorption induced by UV photons, namely UV photodesorption, which has been studied for various molecular ices including CO[1,2] for which it has been shown that the UV photodesorption follows a "Desorption Induced by Electronic Transition (DIET)" mechanism.[3] In this astrochemical context and in the framework of the ANR PIXyES *(Photodesorption Induced by UV-X-rays and Electrons on ice Surfaces)*, this study aims at understanding, at the molecular level, the energy redistribution after VUV excitation in pure CO ice by means of molecular dynamics using a classical force field.[4] The focus is on the end of the DIET mechanism where the electronic energy of the excited molecule redistributes on the vibrational states of its electronic ground state which leads to photodesorption of a neighbouring molecule from the ice surface. To do so, a cluster approach is used to model the ice amorphous structure. The obtention, optimization and characterization of the theoretical samples is detailed in this work. Then, the energy profile to observe the desorption of a CO molecule from the cluster surface is presented using different approximations. These preliminary results show that the energy required to desorb a CO molecule from the cluster surface is much lower (≈ 60 meV) than the vibrational energy acquired by the excited CO molecule after the VUV irradiation (≈ 8 eV). This observation suggests that the CO photodesorption should be highly probable as has been reported in the experimental works.

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* correspondence : samuel.del-fre@univ-lille.fr

Spectroscopie IRMPD et calculs de chimie quantique de complexes ioniques or-phosphine ou or-thiol

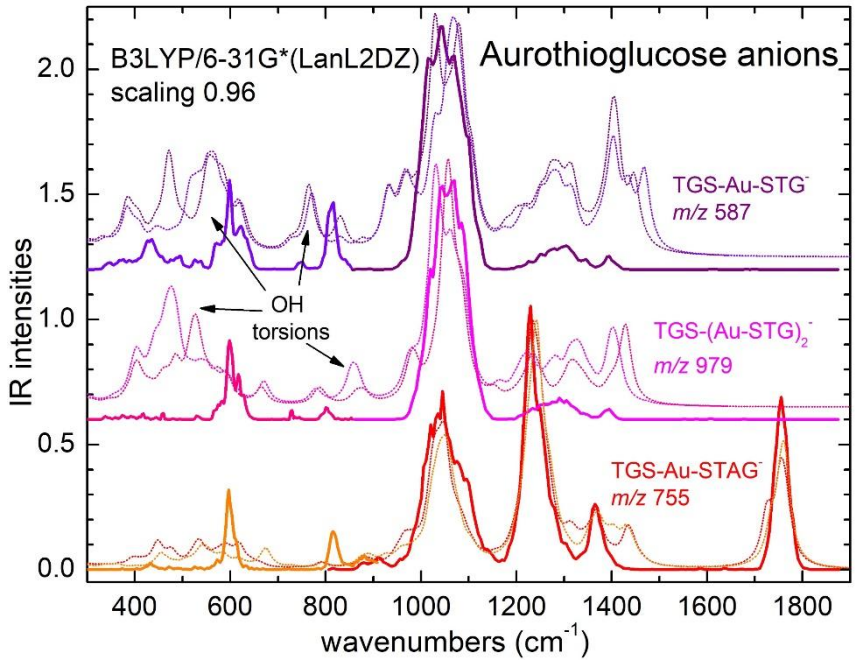
G. Berden[1], J. Oomens[1], N. Nieuwjaer[2], A. Beydoun[2], F. Lecomte[2], B. Manil[2], C. Desfrançois[2]

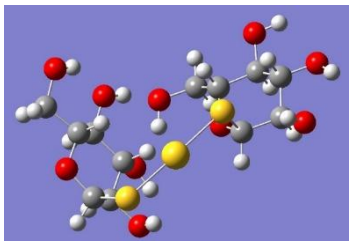
[1] *HFML – FELIX, Radboud University , Toernooiveld 7c, 6525 ED Nijmegen , Nederland*
[2] *Laboratoire de Physique des Lasers, CNRS, Université Sorbonne Paris Nord, 93430 Villetaneuse, France*

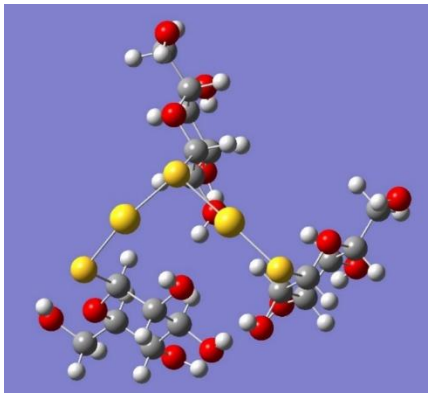
Nous présentons ici quelques résultats récents sur des complexes ioniques or-phosphine ou or-thiol étudiés expérimentalement par spectroscopie IRMPD (InfraRed Multiple Photon Dissociation), après sélection et piégeage par spectrométrie de masse, et par des calculs de chimie quantiques des structures et des spectres infrarouges associés.

Ces études sont motivées par la recherche de signatures spectrales IR qui puissent donner des indications sur la structure et les propriétés physico-chimiques des liaisons Au-P ou Au-S dans ces complexes covalents qui sont intéressants pour leur utilisation dans les nanoparticules fonctionnalisées souvent utilisées en nano-médecine.

Les résultats présentés ici concernent des complexes de l'or soit avec des triphenyl ou triéthyl phosphines soit avec des thio(acétyl)glucoses. Si les spectres IR sont globalement dominés par les bandes vibrationnelles propres à ces ligands, on note quand même des bandes ou des décalages spectraux qui peuvent être caractéristiques soit d'un type de structure soit des liaisons Au-P ou Au-S. Les calculs DFT classiques (B3LYP/6-31G*(LanL2DZ)) reproduisent bien les spectres IR expérimentaux, en particulier pour les positions des bandes au-dessus de 1000 cm^{-1}, mais pas toujours dans le domaine des plus basses fréquences (200-800 cm^{-1}) qui reste encore à mieux explorer, notamment pour y chercher d'autres signatures de l'interaction or-ligand.







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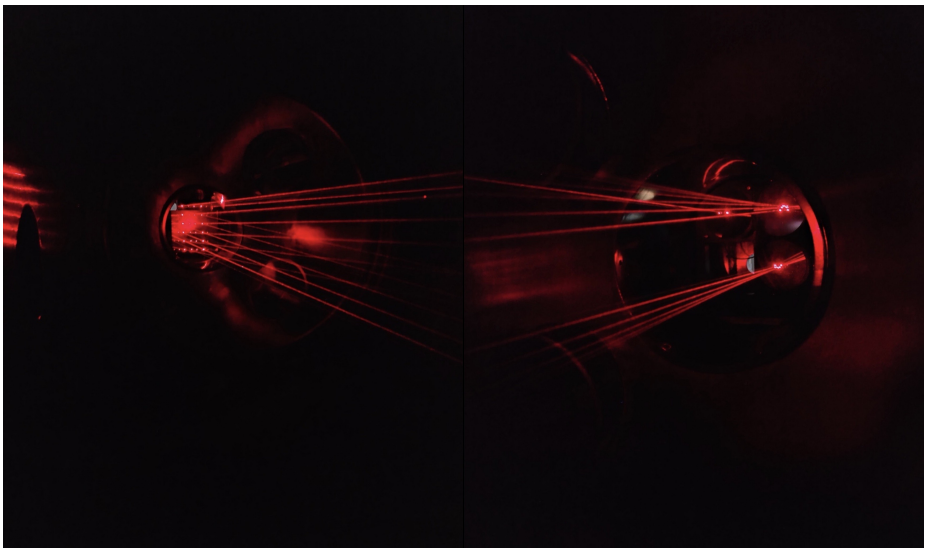
MULTICHARME: a modified Chernin-type multi-pass cell designed for IR and THz long-path absorption measurements in the CHARME atmospheric simulation chamber

Eric Fertein, Jean Decker, Pierre Kulinski, Nicolas Houzel, Jonas Bruckhuisen, Frank Hindle, Gaël Mouret, Robin Bocquet, Guillaume Dhont, Cécile Cœur and Arnaud Cuisset.
Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale Dunkerque, France
* Email: fertein@univ-littoral.fr

We have developed MULTICHARME, a modified Chernin-type multi-pass cell especially designed for IR and THz long-path absorption measurements in the CHamber for Atmospheric Reactivity and Metrology of the Environment (CHARME). The pathlenghts could be adjusted from 120m. (24paths) to 280 m. (56 paths) in THz and 480 m. (96 paths) in Near IR. By measuring the output power using a near-IR diode-laser and a THz amplified multiplication chain, we have established that the effective reflectivity of MULTICHARME is better than 94 % over approximately three decades of frequency. Absorption measurements of N_2O have been performed by probing highly excited rovibrational transitions in the near-IR and ground state rotational transitions at submillimeter wavelengths. In each case the linearity of the absorbance with the path lengths was verified. Finally, we demonstrate that THz spectroscopy is able to study the isotopic composition of greenhouse polar gases such as N_2O and to absolutely quantify stable (N_2O) and reactive (O_3) species at trace levels. At low pressure the ozone concentration was continuously monitored and its decay characterized. The deduced ozone lifetime of 3.4 ± 0.1 h is shorter compared with previous measurements performed in CHARME at atmospheric pressure. For the first time, the ability of THz rotational spectroscopy to monitor, with a very high degree of selectivity, stable and reactive polar compounds at trace level in an atmospheric simulation chamber is demonstrated.



The back and forth of the HeNe laser beam in MULTICHARME

Spectroscopie du 4(5)-méthylimidazole et de ses hydrates, hébergés en gouttelette d'hélium

F. Grollau[1], J.-M. Mestdagh[1], B. Soep[2], E. Gloaguen[1], V. Brenner[1], L. Poisson[2], M. Mons[1] et M. Briant[3*]

[1] *Univ. Paris-Saclay, CEA, CNRS, LIDYL, 91191 Gif-sur-Yvette, France*
[2] *Univ. Paris-Saclay, CNRS, ISMO, 91405, Orsay, France*
[3] *Univ. Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France*

L'histidine est l'un des deux acides aminés qui présente un équilibre tautomérique. Cette molécule est par ailleurs, à la fois accepteur et donneur de proton, ce qui lui donne un rôle essentiel dans les processus biologiques où le transfert d'un proton intervient (ex. régulation du pH sanguin). Des études antérieures ont montré que l'équilibre tautomérique de cet acide aminé est modifié par son environnement[1], ce qui rend ses propriétés intrinsèques délicates à obtenir expérimentalement. Connaître ces propriétés est pourtant important pour comprendre le comportement de cet acide aminé lorsqu'il est environné. Les caractéristiques mentionnées ci-dessus sont uniquement portées par le cycle imidazole qui est la chaîne latérale de l'histidine. Ainsi, nous nous sommes intéressés à une molécule modèle de l'histidine, le 4(5)-méthylimidazole (MeIm) (Figure 1).

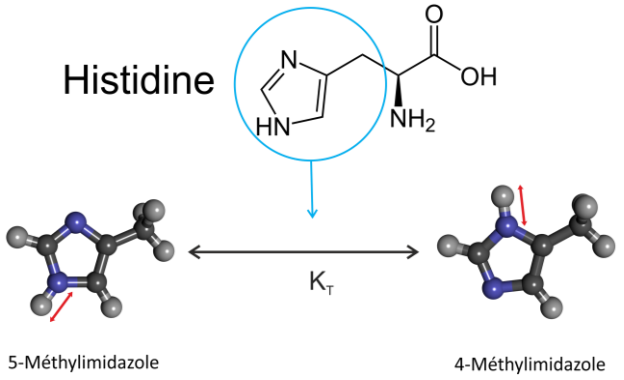


Figure 1: L'histidine et sa molécule modèle, le méthylimidazole.

Sur le plan expérimental, nous avons caractérisé les isomères du MeIm et ses hydrates, par spectroscopie infrarouge (IR). Le dispositif Gouttelium[2] a permis d'enregistrer les spectres IR de ces espèces en utilisant la technique "Helium NanoDroplet Isolation"[3]. Les gouttelettes d'hélium sont des systèmes quantiques froids (0,37 K[4]), superfluides[5] et très fragiles. Elles thermalisent les espèces qui y sont hébergées et interagissent peu avec ces dernières, ce qui permet d'obtenir des spectres d'absorption IR proche de ceux attendus sur des molécules totalement isolées. Néanmoins, cette observation porte essentiellement sur la structure vibrationnelle des spectres car la structure rotationnelle est affectée par la présence de la gouttelette.

Nous avons caractérisé sans ambiguïté les deux tautomères du MeIm via l'élongation NH dont la fréquence est très sensible à la position du groupe méthyle. L'attribution des bandes IR observées à un conformère spécifique a été faite par comparaison avec des calculs de DFT-D. Les intensités relatives entre bandes nous ont permis d'estimer la constante de tautomérisation, $K_{5 \leftrightarrow 4}$(T=43°C)= 5,3 ± 0.8, qui n'était pas connue avec précision. Les constantes de rotation du 4-méthylimidazole dans les gouttelettes ont été déterminées grâce à une simulation du spectre et montrent une interaction forte de la rotation avec la gouttelette d'hélium. Ce résultat est attendu car la molécule entraîne une couche d'hélium non superfluide dans sa rotation.

Enfin, les complexes 4(5)-MeIm-eau ont été formés par le dépôt des deux espèces dans les gouttelettes d'hélium. Une recherche du signal de l'élongation NH du MeIm et de l'élongation symétrique et antisymétrique OH de l'eau a été effectuée.

Les différents spectres et leur interprétation seront présentés, ainsi qu'une discussion.

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A system-bath approach for the quantum vibrational dynamics of large molecules

Loïse Attal[1], Cyril Falvo[1,2], Florent Calvo[2], Pascal Parneix[1]

[1]*Institut des Sciences Moléculaires d'Orsay, CNRS, Université Paris-Saclay, 91405 Orsay, France*
[2]*LiPhy, CNRS, Université Grenoble Alpes, 38000 Grenoble, France*

Addressing the relaxation dynamics and spectral properties of large molecules is of interest for different scientific communities and in particular in astrophysics, owing to the increasingly large number of complex molecules that have been detected in the interstellar medium. For example, fullerene C_{60} [1,2], indene [3] and cyanonaphthalenes [4] have been identified from their vibrational or rotational signature.

In this context, we are developing a new theoretical model for the simulation of the quantum vibrational dynamics of relatively large molecules (> 20 atoms) that takes into account their vibrational anharmonicity and allows for an explicit coupling to an electromagnetic field. Our approach is based on a system-bath model in which one particular vibrational mode of interest, for which we want to obtain the spectral or dynamical information, is in contact with a bath formed by the remaining vibrational modes of the molecule. The mode of interest and its couplings to the other modes are treated as rigorously as possible but the bath part of the Hamiltonian is simplified with its modes being replaced by a ladder of energy-dependent effective quantum states that describe the energy stored in those modes. Such an approach scales very mildly with the number of degrees of freedom, allowing for large systems to be considered. With this model it is possible to analyze the response of the bath to the excitation of the mode of interest [5] and to study the infrared spectrum and relaxation dynamics of relatively large molecules at finite temperature.

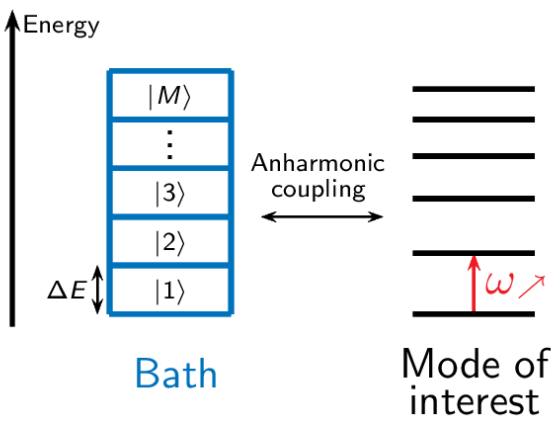

Figure 1: Schematic view of our model with the vibrational levels of the selected mode (in black), the effective states of the bath (in blue) and the anharmonic coupling between the two. In our model the electromagnetic field is only coupled to the mode of interest.

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Analyse structurale des épitopes d'immunoglobuline G (IgG) par MS-IR

INFANTINO Alicia*, YENI Oznur, MOGE Baptiste, COMPAGNON Isabelle

Institut Lumière Matière, Université Lyon 1/CNRS, Villeurbanne, France

La spectrométrie de masse (MS) est un outil analytique très répandu pour identifier la structure des biopolymères. Par exemple, celle-ci permet d'accéder à la structure du cœur des N-glycanes, une modification post traductionnelle souvent mise de côté dans l'analyse de protéines. Cependant, la MS ne permet pas de décrire l'ensemble des variations structurelles que constituent les épitopes, c'est-à-dire la partie terminale des N-glycanes, partie extrêmement critique puisqu'au premier plan des interactions glycoprotéine/environnement. Ceci est dû aux diverses modifications fonctionnelles qui complexifient la structure moléculaire des monosaccharides terminaux (sulfatations, sialylations, …) et aux divers branchements possibles au niveau de leurs extrémités. Nous nous intéressons à la description de la « structure fine » de ces épitopes de N-glycanes qui sont impliqués dans plusieurs processus biologiques et en particulier la polyarthrite rhumatoïde (PR).

Nous proposons l'utilisation de la spectroscopie IRMPD (InfraRed Multiple Photon Dissociation) [1] afin de mieux décrire la structure des épitopes et leurs isoméries (voir figure 1). Dans le cadre de la PR, une variation au niveau des épitopes sialylés est attendue étant donnée que les acides sialiques semblent être reliés aux effets anti-inflammatoires [2].

Nous nous intéresserons dans un premier temps à ce type d'épitope qui sont présents à la surface des immunoglobulines G, une protéine essentielle du système immunitaire, sous deux formes possibles : l'isomère 3'-sialyl-N-acetyllactosamine ou 6'-a-sialyl-N-acetyllactosamine. Je présenterai les premiers résultats obtenus depuis le démarrage de ma thèse en décembre 2021.

Ce projet est financé par l'ANR et rassemble le consortium GEPHIR : l'équipe DYNAMO de l'Institut Lumière Matière, les plateformes Lilloises en Biologie et Santé, les Hospices Civils de Lyon et l'Institut de Chimie et Biochimie Moléculaires et Supramoléculaires.

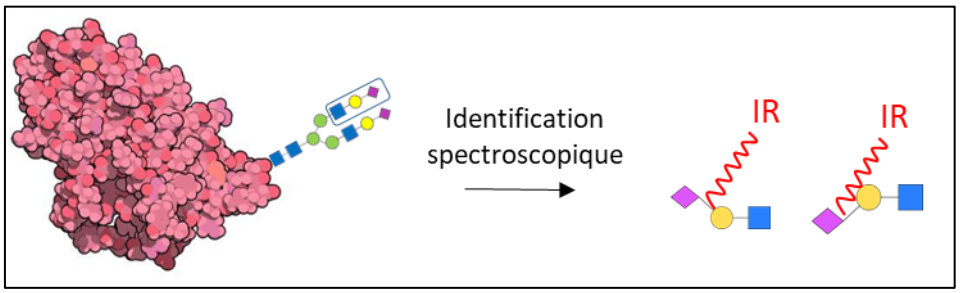

Figure 1 : schéma de l'identification spectroscopique d'un trisaccharide sialylé

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* correspondant : alicia.infantino@univ-lyon1.fr

Synthèse de complexes organométalliques d'or(I) et d'or(III) et détermination de leur énergie de dissociation par spectrométrie de Masse

Clément Soep[1], Lyna Bourehil[1,2], Benoît Bertrand[1], Denis Lesage[1], Héloïse Dossmann[1]

[1] *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France*

[2] *Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France*

Les complexes organométalliques sont des composés indispensables en catalyse homogène, leur réactivité est intimement liée aux ligands qui les composent. En effet les ligands ont la possibilité d'orienter la réactivité du centre métallique auquel ils sont liés de par leurs effets électroniques et stériques. La connaissance de ces effets est ainsi essentielle pour choisir le ligand le plus adapté lors de la synthèse de complexes organométalliques en vue d'une application donnée [1,2]. L'interaction métal-ligand est habituellement considérée comme étant due à la combinaison de deux effets électroniques principaux : une donation σ du ligand au métal et une rétrodonation π du métal vers le ligand (modèle de Dewar-Chatt-Duncanson) [3,4].

Expérimentalement, la détermination des effets de ligands peut se faire au moyen de méthodes indirectes telles que la spectroscopie infrarouge de la bande d'élongation νCO dans des complexes de type métal-carbonyle (méthode de Tolman) [5]. Cette approche a permis de produire des classements relatifs des ligands de type phosphine ou NHC en fonction de leur caractère donneur [6]. Ces méthodes sont cependant limitées aux complexes possédants des ligands sondes comme CO (par exemple de type LMCO). Très peu de méthodes expérimentales fiables permettent de déterminer les propriétés électroniques des ligands dans les complexes ne possédant pas de ligands sondes. Dans ce contexte, nous nous sommes intéressés à l'étude de l'influence de ligands sur des complexes d'or (I) et (III) de type $[(NHC)AuL]^+$ $[(C^C)Au(NHC/PPh_3)L]^+$ et $[(C^N^C)AuL]^+$avec L un ligand de type pyridine (Figure 1). L'effet de la substitution de la pyridine sur l'enrichissement (en densité électronique) du centre métallique a été évaluée par la détermination de l'énergie de dissociation M-L -> M + L (bond dissociation energy, BDE) par spectrométrie de masse grâce à une activation par higher energy colision dissociation (HCD). Les ions d'intérêts sont isolés dans un piège à ions linéaire puis focalisé dans un C trap avant d'être collisionné avec N_2 dans un octopole. Les fragments formés sont renvoyés dans le C trap qui les envoient de manière pulsé dans un Orbitrap. Les BDEs ont ensuite été estimées à partir des données expérimentales au moyen d'une modélisation cinétique du processus de fragmentation. Les résultats obtenus ont ensuite été rationalisés grâce à des calculs de structures électroniques avec la théorie de la fonctionnelle de la densité (DFT).

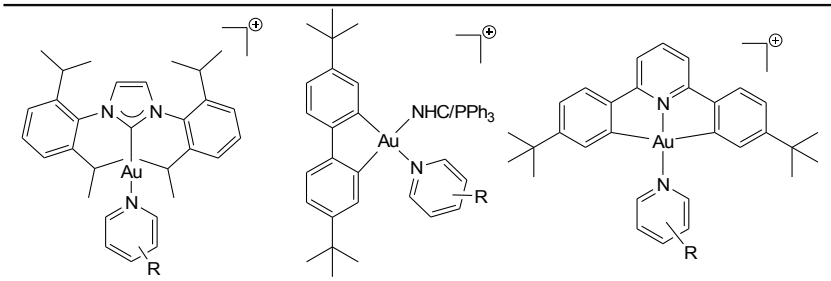

Figure 1: Structures des complexes synthétisés et étudiés $[(C^N^C)AuL]^+$, $[(C^C)Au(NHC/PPh_3)L]^+$ et $[(NHC)AuL]^+$. R est un substituant variable de la pyridine (position ortho, méta ou para).

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TeraWaste : In-situ/real time TeraHertz analysis of gaseous emission in the Dunkirk Urban Community's waste incineration/power plant

Jean Decker[1*], Frank Hindle[1], Eric Fertein[1], Nicolas Houzel[1], Patrick Augustin[1], Marc Fourmentin[1], Yamina Allouche[2], Fabrice Cazier[2], Frédéric Desmedt[3], Marion Philippon[4], Julien Dumont[3] and Arnaud Cuisset[1]

[1] Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France
[2] Centre Commun de Mesures, Université du Littoral Côte d'Opale, Dunkerque, France
[3] Biogie, Groupe Paprec, Pôle de Valorisation des Déchets, Dunkerque, France
[4] Direction Déchets, Communauté Urbaine de Dunkerque, Dunkerque, France

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.

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* correspondant : jean.decker@univ-littoral.fr

High-resolution spectroscopy and analysis of combination bands of SiF_4

M. Merkulova[1,2*,**], V. Boudon[2], L. Manceron[3,4]

[1] *Research School of High–Energy Physics, National Research Tomsk Polytechnic University, Tomsk 634050, Russia*
[2] *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS - Université Bourgogne Franche-Comté, 9 avenue Alain Savary, BP 47870, F-21078 Dijon Cedex, France*
[3] *Synchrotron SOLEIL, AILES Beamline, L'Orme des Merisiers, BP48, F-91192 St-Aubin Cedex, France*
[4] *MONARIS, UMR 8233, Université Pierre et Marie Curie, 4 Place Jussieu, case 49, F-75252 Paris Cedex 05, France*

Silicon tetrafluoride (SiF_4) is a trace component of volcanic gases and is gaining industrial importance. However, a better knowledge of spectroscopic parameters is needed for this molecule in order to derive accurate concentrations. Recently, we have undertaken a systematic study of its different rovibrational bands. We first published the analysis of the ν_3, ν_4 and $2\nu_4$ bands of it different isotopologues [1], followed by the fit of all fundamental levels of $^{28}SiF_4$ that led to an accurate determination of the Si–F equilibrium bond length.

In this poster, we present a continuation of this global investigation concerning four combination bands, namely $\nu_1+\nu_3$, $\nu_1+\nu_4$, $\nu_2+\nu_3$ and $\nu_2+\nu_4$. 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.

For each band, between 1000 and more than 2000 lines could be assigned for *J* values higher than 55 (up to 82 for $\nu_1+\nu_3$) 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 $\nu_1+\nu_3$ band, the $^{29}SiF_4$ and $^{30}SiF_4$ isotopologues could also be assigned and fitted. These results will allow the calculation of hot bands like $\nu_3+\nu_2-\nu_2$, *etc.*, in the regions of strong atmospheric absorption.

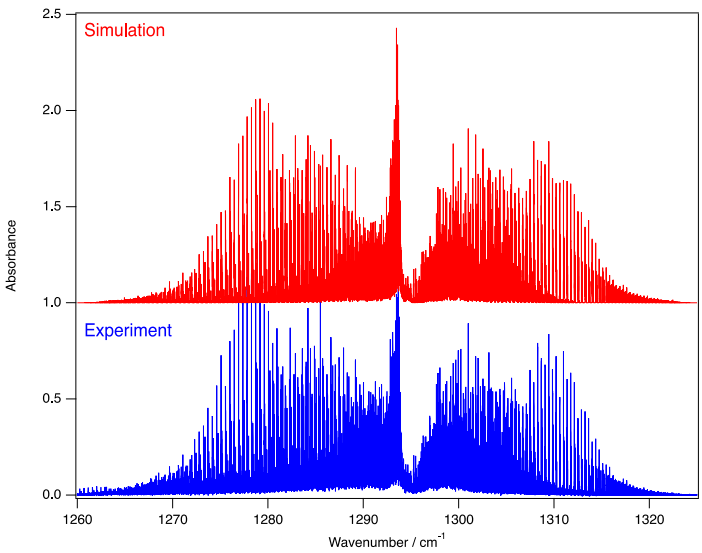

Figure 1: Comparison between the experimental and the simulated spectrum for the $\nu_2+\nu_3$ combination band of $^{28}SiF_4$ at 163 K.

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* Corresponding author: mari_andrew@mail.ru
* PhD Thesis supervised by V. Boudon in Dijon, France and O. Ulenikov in Tomsk, Russia

Rotation de molécules méthylées en matrice de para-hydrogène : analyse par conversion de spin nucléaire

Florian Lorin[1*], Claudine Crépin[1]

[1] *Institut des Sciences Moléculaires d'Orsay, UMR8214, CNRS-Université Paris-Saclay, 91405 Orsay Cedex*

Le para-hydrogène (pH_2) solide est considéré comme un environnement peu perturbateur pour les molécules qui y sont piégées et en particulier, les mouvements moléculaires de grande amplitude y sont grandement préservés [1]. Nous nous sommes intéressés à la rotation ou la torsion des groupements méthyle qui n'y sont pas bloqués et qui offrent ainsi une observable des effets de faible perturbation par le pH_2. Pour des raisons de symétrie au sein du groupe CH_3, les deux premiers niveaux de rotation (K=0 et K=1 sur l'axe C_{3v} du groupe méthyle) sont peuplés par des molécules avec les spins nucléaires des H différents : I=3/2 pour K=0 et I=1/2 pour K=1. Les deux niveaux sont peuplés lors de la formation de l'échantillon solide à 3 K et on peut suivre par spectroscopie IR l'évolution des populations due à la conversion de spin nucléaire (CSN) sur des temps très longs jusqu'à l'équilibre thermique.

Nous étudions la rotation des méthyles sur des chaînes linéaires méthylées de différentes tailles, à comparer aux travaux antérieurs de Lee et al. [2] sur CH_3F. De premiers résultats sur le propyne ont mis en évidence des évolutions temporelles importantes dans les spectres IR, attribuées à la CSN. L'ensemble du spectre montre que la rotation d'ensemble du propyne est bloquée ; seule la rotation autour de l'axe C_{3v} de la molécule semble préservée dans le pH_2. Les transitions perpendiculaires liées aux mouvements du méthyle présentent une structure attribuée en partie à la rotation gênée autour de cet axe [3], mais l'attribution publiée n'est pas totalement satisfaisante. Une partie des structures de ces bandes suit une dynamique beaucoup plus lente qui n'a été observée que récemment (voir Figure). Elle pourrait être attribuée à des molécules dont la rotation autour de l'axe C_{3v} est suffisamment bloquée pour que le mouvement associé ne soit plus qu'un mouvement de torsion. L'éclatement par effet tunnel des niveaux de torsion produit également des populations de niveaux dépendant du spin des H, et la CSN entre niveaux de torsion peut être suivie dans le pH_2 [4].

L'attribution du spectre propyne/pH_2 est en cours. Nous avons également obtenu des spectres de chaînes méthylées plus longues montrant de nouvelles structures en cours d'analyse.

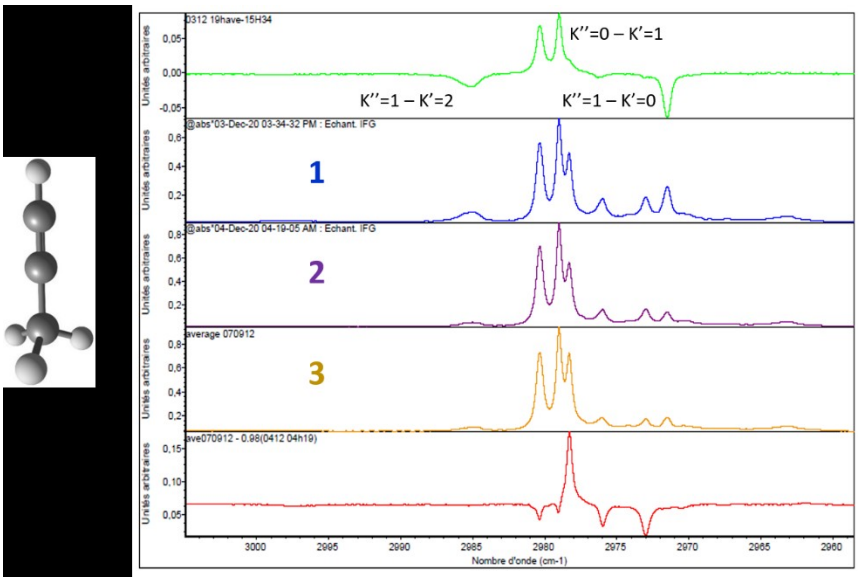

Figure : Bande ν_6 du propyne (étirement asymétrique des C-H du méthyle) dans pH_2 à 3 K. 1 : spectre 90' après déposition, 2 : 14h après, 3 : 4 jours après (spectre stabilisé à 3K). Haut : spectre de différence 2 – 1 montrant la dynamique « rapide » (200') sur certaines composantes avec leurs attributions ; cela correspond à l'équilibre des populations rotationnelles des molécules ayant une rotation gênée autour de l'axe C_{3v}. Bas : spectre de différence 3 – 2 montrant la dynamique « lente » (> 1000') sur les autres composantes ; cela peut correspondre à l'équilibre des populations des molécules ayant une rotation bloquée autour de l'axe C_{3v}.

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* correspondant : florian.lorin@student-cs.fr

QUANTUM AND SPECTROSCOPIC ANALYSIS IN THE MICROWAVE DOMAIN OF CYANOPROPENE

Truong Anh Nguyen[1], Isabelle Kleiner[1], Martin Schwell[1], and Ha Vinh Lam Nguyen[1]

[1] *Univ. Paris Est Creteil, Université Paris Cité, LISA, CNRS UMR 7583, Créteil, France*

The microwave spectrum of cyanopropene, was measured using a pulsed molecular jet Fourier transform microwave spectrometer in the frequency range from 2 to 26.5 GHz. Quantum chemical calculations were performed at the B3LYP/6-311++G(d,p), MP2/6-311++G(d,p) and MP2/6-31G(d,p) levels of theory to obtain optimized molecular geometries. Due to the internal rotation of the methyl group, all rotational transitions split into an A and an E torsional species. In addition, each of these two torsional species contains further hyperfine splittings due to the quadrupole coupling of the ^{14}N nucleus. The complex spectral splittings were analyzed and modeled using the *XIAM* and the *BELGI-C_s-hypefine* code to measurement accuracy.

Évaporation de molécules neutres en fluide supercritique pour une caractérisation structurale par spectroscopie laser résolue en conformation

Jean-Xavier Bardaud[1*], Marc-André Gaveau[1], Michel Mons[1], Eric Gloaguen[1]

[1] *Université Paris-Saclay, CEA, CNRS, LIDYL, 91191 Gif-sur-Yvette, France*

L'évaporation d'un échantillon liquide ou solide donne accès à de nombreuses techniques d'analyse (spectrométrie de masse, spectroscopies résolues), et tient une place importante dans l'analyse de molécules biologiques. L'introduction de systèmes neutres en phase gazeuse s'avère toutefois délicate dans le cas de ces molécules fragiles pour lesquelles les techniques existantes (chauffage, désorption par laser) ne conviennent pas toujours. [1]

Dans ce contexte, une nouvelle source comprenant un appareil de chromatographie à fluide supercritique (SFC) utilisant du CO_2 [2] (voir Fig.1) couplé à un jet moléculaire pulsé, a été développée afin d'améliorer un procédé déjà exploré en 2006. [3] Appliquée à des molécules d'intérêt biologique tel que des petits peptides, [4] cette technique a pour objectif de caractériser la structure de systèmes isolés au moyen d'expériences de spectroscopies laser IR et UV résolues en conformation interprétées à l'aide de calculs de chimie quantique. [5]

Les molécules d'intérêt sont dissoutes dans la phase supercritique et acheminées jusqu'à la vanne pulsée qui permet une détente supersonique du mélange sous vide. L'analyse est ensuite réalisée par un spectromètre de masse à temps de vol double (anion/cation) permettant d'enregistrer les spectres résolus en masse.

Les premiers essais ont été menés avec le toluène en solution dans l'éthanol et ont permis de caractériser la source, notamment la stabilité du signal d'ions, la température du jet moléculaire ainsi que les conditions de formation d'agrégats.

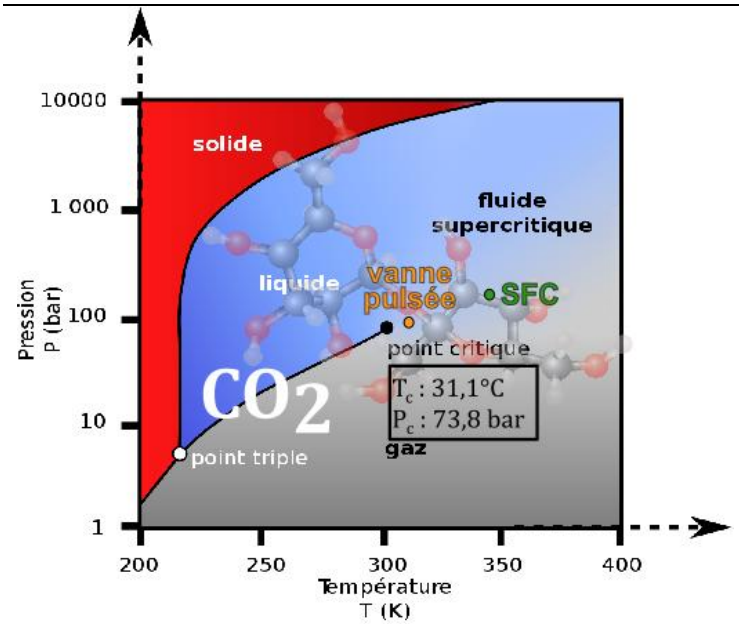

Figure 1 : Diagramme P, T du dioxyde de carbone avec les points de fonctionnement de la SFC (vert) et de la vanne pulsée (jaune).

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* correspondant : jean-xavier.bardaud@cea.fr

Characterization of irradiated sulfur-containing cyclic dipeptides by mass spectrometry and IRMPD spectroscopy

Yining Jiang[1], Enrico Bodo[2], Carine Clavaguéra[1], Marc Lecouvey[3], Suvasthika Indrajith[4], Giel Berden[5], Jos Oomens[5, 6], Chantal Houée-Levin[1] and Debora Scuderi[1*]

[1] *Institut de Chimie Physique (ICP), UMR8000, Université Paris Saclay, Orsay, France*
[2] *Chemistry Department, University of Rome "La Sapienza", Rome, Italy*
[3] *Department of Chemistry, Université Sorbonne Paris Nord, Bobigny, France*
[4] *Stockholm University, Stockholm, Sweden*
[5] *Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Nijmegen, Netherlands*
[6] *Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands*

Oxidative stress induced by an excess of free radicals in the cellular environment may cause deleterious effects affecting the normal biological conformation of proteins, which can be accumulated with age to lead to pathology such as Alzheimer's disease. Due to the high redox reactivity, sulfur-containing methionine (Met) is one of the main targets of reactive oxygen species (ROS) and evidence for oxidation of Met^{35} in the Alzheimer's disease β–amyloid peptide (βAP) has been demonstrated [1]. Recently, calmodulin, which has nine methionine in its sequence, and in particular, two pairs of adjacent methionine residues (Met^{71}-Met^{72} and Met^{144}-Met^{145}) has been investigated for one-electron oxidation by hydroxyl radicals [2]. Cyclic dipeptides (c-(L-Met-L-Met), c-(L-Met-D-Met) and c-(Gly-L-Met)) have been chosen as models for the interior of protein where there are no terminal groups (Figure 1). In linear peptide, the amide bond is in *trans* configuration. In c-(L-Met-L-Met), the amide bond has a *cis* configuration and thus the side chains are on the same side of the diketopiperazine ring. The L-D one has its chains pointing in opposite directions and so it is a good model for the interior of proteins. In c-(Gly-L-Met), one of the methionine is replaced by a glycine and the only possibility to stabilize the sulphur radical cation should be by interaction with the heteroatoms of the peptide bonds or with another peptide.

Some work has been done on the exploitation of chemical mechanisms from a transient scope [3-6]. In our group, the investigation of the oxidation in various linear peptides has already been carried out [7-9]. We present here, a combined study of MS^2-CID, Infrared multiple photon dissociation (IRMPD) spectroscopy and density functional calculation (DFT). Our goal is to investigate the cyclic di-methionine oxidation as model systems and to identify their final products of oxidation.

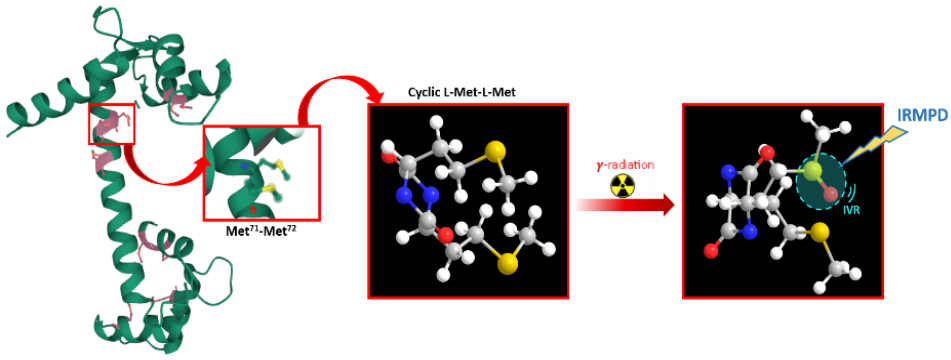

Figure 1: Schematic representation of the cyclic dipeptide modeling process. Left : 3D structure (PDB file 1CLL) [10] of calmodulin (green) with highlighted met-containing sequence (pink); Middle : 3D simulation of cyclic Met-Met; Right : 3D simulation of singly oxidized product of cyclic Met-Met, which can be characterized by IRMPD spectroscopy.

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* correspondant : debora.scuderi@universite-paris-saclay.fr

Transférabilité de la DFTB
De l'atome isolé au solide

Guibourg Paul*

* Normandie Univ., ENSICAEN, UNICAEN,CEA, CNRS, CIMAP, Caen Cedex 4, France

Dans le cadre du projet BreakinGAP, on étudie les mécanismes d'émission d'ions au sein de l'expérience de Sonde Atomique Tomographique [3] (SAT). La SAT consiste en l'évaporation d'atomes et de molécules, d'une pointe sous effet de champs fort, dans l'objectif d'en déduire la structure des matériaux et leurs compositions. La finalité de nos simulations est l'étude des dissociations d'ions depuis la surface chargée d'un agrégat, de manière à simuler la pointe. Pour ce faire, on a besoin de répondre à quelques critères tels que l'efficacité de calcul de système de grande taille sous la forme d'agrégats (quelques milliers d'atomes) ainsi que la nécessité de pouvoir décrire raisonnablement les surfaces d'énergies potentielles. On choisit la DFTB [1] (pour Density Functionnal based Tight-Binding) qui est une méthode semi-empirique basée sur la DFT moyennant certaines approximations. Bien que l'emploi de la DFTB peut être sollicité pour des systèmes très variés [2] — de composés organiques aux cristaux denses — les paramètres et le formalisme de la DFTB présentent des lacunes de description des systèmes chargés et neutres dans des environnements différents. Pour améliorer la transférabilité de la DFTB ainsi que sa description électronique des systèmes, on a mis en place une méthode paramétrique dépendante d'un seul paramètre additionnel. Ce dernier correspond au confinement des atomes en DFTB que l'on ajuste à différentes structures. Par la suite, on estime à l'aide d'une méthode de régression logistique pour chaque atome suivant son environnement immédiat. Cette procédure augmente significativement la capacité de la DFTB à répondre à l'exigence de transférabilité entre des systèmes denses et isolés.

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Developement of an Intracavity Quartz Enhanced Photoacoustic Spectroscopy (I-QEPAS) system

Tong Nguyen-Ba[1], Minh-Nhut Ngo[1], Pierre Kulinski[1], Vincenzo Spagnolo[2], Weidong Chen[1*]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*

[2] *PolySense Lab - Dipartimento Interateneo di Fisica, University and Politecnico of Bari, Via Amendola 173, Bari, Italy*

The development of compact optical sensor for trace gas species is more and more interesting for diverse fields of applications such as environmental monitoring, industrial process control and medical diagnostics. Quartz Enhanced Photoacoustics Spectroscopy (QEPAS) has been proved to be an attractive tool for selective and sensitive detection and quantification of molecular trace gas [1]. This technique has shown a large range of applications with compact and cheap setups, based on the use of a small size quartz tuning fork (QTF) as an efficient acoustic transducer. The optical energy absorbed by the gas results in a periodic thermal expansion which gives rise to a weak acoustic pressure wave. This pressure excites a resonant vibration of the QTF thereby generating a electrical signal via piezoelectric effect. Because the photoacoustic signal is directly proportional to excited optical power, enhancing excitation light power is essential to achieve high sensitivity, which can be realized through the use of high power laser sources, through multipass of laser beam between the QTF inside the photoacoustic module [2] or using optical cavity to enhance the intracavity laser power [3,4].

In this paper, we report on the development of an Intracavity Quartz Enhanced Photoacoustics Spectroscopy (I-QEPAS) system that was realized by placing a QTF in the center of a high finesse cavity. A buildup factor about 200 of optical power inside cavity was obtained. The experimental detail and the preliminary results will be presented and discussed.

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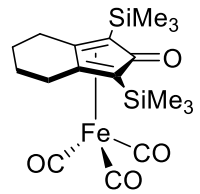
* correspondant : weidong.chen@univ-littoral.fr

Investigation of ligand electronic effects on iron cyclopentadienyl complexes using photoelectron spectroscopy

Lyna Bourehil[1,2], Denis Lesage[1], Léo Bettoni[4], Nicolas Joly[4], Sylvain Gaillard[4], Jean-Luc Renaud[4], Yves Gimbert[1,3], Gustavo Garcia[2], Héloïse Dossmann[1]

[1] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75005 Paris, France
[2] Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France
[3]Université Grenoble Alpes, CNRS, DCM, F-38000 Grenoble, France.
[4] Université Normandie, LCMT, ENSICAEN, UNICAEN, CNRS, F-14050 Caen, France.

Organometallic chemistry is a key process in homogenous catalysis and gives access to a wide range of products and reactions. Through their steric and electronic effects, ligands are able to orientate the reactivity of the complexes and can thus influence the selectivity in the chemical transformations. Usually, the metal-ligand bond is depicted by the Dewar-Chatt-Duncanson model [1,2] involving two opposite interactions, a σ-donor and a π-acceptor effect. Over the years, many experimental methods have been developed to measure these electronic effects, the most common being that of Tolman (Tolman electronic parameter), which is based on the A1-symmetrical CO-stretching frequency shift in carbonyl complexes [3]. We have recently developed the use of new experimental gas-phase approaches to measure these effects, one based on photoelectron spectroscopy (PES) coupled to synchrotron radiation. The satisfying results obtained on model systems [4] have encouraged us to apply this method to catalysts developed for hydrogenation reactions [5], and to probe the electronic interaction between the ligand and the metal centre. Results obtained for tricarbonyl iron complexes of the ($Fe(CO)_3L$) type, with L being substituted cyclopentadiene ligands, are presented here. The experiments were carried out at the DESIRS monochromatized branch using the SAPHIRS experimental station equipped with the DELICIOUS III double imaging-PEPICO spectrometer. The photoelectron spectra (Figure 1) provide access to the ionisation energies and state-selected Fe-CO dissociation energies. Rationalization of the experimental results is made using density functional theory and bond description methods to get information on the electronic structure of the complexes and thus on the metal-ligand interaction.



Scheme 1. One of the cyclopentadiene complex studied

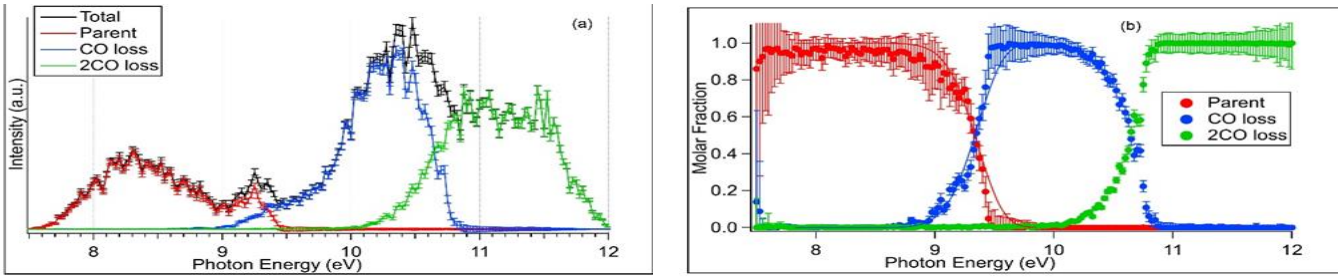


Figure 1 : (a). Slow Photoelectron Spectra (SPES) of state-selected iron complex recorded in the 7.5 - 12.0 eV energy range. (b). Breakdown diagram of iron complex recorded in the 7.5 - 12.0 eV energy range and obtained with a 30 meV energy resolution.

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Vers un spectromètre 2D-IR à haute résolution

Wutharath Chin[1], Jan Helbing[2], Mindaugas Jonusas[1*], Armel Jouan[1], Claudine Crépin[1]

1. ISMO-CNRS, Université Paris-Saclay, Orsay, France
2. Department of Chemistry, University of Zürich, Zürich, Switzerland

La spectroscopie infrarouge bi-dimensionnelle (2D-IR) est un outil puissant pour explorer la structure et la dynamique de nombreux systèmes. Cette technique de spectroscopie non-linéaire, plus poussée que la spectroscopie d'absorption IR**, permet d'accéder aux informations structurales (anharmonicité, couplage des modes) et dynamiques (transferts d'énergie, diffusion spectrale),** à des échelles d'une centaine de femtosecondes [1].

Nous avons mis en place un spectromètre 2D-IR permettant l'acquisition de cartes 2D-IR de systèmes moléculaires. Ce **dispositif 2D-IR est polyvalent : combiné à un système cryogénique, il permettra de mener des expériences sur une large gamme de températures, et de sonder des systèmes en solution ou piégés dans des environnements cryogéniques.** La caméra infrarouge multipixel (320x256) apporte une meilleure résolution spectrale (<0,5 cm^{-1}) que les détecteurs conventionnels [2]. Nous présentons ici des résultats préliminaires sur des petits complexes organométalliques en solution.

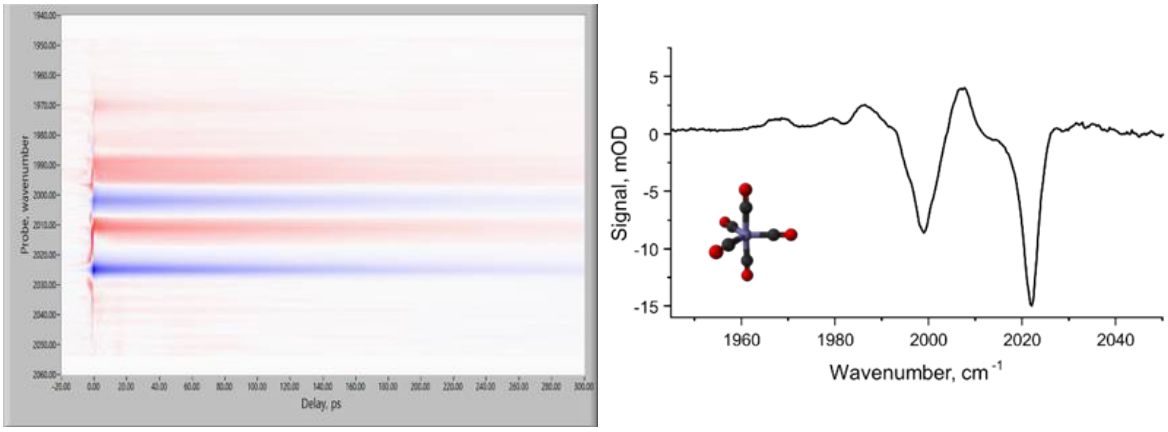

Fig. 1 : A gauche : Signal pompe-sonde du Fe(CO)5 dans le dodécane mesuré avec la caméra. A droite : spectre d'absorption transitoire correspondant.

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** Affiliation actuelle : LOB, Ecole Polytechnique, IPP, Palaiseau.*

Instrumentation for High resolution THz Spectroscopy

A. Khabbaz[1,2], G. Ducournau[2], G. Mouret[1], J.-F. Lampin[2]

[1] *Laboratoire de Physico-Chimie de l'Atmosphère (LPCA), Université du Littoral Côte d'Opale, Avenue Schumann F-59140 Dunkerque*
[2] *Institut d'Electronique Microélectronique et Nanotechnologie (IEMN), CNRS UMR 8520, Université de Lille, Avenue Poincaré F-59652 Villeneuve d'Ascq Cedex, France*

The terahertz (THz) band possess unique properties, these frequencies lie between microwave and infrared frequencies. Despite progress and investigations, powerful continuous wave THz source are still bulky and expensive. New possibilities are offered by exploiting the newly demonstrated THz molecular laser optically pumped by a mid-infrared (MIR) quantum cascade laser (QCL) based on ammonia (NH_3)[1]. NH_3 was used in the first maser experiment in 1953 and has several advantages for optical pumping: strong dipolar moment, small mass, high vapor pressure and strong absorption near 10 µm. By identifying the MIR/THz transitions pairs we have recently shown that optical pumping of NH_3 will potentially generate a huge quantity of new THz frequencies [2]. In order to design a laser, experimental values of the gain for each transition are needed even if the gain factor can be estimated using databases. Gain values were previously measured for two transitions[3] and showed that the gains were the highest measured in a continuous wave pumped gas. Here we report new gain measurements for several pure-inversion transitions of NH_3. The experimental setup is based on a 750–1100 GHz vector network analyzer (VNA), a 46-cm long copper tube is used as a gas cell for NH_3. To avoid any reflection, a THz and MIR transparent high resistivity silicon window inclined at the Brewster angle is placed at both ends of the cell. The THz beam from the VNA is superposed to the MIR beam of a QCL tunable from 10 to 10.6 µm. The gain value is obtained by calculating the ratio between the THz transmission measured with and without the gain medium inside the cell. Figure 1 shows a typical experimental result for the strongest transition, a maximum gain of 7.4 dB is measured for a pump power of 23mW and a pressure of 1.6 µbar.

This laser is going to be used as local oscillator as part of project TIGER (partners: IEMN, LPCA, Thales R&T and ICB) that aims to design a unique THz spectrometer with unprecedented capabilities in terms of frequencies accuracy (<50kHz), resolution (<50 kHz) and spectral coverage (0.5 - 4 THz).

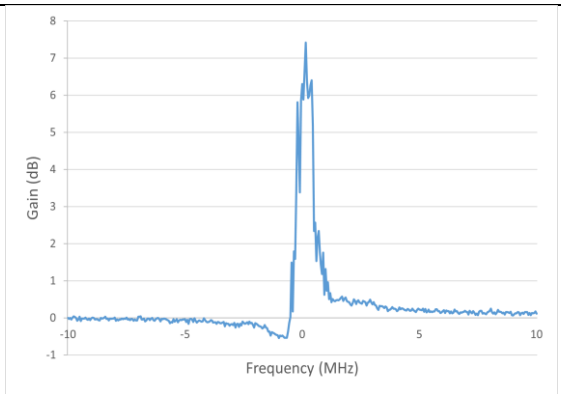

Figure 1 THz gain measured for the (J=3, K=3) pure inversion transition of NH_3. The spectrum is shifted by 1073049.9 MHz

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* Corresponding author: jean-francois.lampin@univ-lille.fr

Theoretical study of butadiene clusters

Julie Douady[1*], Aude Simon[2], Mathias Rapacioli[2], Florent Calvo[3]

[1] *CIMAP,UMR6252,Normandie Univ, ENSICAEN, UNICAEN, CEA, CNRS,Caen, France*
[2] *Laboratoire de Chimie et Physique Quantiques (LCPQ),Fédération FeRMI, UMR5626,Université de Toulouse, CNRS, Toulouse, France*
[3] *LiPhy,University Grenoble Alpes, CNRS,Grenoble France*

We present a theoretical study of clusters of 1,3-butadiene containing up to 20 monomers (trans and gauche conformers) [1]. Our study was motivated by some recent experiments [2] in which clusters of butadiene were found to undergo intracluster reactivity upon collision with a high-energy cation and produce a diversity of larger hydrocarbon molecules. From a theoretical point of view these molecular clusters were investigated using several methods, encompassing classical force fields (Amber ff99), different *ab initio* calculations (DFT-M06-2X, MP2, CCSD(T)) and a specific parametrization of the density-functional-based tight-binding in its self-consistent-charge version (SCC-DFTB). This new parametrization reproduces the energy difference and torsional barrier of the trans and gauche conformers of the monomer predicted at the quantum chemical level. The energy landscape of the pure clusters was explored using the classical force fields method and locally reoptimized using both the DFT and SCC-DFTB methods. The pure trans clusters are generally found to be lower in energy and produce well-ordered structures in which the planar molecules are arranged according to a herringbone motif (see T_{10} in Fig.1). In contrast the lower symmetry of the gauche conformer favors more isotropic packings and the molecular centers of mass adopting distorted icosahedral shapes (see G_{10} in Fig. 1). Mixed clusters containing a single gauche molecule were also studied and found to keep the herringbone motif, the gauche impurity usually residing outside (see $T_{10}G$ in Fig. 1). In those clusters, the strain exerted by the cluster on the gauche molecule leads to significant geometrical distortion of the dihedral angle already at zero temperature. Finally, the finite temperature properties were addressed at the force field level, and the results indicate that the more ordered all-trans clusters are also prone to sharper melting mechanisms.

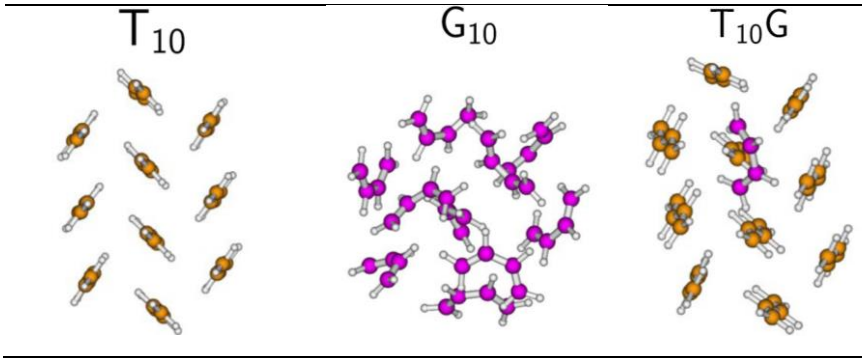

Figure1

Lowest-energy structures of pure and mixed butadiene clusters.

The color of the trans and gauche conformers are respectively orange and pink.

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* correspondant : julie.douady@ensicaen.fr

Keto-gem diol equilibrium reaction from first principle molecular dynamics

Wutharath Chin [1*], Rodolphe Pollet[2],

[1] *ISMO-CNRS, Université Paris-Saclay, 91400 Orsay*
[2] *NIMBE, CEA, CNRS, Université Paris-Saclay, 91191, Gif-sur-Yvette*

Atmospheric aerosols have a strong impact on the climate and on human health: they can absorb or reflect solar radiations; they play an important role in cloud formation; they contribute to the formation of particle matter which badly affect human health. Carboxylic acids, especially glyoxylic acid and pyruvic acid, are very abundant in marine aerosols. In the aqueous phase, glyoxylic and pyruvic acids adopt two forms in equilibrium: The keto form with two carbonyl groups and the gem-diol form that bears two hydroxyl groups on the same carbon [1]. While the gem-diol form is transparent to solar radiation, the keto moiety is light sensitive, thereby contributing through its photochemistry to the production of larger compounds involved in the formation of secondary organic aerosols [2].

By means of ab-initio simulations well suited to the observation of rare events, our theoretical study on the keto/gem-diol equilibrium sheds light on the hydration mechanism of glyoxylic and pyruvic acids. Our investigation also provides a detailed description of the solvation sites and of their conformational landscape in solution [3].

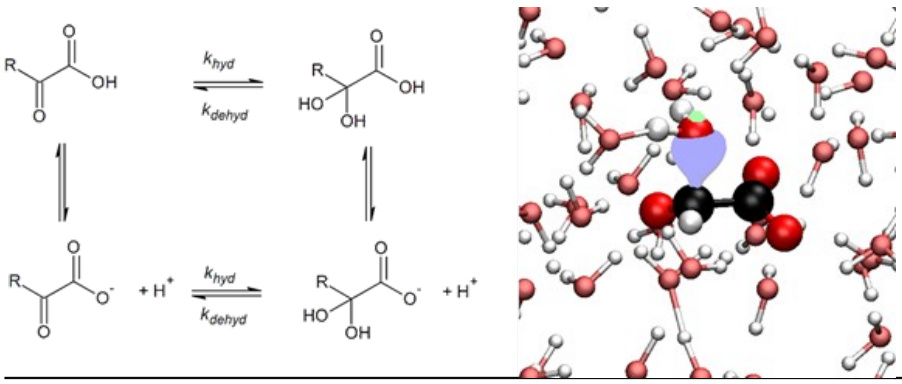

Figure 1 : Left: Scheme of the ketone/gem-diol equilibrium of the R-CO-COOH acid in solution (R=H: glyoxylic acid, R=CH_3: pyruvic acid). Right: Typical configuration for the transition state of glyoxylic acid showing a water lone electron pair (blue and green isosurfaces of a maximally localized Wannier function) interacting with the α-carbon.

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* correspondant : wutharath.chin@universite-paris-saclay.fr

Chemistry and spectroscopy of $CH_3C(O)O_2$ radicals

Christa Fittschen[1*], Mohamed Assali[1]

[1] *PC2A, Université de Lille, UMR CNRS 8522, Lille, France*

Peroxy radicals, RO_2, are key species in the atmosphere. They are formed from a reaction of OH radicals with hydrocarbons:

$$RH + OH + O_2 \rightarrow RO_2 + H_2O$$

In polluted environments, RO_2 radicals react predominantly with NO, leading to formation of NO_2, and eventually through photolysis of NO_2 to formation of O_3.

At low NO_x concentrations such as in the marine boundary layer or the background troposphere, the lifetime of RO_2 radicals increases and other reaction pathways such as self- and cross reaction with other RO_2 or with HO_2 radicals become competitive. To study these reactions, UV absorption spectroscopy has been employed in the past: this technique gives good sensitivity for peroxy radicals, but poor selectivity as these radicals have broad absorption features in the UV. We have established a technique allowing to follow peroxy radicals with a better selectivity compared to UV, but with still good sensitivity by coupling laser photolysis to cw-Cavity Ring Down Spectroscopy in the near IR [1].

Here, we will present results on the measurement of the rate constant of the self-reaction of the acetylperoxy radical, $CH_3C(O)O_2$. Studying this reaction is much complicated due to unavoidable secondary chemistry: the self-reaction leads to formation of CH_3O_2 radicals, which in turn react with $CH_3C(O)O_2$. This reaction has two different paths, one leading to stable products, the other to CH_3O_2 and HO_2 radicals. The HO_2 radicals from this reaction in turn react with both, $CH_3C(O)O_2$ and CH_3O_2 radicals, leading also to either stable products or recycling the radicals. Therefore, the branching ratios of both secondary reactions will influence the decay of the acetylperoxy radical and need to be determined [2].

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Photo-catalysis for the environment, sustainable energy and CO_2 recycling

Aikaterini Tsirkou,[a] Nina Tyminska,[b] Karine Costuas,[b] Stephane Cordier,[b] Fabien Grasset,[b] and Luke MacAleese,[a]

[a] Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622 Lyon, France
E-mail : aikaterini.tsirkou@univ-lyon1.fr , luke.mac-aleese@univ-lyon1.fr
[b] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

The project PHOTOCAT aims at investigating the reaction mechanisms of two alternative photo-catalytic processes, leading to the reduction of CO_2 into methanol (recycling into commodity chemicals) and the generation of H_2 from water (production of decarbonated energy). These two processes involve octahedral clusters of molybdenum (Mo), a non-critical raw material for EU, as photocatalytic centers. These nanoscale aggregates of molybdenum have the structure $[\{Mo_6X^i_8\}X^a_6]^{2-}$ (X=halogen) and possess inner ligands (X^i) in face capping positions and apical ligands (X^a) in terminal position. In the solid state, they crystallize with counter cations to form $A_x[\{Mo_6X^i_8\}X^a_6]$ (A=Alkali). The exchange of X^a ligands with inorganic or organic ligands may be the first step of their reactivity. The proof of concept of the photo-reactivity of these complexes has been recently provided, but any attempt to develop applications requires the rationalization of the mechanisms involved. At the heart of the hypotheses is the involvement of triplet states strongly coupled to singlet states by very efficient spin-orbit couplings in these heavy species.

The gas-phase molybdenum clusters are investigated after electrospray by mass spectrometry in order to determine their molecular weight, obtain information on their molecular structure and study their chemical modifications which depend on the solution conditions. The nature of solvent (CH_3CN, H_2O) and solution composition, in particular the presence of a base (NH_3, NaOH, $(C_4H_9)_4OH$, KOH) is investigated in an attempt to identify important steps on the ligand substitution mechanisms. In addition, the influence of light on the progress of the ligand exchange reaction in the various conditions above is also investigated: theoretical calculations suggest that the reactivity leading to halogen substitution by hydroxide (OH^-) involves a photo-excited triplet state.

The project PHOTOCAT aims at the identification of the major reaction steps in the selected photo-catalytic processes, a necessary step towards the optimization of the catalytic process.

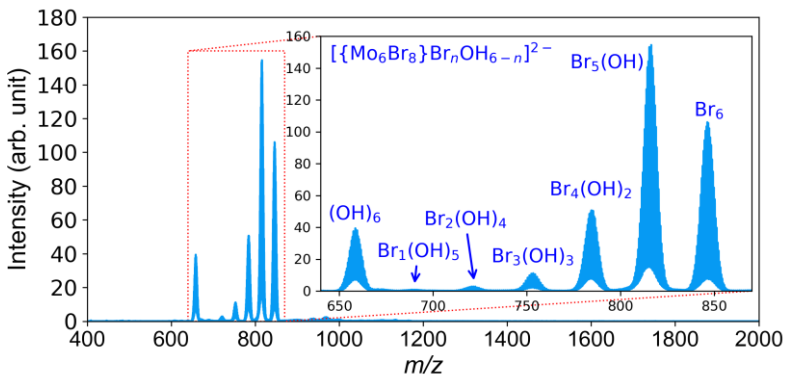

Figure 1 - Mass spectrum of a solution of $Cs_2Mo_6Br_{14}$ in an acetonitrile: water mixture in the presence of NH_3. Up to 6 Br^-/OH^- exchanges are observed.

Millimeter-wave spectroscopy of 3-methylcatechol

L. Manuel Roca[1], Jonas Bruckhuisen[1], Anthony Roucou[1]*, Manuel Goubet[2], Francis Hindle[1], Guillaume Dhont[1], Qian Gou[3,4], Xiujuan Wang[3], Arnaud Cuisset[1]*.

[1] Laboratoire de Physico-Chimie de l'Atmosphère (LPCA), Université du Littoral Côte d'Opale (ULCO), France
[2] Laboratoire de Physique des Lasers Atomes et Molécules (PhLAM), Université de Lille, France
[3] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China
[4] Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, Chongqing, China

Secondary Organic Aerosol (SOA) formation during the ozonolysis of 3-methylcatechol (3-methyl-1,2-dihydroxybenzene) and 4-methylcatechol (3-methyl-1,2-dihydroxybenzene) was identified from atmospheric simulation chamber studies at the LPCA [1]. These molecules are generated in our atmosphere by lignin pyrolysis [2] and belong to Semi Volatile Organic Compounds (SVOC) whose millimeter-wave spectroscopy is limited by their low vapour pressure at room temperature for absorption cell measurements.

The present work focus on the development of a heated absorption cell for the measurement of the millimeter-wave spectrum of 3-methylcatechol with an amplified frequency multiplication chain [3]. As presented in figure 1, different spectra have been measured for temperatures ranging from 23°C to 130°C. Based on a preliminary microwave study performed at Chongqing University, a first calculated spectrum of two conformers of 3-methylcatechol is also presented. A competition between the vapour pressure which increases the line intensity and the partition function which decreases it was interpreted from these measurements. As a result, we selected 50°C for the measurement of the complete millimeter-wave spectrum of 3-methylcatechol in the 70-220 GHz range. These results constitute a preliminary step for the study of a large variety of atmospheric or military-interest SVOC at the LPCA.

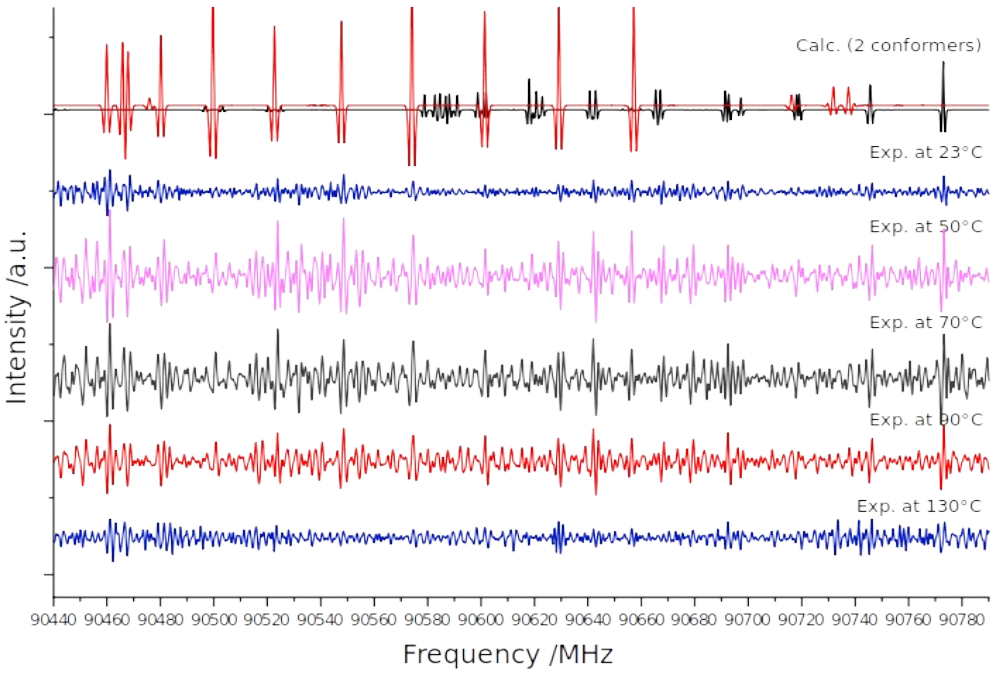

Fig. 1 : millimeter-wave rotational spectrum of 3-methylcatechol measured at different temperatures and compared with a first calculation based on microwave study.

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* correspondant : anthony.roucou@univ-littoral.fr, arnaud.cuisset@univ-littoral.fr

Liste des participants

- Abouhaidar Rawan : rawan.abouhaidar.ra@gmail.com
- Al Ali Fatima : al-ali@univ-littoral.fr
- Ander Camiruaga : ander.camiruaga@universite-paris-saclay.fr
- Antonelli Eléonore : eleonore.antonelli@lisa.ipsl.fr
- Asselin Pierre : pierre.asselin@upmc.fr
- Attal Loïse : loise.attal@universite-paris-saclay.fr
- Augustin Patrick : augustin@univ-littoral.fr
- Bardaud Jean-Xavier : j.xavier.bardaud@gmail.com
- Ben Fathallah Ons : ons.ben.fathallah.1994@gmail.com
- Berthomier Julien : julienberthomier5@gmail.com
- Beydoun Ali : baydoun62@hotmail.com
- Bichon Jeyan : jeyan.bichon@iemn.fr
- Biennier Ludovic : ludovic.biennier@univ-rennes1.fr
- Bocquet Robin : robin.bocquet@univ-littoral.fr
- Boudon Vincent : Vincent.Boudon@u-bourgogne.fr
- Bourehil Lyna : lyna.bourehil@sorbonne-universite.fr
- Bracquart Colwyn : colwyn.bracquart@gmail.com
- Brenner Valérie : valerie.brenner@cea.fr
- Briant Marc : marc.briant@cea.fr
- Broquier Michel : michel.broquier@u-psud.fr
- Bruckhuisen Jonas : jonas.bruckhuisen@univ-littoral.fr
- Calvo Florent : florent.calvo@univ-grenoble-alpes.fr
- Campargue Alain : alain.campargue@univ-grenoble-alpes.fr
- Carcabal Pierre : pierre.carcabal@universite-paris-saclay.fr
- Chawananon Sathapana : sathapana.chawananon@upmc.fr

- Chawananon Sathapana : sathapana.chawananon@sorbonne-universite.fr
- Chen Weidong : chen@univ-littoral.fr
- Chin Wutharath : wutharath.chin@universite-paris-saclay.fr
- Chirot Fabien : fabien.chirot@univ-lyon1.fr
- Chrayteh Mhamad : mhamad.chrayteh@univ-littoral.fr
- Claus Jordan : jordan.claus@univ-lille.fr
- Compagnon Isabelle : isabelle.compagnon@univ-lyon1.fr
- Coussan Stéphane : stephane.coussan@univ-amu.fr
- Crépin Claudine : claudine.crepin-gilbert@u-psud.fr
- Cui Ruyue : cuiruyue1993@163.com
- Cuisset Arnaud : arnaud.cuisset@univ-littoral.fr
- Decker Jean : jean.decker@univ-littoral.fr
- Del Fré Samuel : samuel.del-fre@univ-lille.fr
- Delahaye Thibault : thibault.delahaye@lmd.polytechnique.fr
- Desfrancois Charles : charles.desfrancois@univ-paris13.fr
- Desmedt Arnaud : arnaud.desmedt@u-bordeaux.fr
- Dhont Guillaume : guillaume.dhont@univ-littoral.fr
- Dontot Léo : leo.dontot@gmail.com
- Dossmann Héloïse : heloise.dossmann@sorbonne-universite.fr
- Douady Julie : julie.douady@ensicaen.fr
- Drean Pascal : pascal.drean@univ-lille.fr
- Eliet Sophie : sophie.eliet@univ-lille.fr
- Elmaleh Coralie : coralie.elmaleh@univ-littoral.fr
- Fakhardji Wissam : wissam.fakhardji@lmd.ipsl.fr
- Fertein Eric : fertein@univ-littoral.fr
- Fittschen Christa : christa.fittschen@univ-lille.fr
- Fréreux Joffrey : joffrey.frereux@uclouvain.be
- Georges Robert : robert.georges@univ-rennes1.fr
- Gloaguen Eric : eric.gloaguen@cea.fr
- Goubet Manuel : manuel.goubet@univ-lille.fr
- Guibourg Paul : paul.guibourg@outlook.fr
- Gutiérrez Quintanilla Alejandro : alejandro.gutierrez-quintanilla@univ-amu.fr

- Hearne Thomas S : thomas.hearne@universite-paris-saclay.fr
- Hindle Francis : francis.hindle@univ-littoral.fr
- Hochard Erwan : ErwanHochard.Phy@gmail.com
- Infantino Alicia : alicia.infantino@univ-lyon1.fr
- Jacquet Emmanuelle : emmanuelle.jacquet@unicaen.fr
- Jouan Armel : armel.jouanpourchet@gmail.com
- Khabbaz Alexandra : alexandrakhabbaz@gmail.com
- Kulinski Pierre : pierre.kulinski@univ-littoral.fr
- Lacinbala Ozan : ozan.lacinbala@universite-paris-saclay.fr
- Lampin Jean-François : jean-francois.lampin@univ-lille.fr
- Laurent Adèle : Adele.Laurent@univ-nantes.fr
- Lauzin Clément : clement.lauzin@uclouvain.be
- Leboucher Héloïse : heloise.leboucher@irsamc.ups-tlse.fr
- Lecomte Julien : julien.lecomte@univ-rennes1.fr
- Leroux Juliette : juliette.leroux14@gmail.com
- Liger-Belair Gérard : gerard.liger-belair@univ-reims.fr
- Lorin Florian : florian.lorin@sfr.fr
- M Nair Arya : arya.nair@irsamc.ups-tlse.fr
- Macaleese Luke : luke.macaleese@univ-lyon1.fr
- Mammez Marie-Hélène : marie.mammez@laposte.net
- Manceron Laurent : laurent.manceron@synchrotron-soleil.fr
- Marciniak Alexandre : alexandre.marciniak@irsamc.ups-tlse.fr
- Mascetti Joëlle : joelle.mascetti@u-bordeaux.fr
- Merkulova Mariia : mari_andrew@mail.ru
- Mons Michel : michel.mons@cea.fr
- Mouret Gael : mouret@univ-littoral.fr
- Neeman Elias : elias.neeman@univ-lille.fr
- Ngo Nhut : minh-nhut.ngo@univ-littoral.fr
- Nguyen Truong Anh : tranh18694@gmail.com
- Nguyen Ha Vinh Lam : lam.nguyen@lisa.ipsl.fr
- Nguyen Ba Tong : tong-nguyen.ba@univ-littoral.fr
- Nieuwjaer Nicolas : nicolas.nieuwjaer@univ-paris13.fr

- Parneix Pascal : pascal.parneix@universite-paris-saclay.fr
- Perot Solène : solene.perot@univ-rennes1.fr
- Rabilloud Franck : ranck.rabilloud@univ-lyon1.fr
- Rey Michael : michael.rey@univ-reims.fr
- Rivero Santamaria Alejandro : alejandro.rivero@univ-lille.fr
- Roca Gallardo Luis Manuel : luis.roca.etu@univ-lille.fr
- Roucou Anthony : anthony.roucou@univ-littoral.fr
- Sacquin-Mora Sophie : sacquin@ibpc.fr
- Scuderi Debora : debora.scuderi@u-psud.fr
- Simon Fabien : fabien.simon@univ-littoral.fr
- Simon Aude : aude.simon@irsamc.ups-tlse.fr
- Sobanska Sophie : sophie.sobanska@u-bordeaux.fr
- Soep Clément : clement.soep@etu.sorbonne-universite.fr
- Soorkia Satchin : satchin.soorkia@u-psud.fr
- Sublemontier Olivier : olivier.sublemontier@cea.fr
- Sun Haoyue : haoyue.sun@lisa.ipsl.fr
- Tchana Betnga Wilfried : w_tchana@yahoo.com
- Toubin Céline : celine.toubin@univ-lille.fr
- Tran Ha : ha.tran@lmd.jussieu.fr
- Troitsyna Larisa : larisa.troitsyna@univ-fcomte.fr
- Tsirkou Aikaterini : aikaterini.tsirkou@univ-lyon1.fr
- Vallet Valérie : valerie.vallet@univ-lille.fr
- Vanvincq Veronique : veronique.vanvincq@univ-littoral.fr
- Wei Tingting : waitingonce@163.com
- Yining Jiang : yining.jiang@universite-paris-saclay.fr
- Yusef Buey Maysa : myusef@irsamc.ups-tlse.fr
- Zamith Sébastien : Sebastien.Zamith@irsamc.ups-tlse.fr