Book of abstract

8-12 juin 2026

Toulouse

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Programme

lundi 8 juin 2026

HEURES	ÉVÉNEMENT
16:00 - 17:00	Accueil des participant.e.s
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17:00 - 18:00	› Quantum Computing for Quantum Chemistry - *Saad Yalouz, Laboratoire de Chimie Quantique de Strasbourg*
18:00 - 18:30	› Molécules ultra-froides : Dynamique, contrôle et applications - *Goulven Quéméner, Laboratoire Aimé Cotton*
18:30 - 19:30	Poster - Cocktail apéritif

mardi 9 juin 2026

HEURES	ÉVÉNEMENT
09:10 - 10:20	Chair - Cyril Falvo
09:10 - 09:40	› How collisional rate coefficients contribute to investigating the journey of molecules in space - *Amélie Godard Palluet, Centro de Astrobiologia [Madrid]*
09:40 - 10:00	› Experimental state-to-state rate coefficients of gas-phase inelastic molecular collisions - *Alberto Macario Farto, Laboratoire de Physique des Lasers*
10:00 - 10:20	› Spectroscopie Rotationnelle des Isomères du Cyanocyclopentadiène et du Diazocyclopentadiène pour la Recherche Astronomique dans les Milieux Interstellaires Chauds et Froids - *Noé Gallifa, Physique Moléculaire aux Interfaces, Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523*
10:20 - 10:50	Pause café
10:50 - 12:00	Chair - Mathias Rapacioli
10:50 - 11:20	› A la recherche des processus primitifs des mécanismes concertés – Apports de la DFT conceptuelle et des outils d'analyse topologique (QTAIM / ELF) - *Vanessa Labet, MONARIS*
11:20 - 11:40	› De la spectroscopie d'électron au contrôle de réactions chimiques - *Hassan Abdoul-Carime, Université Claude Bernard Lyon 1 - Institut de Physique des 2 Infinis de Lyon*
11:40 - 12:00	› Photodissociation et photodétachement : cas des anions de la famille du méta nitrophénolate - *Satchin Soorkia, ISMO*
12:00 - 14:30	Déjeuner
14:30 - 15:40	Chair - Goulven Quéméner
14:30 - 15:00	› Dicke-narrowed spectroscopy of molecules confined in gas cells of sub-wavelength thickness - *Athanasios Laliotis, Laboratoire de Physique des Lasers*
15:00 - 15:20	› High-resolution study of the spectrum of allene around 11 µm - *Solène Perot, Université libre de Bruxelles*
15:20 - 14:40	› Density-dependent intensity in CO2 absorption spectra from requantized molecular dynamics simulations - *Emile DUCREUX, Laboratoire de Météorologie Dynamique*
15:40 - 17:20	Pause café
16:10 - 17:20	Chair - Robert Georges
16:10 - 16:40	› Experimental tests for non covalent interactions in large molecules - *Alexandra Tsybizova, Institut Parisien de Chimie Moléculaire*
16:40 - 17:00	› Probing Environment-Induced Vibrational Stark Effects in Benzyl Alcohol Derivatives in Gas Phase - *Fernando Torres Hernandez, Institut des Sciences Moléculaires d'Orsay*
17:00 - 17:20	› Formation and transfer of HCl in a macromolecular noncovalent complex: does the roaming atom mechanism play a role? - *jean-christophe poully, Centre de recherche sur les Ions, les MAtériaux et la Photonique*
17:20 - 19:00	Poster - Cocktail apéritif

mercredi 10 juin 2026

HEURES	ÉVÉNEMENT
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09:40 - 10:00	› Measurements of dissociation rates of naphthalene and azulene cations close to threshold energy. - *Suvasthika INDRAJITH, Institut de la matière condensée et des nanosciences*
10:00 - 10:20	› Modeling the emission spectra of polycyclic aromatic hydrocarbons by recurrent fluorescence - *Damien Borja, ISMO*
10:20 - 10:50	Pause café
10:50 - 12:00	Chair - Arnaud Cuisset
10:50 - 11:20	› Du spectre à la structure : visualisation interactive et immersive d'édifices moléculaires, des petits agrégats aux assemblages complexes - *Marc Baaden, Laboratoire de biochimie théorique*
11:20 - 11:40	› Modeling the DABCO molecule in various environments (Ar, H_2O, CO_2, NH_3) with extended Density Functional Tight Binding schemes - *Paul Guibourg, LCPQ*
11:40 - 12:00	› Modéliser la spectroscopie infrarouge et la dynamique intramoléculaire de molécules complexes à l'aide d'états effectifs - *Loïse Attal, Theoretische Chemie, Institut für Chemie, Universität Potsdam*
12:00 - 14:30	Déjeuner
14:30 - 15:40	Chair - Marc Briant
14:30 - 15:00	› High-resolution 2D-IR Spectroscopy in Low Temperature Matrix - *Wutharath Chin, ISMO*
15:00 - 15:20	› CRIUM (Cryogénie, Raman, Infrarouge, UV, Masse, pour des études en volume et surface). Une nouvelle instrumentation cryogénique - *Stéphane Coussan, PIIM*
15:20 - 15:40	› Étude par isolation en matrice cryogénique des voies de photolyse et des réactions radicalaires de molécules organiques d'intérêt atmosphérique - *Alejandro Gutierrez-Quintanilla, IPREM*
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jeudi 11 juin 2026

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09:10 - 09:40	› Computational investigation of multiphase chemical mechanisms in atmospheric aerosols and water droplets - *Céline Toubin, PhLAM*
09:40 - 10:00	› Photolysis of cis-pinonic acid particles at the single-particle scale - *Gwendoline Bourdon, ISM*
10:00 - 10:20	› High resolution infrared measurements of dioxane isomers using Fourier transform and quantum cascade laser spectroscopies coupled to supersonic jet and long path cell - *Pierre Asselin, MONARIS*
10:20 - 10:50	Pause café
10:50 - 12:00	Chair - Manuel Goubet
10:50 - 11:20	› High resolution THz instrumentation - *Francis Hindle, LPCA*
11:20 - 11:40	› Sub-Doppler Spectroscopy of Methane in the THz range - *Andjela Zarin, ISMO*
11:40 - 12:00	› La chiralité et la flexibilité moléculaires sondées par une lumière polarisée circulairement - *Valéria Lepère, ISMO*
12:00 - 14:30	Déjeuner
14:30 - 15:40	Table ronde

HEURES	ÉVÉNEMENT
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16:10 - 17:20	Chair - Stéphane Coussan
16:10 - 16:40	› Spectroscopie optique et spectrométrie de masse pour l'environnement et l'Univers - *Claire Pirim, PhLAM*
16:40 - 17:00	› Temperature Programmed Desorption of SO2 from Water Ice Surfaces: Adsorption Energy Distributions - *Ferdinand Benoit, MONARIS*
17:00 - 17:20	› Simulating steady state spectra of acrolein while accounting Nuclear Quantum Effects - *Mukul Dhiman, INSP*
17:20 - 19:00	Poster - Cocktail apéritif
19:30 - 21:30	Conférence grand public (Eurêkafé)
19:30 - 21:30	› Le nanomètre comme si vous y étiez - la Visualisation Moléculaire - *Marc Baaden, Laboratoire de Biochimie Théorique*

vendredi 12 juin 2026

HEURES	ÉVÉNEMENT
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09:10 - 09:40	› Studying the properties of PAH and hydroxylated PAH in interaction with water in the context of laboratory astrophysics - *Alexandre Marciniak, LCAR*
09:40 - 10:00	› Exploring Structure and Dynamics of Large PAHs clusters using Deep Neural Network Potentials - *Antoine Laurens, LCPQ*
10:00 - 10:20	› Ecoulements hypersoniques et atmosphères exoplanétaires - *Robert Georges, IPR*
10:20 - 10:50	Pause café
10:50 - 11:40	Chair - Sébastien Zamith
10:50 - 11:20	› Experimental insights in gas phase kinetics and conformational dynamics - *Fabien Chirot, ILM*
11:20 - 11:40	› Caractérisation du transfert d'énergie dans la dissociation induite par collision (CID) ; cas du cation n-butylbenzène avec le xénon - *Roland Thissen, Institut de Chimie Physique*
11:40 - 12:00	Conclusions - Luke Mac Aleese

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Sponsors


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3

Conférence d'ouverture

Quantum Computing for Quantum Chemistry

Saad Yalouz

[1] *Laboratoire de Chimie Quantique de Strasbourg Institut de Chimie, UMR7177 4, rue Blaise Pascal, 67000 Strasbourg - France*

In quantum computing, significant efforts are devoted to developing quantum algorithms with the long-term goal of accessing properties of molecular systems beyond the reach of classical computation. However, current quantum devices remain very noisy and limited, requiring adapted algorithmic strategies.

In this introductory talk, I will present how a molecular physics problem can be formulated for implementation on current quantum computer. More specifically, I will discuss how the electronic structure of a molecule can be mapped onto a collection of qubits. Based on this, I will then discuss a key algorithm for approximating molecular ground states that is tailored to near-term devices: the Variational Quantum Eigensolver.

I will then extend this framework to molecular polaritonic systems, where a molecule is strongly coupled to a photonic environment inside an optical cavity. Simulating *ab initio* polaritonic chemistry requires efficient representations of strongly correlated light–matter states, raising the question of whether qubit-based encodings are optimal or whether alternative paradigms may offer advantages. I will then discuss encoding strategies based on quBits, quDits, and quModes, with an emphasis on higher-dimensional representations.

4

Conférence grand public

Le nanomètre comme si vous y étiez - la Visualisation Moléculaire

Marc Baaden[1*]

[1] *Université Paris Cité, CNRS, Laboratoire de Biochimie Théorique, 13 rue Pierre et Marie Curie, F-75005, Paris, France*

Notre monde est une soupe de molécules toutes plus variées les unes que les autres. Qu'elles soient à la base de la vie, de composés dangereux ou bien de simples matériaux, elles structurent l'ensemble du monde matériel à l'échelle du nanomètre. Leur compréhension est donc fondamentale, mais comment se les représenter autrement qu'à travers des schémas ou des notations abstraites ? C'est là tout l'objet de la visualisation moléculaire.

Marc BAADEN est un spécialiste de la visualisation moléculaire reconnu internationalement. Il crée des outils de visualisation et manipulation moléculaire immersif.

Venez découvrir ses travaux, puis tester certains des outils de réalité virtuelle qu'il a développé !

Cette soirée vous est proposée par le groupement de recherche EMIE (Edifices Moléculaires Isolés et Environnés) à l'Eurêkafé de 19h30 à 21h30 le 11 juin 2026.

Faculté sciences et ingénierie Université de Toulouse

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Keynote lectures

Contents

Computational investigation of multiphase chemical mechanisms in atmospheric aerosols and water droplets

Rawan AbouHaidar[2], Sana Bougueroua[2], Denis Duflot[1], Marie-Pierre Gaigeot[2], Barbara Wyslouzil[3], Céline Toubin[1]

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

[2] Université Paris-Saclay, University Evry, CY Cergy Paris Université, CNRS, LAMBE UMR8587, 91025 Evry-Courcouronnes, France

[3]The Ohio State University - William G. Lowrie Department of Chemical and Biomolecular Engineering, Columbus, OH 43210-1226, USA.

Gas–liquid and air–liquid interfaces play a central role in atmospheric chemistry by controlling reaction kinetics, phase partitioning, and chemical transformations. Gaining molecular-level insight into these interfacial processes is essential for predicting atmospheric behavior and its implications for climate and the environment. Molecular dynamics (MD) and quantum mechanical (QM) approaches provide complementary perspectives on the multiphase chemistry and mechanisms of freezing.

This talk highlights applications of these molecular-level methods. MD simulations elucidate interfacial organization and partitioning between surface and bulk phases, which strongly influence uptake processes, surface properties, and ice nucleation. In particular, graph theory analysis has revealed how short-chain alcohols modify the hydrogen-bonding network of interfacial water, offering new perspectives on the early stages of freezing relevant to climate science. In parallel, QM and hybrid QM/QM' methods captured heterogeneous reactivity, including explicit solvent effects, and predict heterogeneous rate constants that may differ by several orders of magnitude from gas-phase reactions.

The French State under the France-2030 programme and the Initiative of Excellence of the University of Lille are acknowledged for the funding and support granted to the R-CDP-24-003-AREA project

References

[1] Abouhaidar, R. ; D. Duflot, C. Toubin, Theoretical characterization of the kinetics of the multiphase ozonolysis of an aqueous maleic acid droplet, *Aerosol Science and Technology*, *58*(4), 337–355. https://doi.org/10.1080/02786826.2023.2286341

[2] AbouHaidar, R., Bougueroua, S., Duflot, D., Gaigeot, M.P., Wyslouzil, B., Toubin C., Unraveling Aqueous Alcohol Freezing: new theoretical tools from graph theory to extract molecular processes in MD simulations, Faraday Discussions 2025. https://doi.org/10.1039/D4FD00165F

Molécules ultra-froides : Dynamique, contrôle et applications

Goulven Quéméner[1*]

[1] *Laboratoire Aimé Cotton, CNRS, Université Paris-Saclay*

Le domaine des molécules ultra-froides a connu ces dernières années un essor impressionnant. Aujourd'hui on peut créer des gaz cohérents d'environ 30000 molécules dipolaires (le plus souvent de bi-alcalins) dans le même état quantique interne, à une température d'une centaine de nano Kelvin. Par le contrôle de ces molécules avec des champs électriques et/ou électromagnétiques, on peut les protéger de collisions néfastes comme des réactions chimiques, les gaz atteignant des durées de vie de quelques secondes. Ainsi, les premiers condensats de Bose-Einstein et gaz de Fermi dégénérés de molécules ont été observés récemment. Par ailleurs, ces molécules peuvent être assemblées de manière périodique dans un réseau optique crée par des lasers et être manipulées et déplacées individuellement par des pinces optiques. Elles peuvent être crées sous forme de paires intriquées pour l'implémentation de portes quantiques, être observées sous forme de phases dipolaires émergentes à N-corps, être utilisées pour l'étude de chimie réactive cohérente et contrôlée, et être assemblées pour former des tétramères à longue portée. Dans cet exposé introductif, je présenterai le domaine des molécules ultra-froides actuel et ses dernières avancées [1]. Je me concentrerai plus particulièrement sur des exemples qui pourraient potentiellement intéresser d'autres disciplines du GDR comme l'étude de complexes moléculaires [2], les réactions chimiques [3], le controle cohérent [4], et l'assemblage de molécules [5], présentés ici dans le contexte du régime ultra-froid.

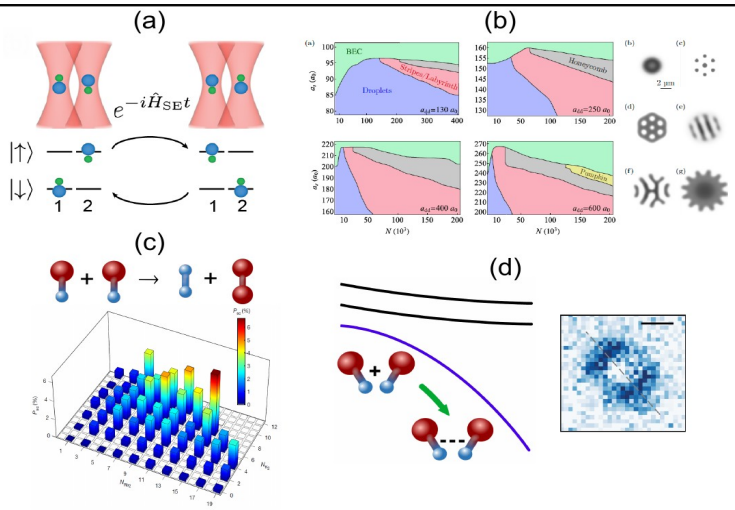

Figure 1 : Molécules ultra-froides pour différentes applications : (a) intrication et portes quantiques [6], (b) phases émergentes [7], (c) réactions chimiques [3], (d) assemblage de molécules [5].

[1] A. Schnidewolf et al., submitted to Rev. Mod. Phys., arXiv:2512.14511 (2025)
[2] J. F. E. Croft et al., Phys. Rev. A **107**, 023304 (2023)
[3] Y. Liu et al., Nature **593**, 379 (2021)
[4] T. Delarue et al., Phys. Rev. A **109**, L061303 (2024)
[5] G. Quéméner et al., Phys. Rev. Lett. **131**, 043402 (2023) ; X.-Y. Chen et al., Nature **626**, 283 (2024)
[6] Y. Bao et al., Science **382**, 1138 (2023) ; C. Holland et al., Science **382**, 1143 (2023) ; D. Ruttley et al., Nature **637**, 827 (2025)
[7] M. Schmidt et al., Phys. Rev. Research **4**, 013235 (2022) ; S. Zhang et al., Nature **651**, 601 (2026)
* correspondant : goulven.quemener@cnrs.fr

How collisional rate coefficients contribute to investigating the journey of molecules in space

Amelie Godard Palluet[1*]

[1] *Centro de Astrobiología (CAB, CSIC-INTA), Ctra. de Torrejón a Ajalvir km 4, 28850 Torrejón de Ardoz, Madrid, Spain*

Astrochemistry tries to unveil the origin and evolution of molecular complexity in space [1]. From molecular clouds to comets, molecular species serve as diagnostic tools, offering insights into the evolution of astrophysical objects and the emergence of life on Earth. By analysing molecular spectra captured by telescopes, we can infer the physical conditions—such as temperature, density, and molecular abundances—of these environments, shedding light on their origins and futures.

However, the analysis of molecular spectra is often performed under the Local Thermodynamic Equilibrium (LTE) approximation, which is not expected to hold in most astrophysical media. Relying solely on the LTE approach raises two critical issues: **(1) uncertainties in molecular line intensities can hinder the detection of new species**, and **(2) poorly constrained physical conditions limit our understanding of the physics and chemistry within these media**. To overcome these limitations, non-LTE radiative transfer models should be employed. However, these models require collisional rate coefficients, which are available for only a fraction of the molecules detected so far.

Such studies are highly interdisciplinary by nature. They require the use of quantum chemistry methods to compute the potential energy surface (PES) of the system (Figure 1.a.), scattering approaches to compute the collisional rate coefficients based on the PES (Figure 1.b), astronomy to capture the molecular spectra, and radiative transfer modeling to determine the physical conditions of the media using the new collisional data and comparing the results with the observations (Figure 1.c.).

In this presentation, I will focus on the methods and challenges involved in determining collisional rate coefficients for astrophysical applications. I will present the full quantum approaches we used to determine these coefficients for the CCS-He system and all its isotopologues [1,2]. These results led to a re-estimation of CCS abundances, and thus to a re-evaluation of its formation process before star formation [3]. I will also introduce statistical approaches, an alternative method employed for the study of molecules in comets [4.5]. This approach led to excellent results and shows great promise, particularly in cometary science where only five molecules can currently be accurately modelled.

By providing sets of collisional data, we enable the robust determination of molecular abundances, gaining valuable insights not only into the formation pathways of these molecules but also into the origins of our Solar System.

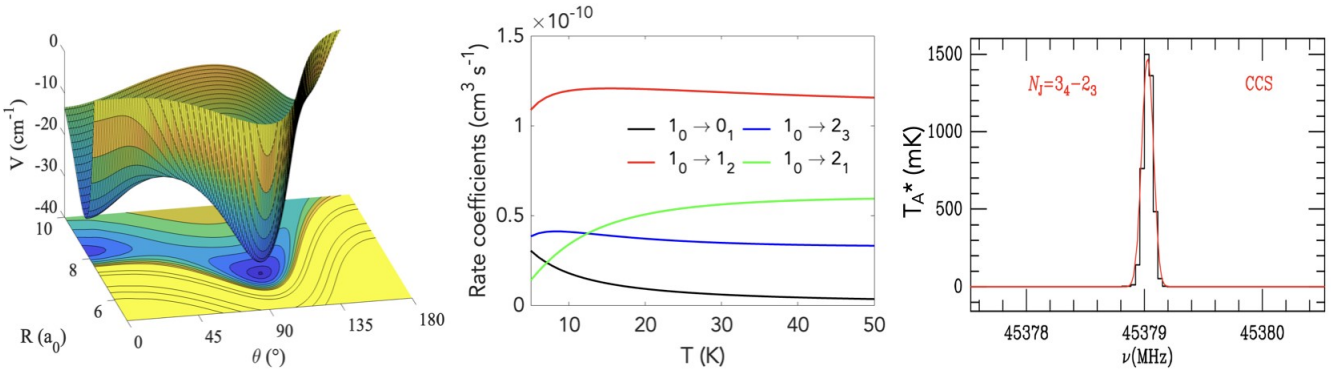

Figure 1: (a) Potential energy surface of the CCS-He system, (b) Collisional rate coefficients of the CCS-He system, (c) Molecular spectra of CCS captured in TMC-1

[1] A. Godard Palluet & F. Lique (2023).
[2] A. Godard Palluet & F. Lique (2024).
[3] R. Fuenteta et al., A&A 702, A23 (2025)
[4] A. Godard Palluet, R. Dawes; E. Quintas-Sánchez, A. Batista-Planas, F. Lique, J. of Chem. Phys. Comm. 162, 241101 (2025)
[5] A. Godard Palluet, J. Klos, D. Kedziera, F. Lique, A&A 707, A55 (2026)

* correspondant : amelie.godard@cab.inta-csic.es

Dicke-narrowed spectroscopy of molecules confined in gas cells of sub-wavelength thickness

Hippolyte Mouhanna[1,2], Athanasios Laliotis[1,2*]

[1] Laboratoire de Physique des Lasers, Université Sorbonne Paris Nord, F-93430, Villetaneuse, France
[2] CNRS, UMR 7538, LPL, 99 Avenue J.-B. Clément, F-93430 Villetaneuse, France

Miniaturized atomic vapor cells of nanometric thickness have become promising platforms for fundamental measurements, metrology and quantum technologies. For example, nanometric cells have been used for exploring Dicke-type effects of confinement [1], measuring Casimir-Polder interactions, fabricating compact atomic clocks and probing collective effects. Extending these experiments to molecular gases is a fascinating prospect for applications in compact frequency referencing and for testing fundamental quantum electrodynamics using increasingly complex quantum objects. Towards this end, experiments have been performed with platforms such as hollow core fibers, tapered nanofibers and integrated waveguides. Moreover, selective reflection experiments with molecules have also been performed [2].

Here, we present our pioneering experiments probing molecular rovibrations of gases confined in micrometric cells, whose thickness is comparable to the excitation wavelengths. We work in two distinct regions of the electromagnetic spectrum, probing $\nu_1 + \nu_3$ resonances of acetylene at 1.530 µm, within the telecommunications wavelength range, as well as the ν_3 and ν_2 resonances of SF_6 and NH_3 respectively, in the mid-infrared fingerprint region around 10.55 µm. Thin-cell confinement allows us to explore and demonstrate Dicke-narrowing effects, probing molecules with linear sub-Doppler transmission spectroscopy. Our first experiment, reported recently in Nature Communications [3], uses a cell with a thickness that varies between 5.2–5.5 µm. This corresponds to $7\lambda/2$ and $\lambda/2$ thickness for acetylene and SF_6 or NH_3 rovibrations respectively. We also report measurements in a second cell of thickness ranging from 600–1200 nm allowing us to explore tighter molecular confinement. The transmission spectra displaying sub-Doppler characteristics due to the coherent Dicke narrowing are analyzed by means of a theoretical model making specific assumptions about the physics and dynamics of confined molecules. In all the above measurements, the model reproduces exceptionally well the experimental data.

We focus our analysis on both the absolute signal amplitude and spectral lineshape. This allows us to confirm, within the limits of our precision, the hypotheses concerning the collisions with the cell-windows, the Maxwell-Boltzmann thermal distribution of velocities and the rotational redistribution (Boltzmann repartition function) of molecules after desorption from the wall. This is an important result, as the equilibrium conditions of confined gases have been put into question [4]. Furthermore, our analysis confirms that our spectroscopic technique can be used to determine molecular transition strengths and therefore enrich molecular databases. We demonstrate this by providing new data on the SF_6 greenhouse molecule for which databases are notoriously incomplete.

A major perspective resulting from this work is the measurement of Casimir-Polder interactions with molecules. For this purpose, we are currently building a new experiment to probe the strong HF rovibration at 2.5 µm. This experiment will allow us to probe strongly confined HF gas in a nanocell (100 nm thickness) and measure the effects of molecular orientation in Casimir-Polder interactions.

[1] G. Dutier et al., Europhys. Lett. EPL, 63, 35–41 (2003.
[2] J. Lukusa Mudiayi et al., Phys. Rev. Lett, 127, 043201 (2021).
[3] G. Garcia Arellano et al., Nat. Commun, 15, 1862 (2024).
[4] P. Todorov and D. Bloch, J. Chem. Phys., 147, 194202 (2017).
* correspondant : laliotis@univ-paris13.fr

High resolution THz instrumentation

Francis Hindle[1], Fabien Simon[1], Arnaud Cuisset[1], Gaël Mouret[1]

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

THz waves can be attractive for the analysis of gas phase samples as they are able to provide an excellent discrimination due to the particularly fine Doppler broadening. This frequency range located between the micro-wave and infrared domains is challenging for the construction of instrumentation because of the lack of mature system components such as sources, detectors, filters etc. Nevertheless, over the last two decades the LPCA has focussed its attention on high-resolution THz spectroscopy of gases. Numerous spectrometers have been constructed with the aim to increase the overall performance in terms of sensitivity, spectral coverage, measurement speed and usability. This development has been accompanied by the use of the instruments for both fundamental spectroscopy and numerous applied studies. Several recent advances will be presented and include the use of a resonant cavity gas cell to achieve high sensitivity [1], high resolution spectroscopy with a frequency comb [2], and heterodyne instrumentation [3] which is pushing available frequency range.

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[2] F. Hindle, A. Khabbaz, A. Roucou, J.-F. Lampin, and G. Mouret, 'Terahertz Frequency Comb High-Resolution Heterodyne Spectrometer', *IEEE Transactions on Terahertz Science and Technology*, vol. 15, no. 4, pp. 566–572, Jul. 2025, doi: 10.1109/TTHZ.2025.3572249.
[3] T. S. Hearne *et al.*, 'Unlocking synchrotron sources for THz spectroscopy at sub-MHz resolution', *Opt. Express*, vol. 30, no. 5, p. 7372, Feb. 2022, doi: 10.1364/OE.448147.

High-resolution 2D-IR Spectroscopy in Low Temperature Matrix

Wutharath Chin[1]*, Armel Jouan[1 #], Daniel Varga[1], Claudine Crépin[1], Jan Helbing[2]

[1] Institut des Sciences Moléculaires d'Orsay ISMO, CNRS, Univ. Paris-Saclay
[2] Département de chimie, Univ. de Zürich, Suisse
 # present adress: Institut de Physique et Chimie des Matériaux de Strasbourg IPCMS, Univ. de Strasbourg

Matrix isolation spectroscopy offers an interesting window into vibrational dynamics free from solvent interactions and broad absorption in liquids. The cryogenic temperatures not only allow for new relaxation pathways, but also make it possible to study reactive and less/meta-stable species. Yet the resulting narrow spectral bandwidths (≤1 cm^{-1}) and the matrix site-effects require techniques that can resolve thin, and sometimes complex overlapping features. Our recent high-resolution two-dimensional infrared (2D-IR) spectrometer rises this challenge, opening the route to detailed vibrational signatures and relaxation pathways so far not accessible through classical linear spectroscopy [1].

We report the high spectral resolution 2D-IR spectra of two benchmark metal carbonyls - $W(CO)_6$ and $Fe(CO)_5$ - and bring new insight into the symmetry-breaking these systems undergo in cryogenic matrices.

In solid nitrogen, the T_{1u} (3-fold degenerate) asymmetric C≡O stretch mode of $W(CO)_6$ splits into multiple bands, with 2/3 of molecules showing fully lifted degeneracy (see Fig. 1). 2D-IR cross-peaks reveal weak negative anharmonic coupling (−1 cm^{-1}) and excitation transfer between non-degenerate modes on tens of picoseconds at 20 K, slowing at 5 K. Energy redistribution within high-symmetry T_{1u} modes remains temperature-independent.

The vibrational spectrum of $Fe(CO)_5$ presents an even complex spectrum with dense and overlapping features in cryogenic matrices [2,3]. This richness is unravelled by 2D-IR spectroscopy, revealing multiple trapping sites with different degrees of symmetry breaking. By mapping anharmonicities and mode couplings, we unambiguously assign the numerous transitions into well-defined trapping site families. Going further, we elucidate the ultrafast dynamical processes through polarisation measurements by evidencing site- and mode-specific relaxation, intramolecular energy transfer, and IR activation of dark modes.

Beyond these showcase examples of symmetry-breaking, our high-resolution 2D-IR spectra of matrix-isolated molecules can directly map the anharmonic coupling between normal modes in the fingerprint region, and disentangle complex spectra, making it the method of choice for probing environmental effects in cryogenic matrices.

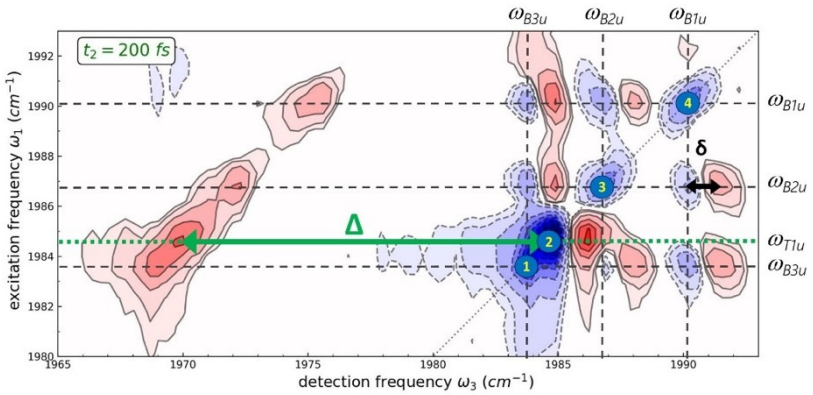

Figure 1: 2D-IR spectrum of $W(CO)_6$ in solid nitrogen at 20 K showing the asymmetric stretch signals for both the degenerate (2) and low-symmetry sites (1,3,4).

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* correspondant : wutharath.chin@cnrs.fr

Experimental tests for non-covalent interactions in large molecules

Alexandra Tsybizova[1], Vladimir Gorbachev, [2] Peter Chen[3]

[1]Sorbonne University, IPCM - Paris (France), [2]University of Basel, Department of Chemistry - Basel (Switzerland), [3]ETH Zurich, Department of Chemistry and Applied Biosciences - Zurich (Switzerland)

Abstract

In classical descriptions of molecular interactions, steric bulk repels. Yet careful experiments on simple model systems have revealed that two large, nonpolar substituents placed in close proximity can attract one another, stabilising the very arrangements that steric arguments would disfavour. This counterintuitive behaviour is a signature of London dispersion: the weak, attractive interaction arising from correlated fluctuations of electron density, which acts between all pairs of atoms in contact. Although each pairwise contribution is small — well below 1 kcal mol^{-1} — the interaction is strictly additive and scales steeply with molecular size. In molecules of 50–200 atoms, the cumulative dispersion energy can reach tens of kilocalories per mole, sufficient to determine conformational preferences, influence reaction barriers, and control stereoselectivity. London dispersion has accordingly become a recognised design element in modern organic and organometallic chemistry, yet its direct, quantitative measurement in large, chemically realistic molecules remains challenging. In solution, interactions with the solvent compensate 40–80% of the gas-phase dispersion energy, obscuring the intrinsic interaction. Isolating and measuring London dispersion therefore calls for the gas phase.

To this end, we have developed a series of gas-phase molecular torsion balances in which London dispersion is placed in direct, tunable competition with a well-defined reference interaction. The systems investigated are substituted pyridinium ions and proton-bound onium ions, electrosprayed into the gas phase and interrogated by a combination of complementary structural probes: cryogenic ion vibrational predissociation (CIVP) spectroscopy, infrared multiphoton dissociation (IRMPD) spectroscopy at a free-electron laser, and trapped ion mobility spectrometry (TIMS).[1,2,3] In each series, the size of the pendant alkyl substituents is varied systematically from hydrogen to methyl to tert-butyl, progressively increasing the dispersion contribution while keeping the molecular framework constant. The N–H stretching mode, whose frequency is exquisitely sensitive to the local non-covalent environment, serves as a diagnostic conformational reporter, complemented by collision cross sections as an independent structural observable.

The talk will present results obtained across three series of test systems of increasing complexity, illustrating how the interplay between London dispersion, electrostatics, and conformational flexibility can be disentangled experimentally, and what these measurements reveal about the reliability of widely used computational models for non-covalent interactions.

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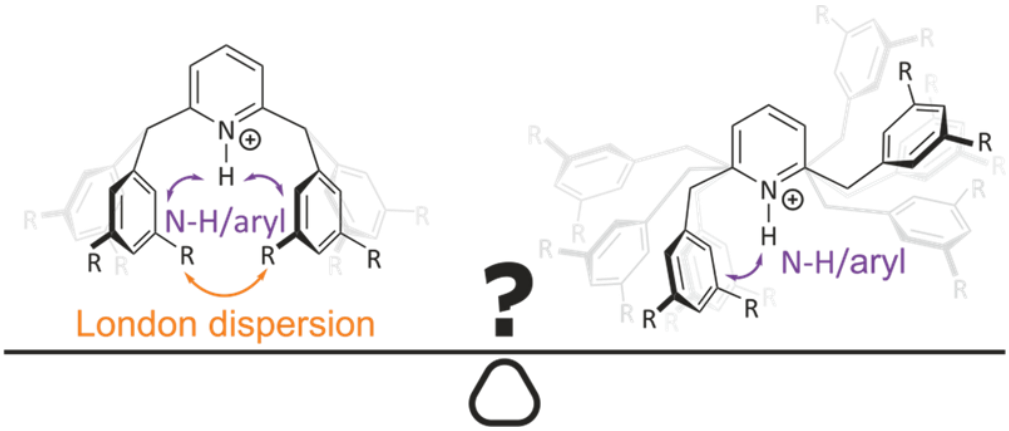


Du spectre à la structure : visualisation interactive et immersive d'édifices moléculaires, des petits agrégats aux assemblages complexes

Marc Baaden[1*]

[1] Université Paris Cité, CNRS, Laboratoire de Biochimie Théorique, 13 rue Pierre et Marie Curie, F-75005, Paris, France

Comprendre les édifices moléculaires — qu'ils soient isolés en phase gazeuse, piégés dans une matrice, ou intégrés à un environnement complexe — passe de plus en plus par une articulation fine entre simulation, expérience et analyse visuelle. Cet exposé présentera comment les outils interactifs et immersifs permettent d'explorer des systèmes moléculaires couvrant plusieurs ordres de grandeur en taille et en complexité: agrégats, nano-objets, biomolécules solvatées, assemblages supramoléculaires. Au-delà de la visualisation, ces approches ouvrent la voie à des manipulations interactives, à la confrontation directe entre données calculées et mesurées, et au partage FAIR des expériences moléculaires. Je discuterai des cas d'usage que j'espère pertinents pour la communauté EMIE — depuis l'interprétation de signatures spectroscopiques jusqu'à l'analyse des effets d'environnement — et des perspectives qu'offrent les jumeaux numériques moléculaires pour la physico-chimie de demain. J'illustrerai mes propos par des expériences développées autour de la plateforme UnityMol et d'outils comme bioSPRING et MolPlay qui sont disponible gratuitement.

Figure 1 : Illustration conceptuelle d'une manipulation interactive et immersive.

[1] https://unity.mol3d.tech
[2] https://molplay.mol3d.tech
[3] https://biospring.mol3d.tech

* correspondant : baaden@smplinux.de

A la recherche des processus primitifs des mécanismes concertés – Apports de la DFT conceptuelle et des outils d'analyse topologique (QTAIM / ELF)

Vanessa Labet[1*], Antoine Geoffroy-Neveux[1], M. Esmaïl Alikhani[1]

[1] *Laboratoire MONARIS, Sorbonne Université, Paris, France*

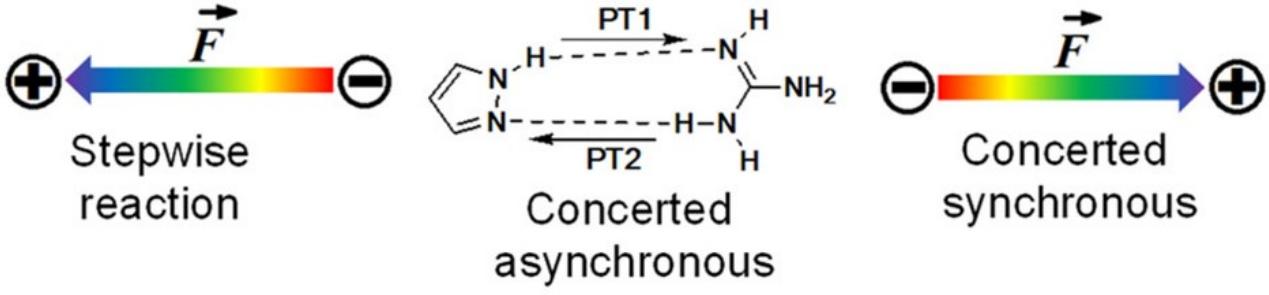
La brique élémentaire d'un mécanisme réactionnel est l'étape élémentaire, définie par une unique barrière d'activation et un seul état de transition. Cependant, certaines étapes élémentaires peuvent être intrinsèquement complexes et impliquer plusieurs processus couplés, que nous qualifierons de processus primitifs. C'est le cas des mécanismes concertés qui seront au cœur de cette communication.

De nombreuses réactions, telles que les réactions de Diels–Alder ou encore les réactions de doubles transferts de protons (DTP), sont connues pour pouvoir suivre, selon les conditions expérimentales, soit un mécanisme concerté, soit un mécanisme par étapes. Cette dualité suggère que les processus primitifs sous-jacents constituent le niveau pertinent de description pour appréhender et contrôler le degré d'asynchronicité des mécanismes concertés. Une telle approche ouvre la voie à une modulation continue entre mécanismes concertés et mécanismes par étapes, avec des implications directes en termes de contrôle de la sélectivité.

Dans ce contexte, les profils de force de réaction et de constante de force, issus de la DFT conceptuelle, offrent un cadre théorique particulièrement adapté pour analyser l'évolution d'un système réactif le long de la coordonnée de réaction. Ils permettent notamment de définir une région élargie de l'état de transition, au sein de laquelle se concentrent les réorganisations électroniques. Nous montrerons comment ces descripteurs permettent de distinguer mécanismes par étapes, mécanismes concertés synchrones et mécanismes concertés asynchrones.[1]

Par ailleurs, nous montrerons que dans le cas des réactions de DTP l'application d'un champ électrique externe d'orientation et d'intensités adéquates peut permettre de modifier le couplage entre les processus primitifs d'un mécanisme concertés. [2]

Enfin, nous mettrons en évidence que les outils d'analyse topologique (QTAIM ou ELF selon la réaction d'intérêt) peuvent permettre de localiser et caractériser les processus primitifs d'un mécanisme concerté. [3]



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Studying the properties of PAH and hydroxylated PAH in interaction with water in the context of laboratory astrophysics

Alexandre Marciniak[1,2], Fatima Baterdouk[1], Sébastien Zamith[1], Arya M. Nair[1], Anthony Bonnamy[1,2], Héloïse Leboucher[3], Mathias Rapacioli[3], A. Simon[3], Giacomo Mulas[4,5], Sandra Brünken[5], Priyanka Paunikar[5], Donatella Loru[6], Melanie Schnell[6] and C. Joblin[2]

[1] Univ Toulouse, CNRS, LCAR, Toulouse, France
[2] Univ Toulouse, CNRS, CNES, IRAP, Toulouse, France
[3] Univ Toulouse, CNRS, LCPQ, Toulouse, France
[4] INAF - Osservatorio Astronomico di Cagliari, Via della Scienza 5, I-09047 Selargius (CA), Italy
[5] HFML-FELIX, Institute for Molecules and Materials, Radboud University, Nijmegen, Netherlands
[6] Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

Polycyclic Aromatic Hydrocarbons (PAHs) and water molecules are ubiquitous in regions of star and planet formation in which they have an important contribution to the chemical evolution [1,2]. In cold and dense regions, water molecules can adsorb on icy and carbonaceous grains containing PAHs. The irradiation by energetic photons or particles (cosmic rays) may lead to the formation of strongly bounded PAH-water complexes. The latter species correspond to the incorporation of oxygen into PAH by the formation of the carbonyl (C=O) or hydroxyl (C-OH) function leading to ketones, quinones, enols or alcohols [3,4,5] which are key molecules in prebiotic chemistry. Exposure of the icy grains to UV irradiation may then lead to the evaporation of these new species or to weakly bounded clusters made of PAH, functionalized PAH and water [6]. Therefore, studying PAH-water systems in the laboratory by experiments and/or quantum chemistry is needed to better understand the role and the survivability of such molecular systems in these regions in order to support astronomical observations.

We are investigating such topics thanks to a strong collaboration between three laboratories in Toulouse (IRAP, LCAR and LCPQ). This has led us to develop different methodologies to study mixed PAH-water systems. I will focus on the combined experimental techniques which permit us to produce, manipulate, isolate and study such species [7,8] and our recent results which deal with hydroxylated PAHs (OH-PAHs) mixed with water. Our general methodology is to use sources which generate cationic PAHs that act as nucleation seeds for a further aggregation with the surrounding molecules (water or PAH) at low temperature. The formed clusters/complexes are either excited with collisions or photons. The induced modifications are observed by mass spectrometry techniques. These measurements allow us to quantify relevant parameters for astrochemistry such as the dissociation energies, the IR spectra or the collision/photon cross-sections of these species. Besides, these studies give insights on fundamental processes such as photo-excitation and energy redistribution which are at play in astrophysical environments and may be of interest for atmospheric chemistry [9,10].

I will focus my presentation on recent results obtained with the “Agrégats” setup at LCAR and the “FELion” setup at FELIX on the 1-hydroxypyrene (OH-Pyr) and 1-hydroxyphenanthrene (OH-Phen) in interaction with water. These results are obtained either by collision induced dissociation or IR tagging spectroscopy [11]. They demonstrate that OH-PAHs have a specific interaction with water through the hydroxyl function and a higher dissociation energy than the bare PAH. Additionally, the modification of the IR spectrum induced by one water molecule in interaction with $OH\text{-}PAH^+$ is discussed, in particular regarding the expected OH wagging modes around 1000 cm-1 that were not observed experimentally. These studies question isomerization mechanism and the anharmonic couplings in such systems. Finally, I will present the ongoing development in LCAR regarding the “CASSOULExp” setup which aim to systematically perform IR tagging spectroscopy on complexes made of several functionalized or bare PAHs and water molecules.

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Theoretical studies of large molecular systems of astrophysical interest: static and dynamic properties

Aude Simon

Univ Toulouse, CNRS, Laboratoire de Chimie et Physique Quantiques (LCPQ), Toulouse, France.

Exploring the potential energy surface (PES) of large molecular aggregates and unraveling their dynamic evolution under energy input have long been major challenges in theoretical chemistry. To address these issues, efficient algorithms based on Monte Carlo (MC) and molecular dynamics (MD) have been developed and are now routinely combined with electronic structure methods that provide a favorable balance between computational cost and accuracy. Among these, the Density Functional Tight Binding (DFTB) method has emerged as a particularly attractive approach [1].

Using examples from recent studies of astrophysical relevance, we will illustrate:

(i) The structural, energetic, and spectral information accessible for complex systems such as neutral and charged polycyclic aromatic hydrocarbon (PAH)-water aggregates, as well as PAHs complexed with metal atoms. These results are obtained using a multistep approach that combines parallel tempering Monte Carlo (PTMC) with DFTB, followed by local optimization at the density functional theory (DFT) level [2,3].

(ii) How MD/DFTB simulations complement experimental investigations in elucidating unimolecular dissociation mechanisms of large carbon-based molecules such as PAHs [4,5], collision-induced dissociation of protonated PAH-water aggregates, and formation of silver-hydrocarbon complexes in a plasma reactor.

The advantages and limitations of the adopted methodologies will also be discussed.

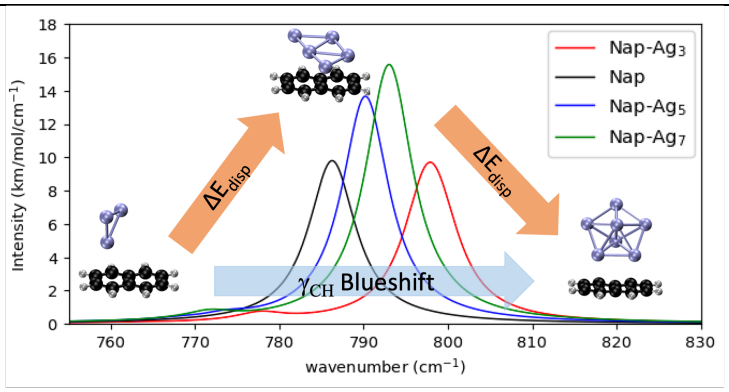

Figure 1 : adapted from [3]. Influence of the coordination of Ag_n (n=3,5,7) on the out-of-plane CH mode of naphthalene.

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Experimental insights in gas phase kinetics and conformational dynamics

Frederik Menn[1], Marium Haq[1], Charlène Bouanchaud[1], Luke Mac Aleese[1], Thomas Robert[2], Julien DeWinter[2], Pascal Gerbaux[2], Fabien Chirot[1*]

[1] *Institut Lumière Matière, UM55306 CNRS Université Claude Bernard Lyon 1, Villeurbanne, France*
[2] *Service de Synthèse et de Spectrométrie de Masse, Université de Mons, Mons, Belgique*

Conformational flexibility is key property of molecular species as it modulates their ability to interact with each other and to adapt to their environment. Flexibility is then not only central to the function of numerous biomolecules, but it is also an important characteristic of synthetic molecules. As a dynamic property however, molecular flexibility can be difficult to capture, especially when molecules are in the gas phase. We developed a method, based on mass spectrometry (MS) and ion mobility spectrometry (IMS) dedicated to the characterization of conformational dynamics of complex molecular systems in the gas phase. Namely, our setup uses the ability of IMS to separate conformers in the gas phase as a way to select ionic species with a defined conformation. The selected species can then be subjected to various stimuli, before a second IMS stage used to readout potential conformational changes. Such IMS-IMS scheme has been used in our group to investigate different types of conformational changes, ranging from photoisomerization [1] to spontaneous conformational rearrangements [2]. In this presentation I will focus on the investigation of the kinetics of structural rearrangements using a trap-and release procedure in which the temperature dependance of the kinetics can be determined. This method was applied to synthetic polymers [3], and also to biomolecular species such as peptides, proteins, and peptide complexes. As exemplified in Figure 1, these experiments allow to extract kinetics parameters associated to the investigated conformational changes.

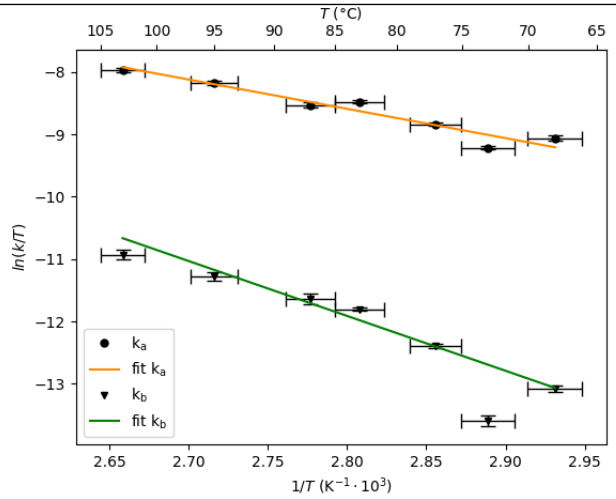

Figure 1 : Eyring's plot representing the evolution of the kinetics constants for the unfolding of two distinct compact states of the Ubiquitin protein. The relative enthalpies and entropies of the associated transition states can be inferred from such plots.

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

Spectroscopie optique et spectrométrie de masse pour l'environnement et l'Univers

Claire Pirim[1], Yvain Carpentier[1], Michael Ziskind[1], Elodie Gloesener[1], Bertrand Chazallon[1] and Cristian Focsa[1]

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

Claire.Pirim@univ-lille.fr

Notre groupe de recherche au laboratoire PhLAM mène des travaux interdisciplinaires en physique moléculaire, avec des applications en sciences de l'environnement et en sciences planétaires.

Dans le domaine de l'environnement, nous étudions le comportement physico-chimique des particules et des molécules impliquées dans les processus atmosphériques, en nous intéressant particulièrement à la phase condensée et aux interfaces solide–gaz. À l'aide d'instruments commerciaux et de dispositifs développés au laboratoire, nous analysons la composition de surface des aérosols, leur nanostructure ainsi que les mécanismes de nucléation de la glace. Nous développons une approche intégrée, combinant échantillonnage, analyses multi-techniques et méthodes statistiques avancées, pour prendre en compte la spécificité de ces différents systèmes moléculaires.

Dans le contexte de la décarbonation et de la transition énergétique, nous explorons les technologies basées sur les hydrates de gaz pour le captage du carbone, la récupération du gaz naturel et le dessalement de l'eau de mer. Nous avons développé une méthode robuste de microspectroscopie Raman permettant d'évaluer les performances des hydrates de gaz et démontré avec succès le captage du CO_2 à partir de gaz simulant des fumées industrielles par séparation fondée sur les hydrates.

Nous avons également étendu nos activités aux études paléoenvironnementales en développant un système unique de spectrométrie de masse laser HR-L2MS permettant l'analyse organique à l'échelle micrométrique de microfossiles et d'échantillons extraterrestres. Cet instrument a permis d'apporter de nouvelles connaissances sur les environnements de la Terre primitive ainsi que sur la composition organique des météorites, fournissant des informations sur leur histoire thermique et sur les poussières carbonées interstellaires.

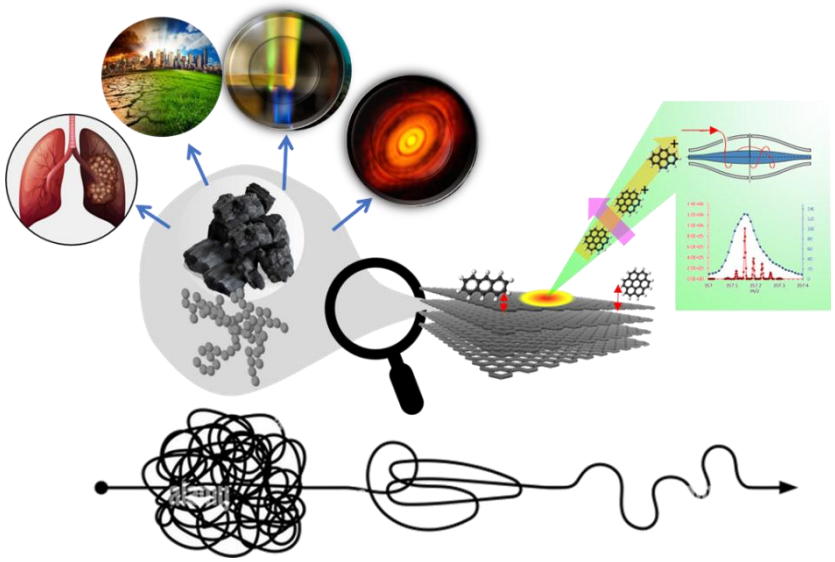


Figure 1 Développements instrumentaux dédiés à la révélation de la complexité moléculaire des échantillons carbonés.

6 Contributions orales

Contents

De la spectroscopie d'électron au contrôle de réactions chimiques

Hassan Abdoul-Carime

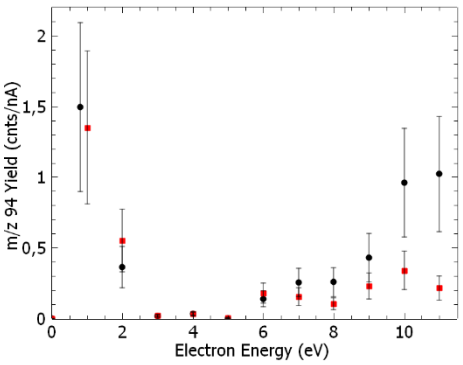
Université Claude Bernard Lyon 1 – Institut de Physique des 2 Infinis de Lyon, UMR5822, F-69003 Lyon, France

Une des tendances en chimie concernent la capacité à maîtriser la synthèse chimique grâce à l'intelligence artificielle [1]. Cibler une réaction spécifique devient probablement l'une des quêtes les actuelles dans le domaine de la synthèse, et le contrôle des processus à l'échelle de l'unité moléculaire par le ciblage de réactifs spécifiques représente la limite ultime.

La photo-activation est un processus bien établi. Les photons d'une longueur d'onde peuvent déclencher spécifiquement des réactions en activant des certaines molécules spécifiques [2]. La photo-synthèse robotisée assistée par l'IA a été récemment proposée [3]. L'avènement des lasers 'atto-seconde' pourront à terme permettre de contrôler la dynamique dans les liaisons chimiques [4].

Les particules tels que les ions et électrons peuvent également d'induire des réactions de synthèse. Jusqu'à maintenant, ces réactions sont réalisées par les particules énergétiques (> keV), illustrés par exemple, en nano-lithogravure par faisceau d'électrons ou d'ions [5]. Toutefois, l'irradiation avec les particules énergétiques ne pas conduire à des processus sélectifs, puisque la déposition d'énergie dans le milieu irradié crée des espèces secondaires tels que les ions, radicaux et électrons balistiques ayant une distribution en énergies < 10 eV qui à leur tour, vont induire différentes réactions.

Lors de cet exposé, je décrirai l'interaction entre les électrons de basses énergies (< 10 eV) avec des molécules en phase gazeuse. Je montrerai que la fragmentation moléculaire est contrôlée par l'énergie de ces particules, tout comme la longueur d'onde pour les photons. Enfin, j'illustrerai, à travers quelques exemples, que les informations obtenues en phase gazeuse permettent de contrôler les réactions de synthèse dans des films moléculaires [6,7].



Synthèse de phénol et benzene par irradiation d'un film de chlorobenzene-eau [7]

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Modeling the emission spectra of polycyclic aromatic hydrocarbons by recurrent fluorescence

Damien Borja[1,2*], Florent Calvo[1], Pascal Parneix[2], Cyril Falvo[1,2]

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

The presence of polycyclic aromatic hydrocarbons (PAH) in the interstellar medium (ISM) was first proposed over 40 years ago, following the observation of the aromatic infrared bands (AIB) [1]. This hypothesis was later confirmed by the detection of Buckminsterfullerene C_{60} [2] and several nitrogen-bearing PAH species [3]. The AIBs results from a transient heating mechanism: isolated molecules absorb a UV or visible photon, reaching an excited electronic state. Non-adiabatic processes then rapidly convert this electronic energy into vibrational energy within the ground electronic state [4], allowing the molecule to relax via spontaneous emission.

Despite this general understanding, many issues remain about the transient heating mechanism and the structure, dynamics and stability of PAHs that play a crucial role in the ISM chemistry.

Recent experiments on the relaxation kinetics of PAH cations trapped in storage rings [5,6,7] reveal a competition between several processes: spontaneous emission, dissociation, isomerization and recurrent fluorescence (RF). The latter in particular, is key to stabilizing PAHs in highly ionized environments found in many regions of the ISM.

In this contribution, we will present a new vibronic model of PAH relaxation by RF mechanism [8]. This model takes into account explicitly the vibrational levels and includes Duschinsky rotations and Herzberg-Teller effects. We will discuss its application to various cations, focusing on the Stokes shift, as well as the vibrational activation of forbidden transitions and their contribution to the total RF emission, in relation with experimental measurements [6].

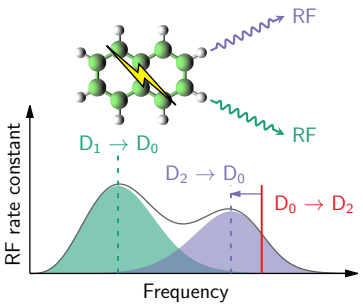

Figure 1 : Typical state-resolved differential RF rate constant for the D_1 and D_2 electronic state of naphthalene cation. The Stokes shift of the D_2 state is highlighted.

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* damien.borja@cnrs.fr

Formation and transfer of HCl in a macromolecular noncovalent complex: does the roaming atom mechanism play a role?

Min Liu[1], Marwa Abdelmouleh[1], Alexandre Giuliani[2,3], Laurent Nahon[2], Jean-Christophe Poully[1*]

[1] CIMAP UMR 6252 Université Caen Normandie, ENSICAEN, CNRS, CEA, Normandie Univ, 14070 Caen, France
[2] Synchrotron SOLEIL, 91190 Saint Aubin, France
[3] INRAE, UAR1008, Transform Department, Rue de la Géraudière, 44316 Nantes, France

In the last twenty years, the “roaming atom” mechanism emerged and gained enormous interest thanks to its success in explaining experimental results that are not accounted for by the widely accepted statistical transition state theory.[1] In the roaming atom mechanism, on the pathway from reactants to products of a given chemical reaction, there is no tight transition state, defined as a saddle point on the potential-energy surface (PES) of the system. Instead, the roaming atom (or group of atoms) explores large and relatively flat regions of the PES, bypassing saddle points. Along its trajectory, “frustrated bonds” between the roaming species and other atoms of the system are successively formed and cleaved.[2] A crucial characteristic is the low total energy required for the roaming atom mechanism to play a major role, once the roaming radical is formed. Another characteristic of the roaming atom mechanism is the asymmetric energy partitioning between the reaction products.

Despite intense efforts for describing this new mechanism, intriguing questions remain. A crucial one is: does it play a role in molecular systems larger than 25 atoms, in particular those relevant to life sciences and pharmacology? Here, we present data on HCl transfer within a noncovalent complex built upon vancomycin, an antibiotic containing more than 170 atoms, and a tripeptide, following UV-VUV photoabsorption in the gas phase. Our experimental results show that the energetics for HCl formation is unusually low, as compared to a straightforward direct abstraction mechanism governed by the transition state, which energy budget has been evaluated by quantum chemistry calculations.[3] Strikingly, we observe an asymmetric internal energy partitioning between the released product anions. Furthermore, the mechanism for HCl formation and transfer implies atypical motion of the reactive Cl radical. We believe that only a roaming atom mechanism can account for these observations. Our results provide a benchmark for future theoretical investigation, not only on HCl loss from molecules, but more broadly on the roaming atom mechanism itself. Moreover, they also raise other questions, for instance whether this mechanism is common in biological molecular systems, and even dominant in some cases.

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* correspondant : poully@ganil.fr

Modéliser la spectroscopie infrarouge et la dynamique intramoléculaire de molécules complexes à l'aide d'états effectifs

Loïse Attal[1*]

[1] *Theoretische Chemie, Institut für Chemie, Universität Potsdam, Germany*

Dès qu'une molécule contient plus d'une dizaine atomes, il devient difficile de modéliser sa dynamique vibrationnelle en résolvant l'équation de Schrödinger pour tous ces modes. Cela est dû à la « malédiction de la dimension » : le nombre d'états à considérer augmente exponentiellement avec la dimension du système [1]. Le problème s'aggrave encore lorsqu'on introduit des effets de température, ce qui demande de considérer un grand nombre d'états initiaux. Dans de tels cas, il peut être intéressant de se concentrer uniquement sur quelques degrés de liberté et de voir le reste de la molécule comme un environnement (ou « bain ») simplifié qui n'est pas traité au même niveau de théorie, et dont la dimension effective est réduite. C'est dans ce contexte que nous avons développé un modèle théorique basé sur une approche « système-bain » où nous considérons un système unidimensionnel (ici un mode vibrationnel) interagissant avec un bain harmonique de grande taille (~10-1000 modes) qui représente le reste de la molécule [2]. Dans la méthode EBS (*Effective Bath State*), le mode d'intérêt et ses couplages avec les autres modes sont traités de manière aussi rigoureuse que possible, mais la partie « bain » de l'hamiltonien est simplifiée. Ainsi, les modes du bain sont remplacés par une unique échelle d'états de bain effectifs qui décrivent l'énergie totale stockée à l'intérieur du bain, on parle de *coarse-graining*. Nous présentons ici l'application de ce modèle à une molécule d'intérêt astrophysique [3], le phénylacétylène (voir Figure 1), pour laquelle nous calculons des spectres infrarouges. Nous montrons aussi que la méthode permet de suivre les transferts de population et d'énergie entre les différents modes vibrationnels de la molécule [4].

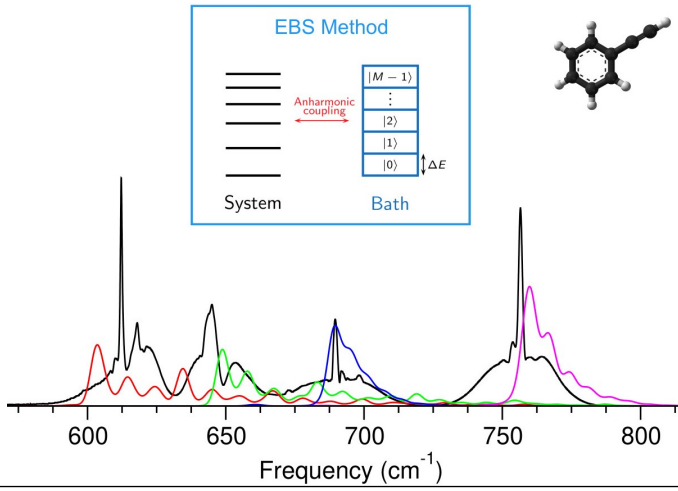

Figure 1 :

Portion du spectre d'absorption de la molécule de phénylacétylène (montrée en haut à droite). Le spectre expérimental est représenté en noir et les spectre partiels obtenus par la méthode EBS, et correspondant aux différents modes normaux impliqués, sont en couleur. L'encadré bleu montre une représentation schématique du modèle, où le mode d'intérêt (le système) est représenté par ses états vibrationnels, et le bain par des états effectifs d'énergie. Des couplages dus à l'anharmonicité de la molécule relie les deux.

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* correspondant : loise.attal@uni-potsdam.de

La chiralité et la flexibilité moléculaires sondées par une lumière polarisée circulairement

Etienne Rouquet[1], Darius Lebeau[1], Sanket Sen[1,2], Valéria Lepère[1*], Anne Zehnacker[1]

[1] *Institut de Sciences Moléculaires d'Orsay (ISMO), CNRS-Université Paris Saclay, Orsay, France*
[2] *Synchrotron SOLEIL, L'Orme des Merisiers, Gif sur Yvette, France*

La chiralité, propriété d'une molécule à ne pas être superposable à son image dans un miroir, est massivement présente dans le domaine du vivant, comme dans les peptides par exemple, ou dans le domaine pharmaceutique via les médicaments. Etudier leur structure et leur flexibilité conformationnelle devient alors une problématique majeure pour comprendre les interactions de tels édifices moléculaires avec leur environnement (complexation ou solvatation) ou leur cible.

Nous avons développé récemment un dispositif qui permet de sonder le dichroïsme circulaire de photoélectrons (PECD) via un schéma d'ionisation résonant sélectif en conformère (RE2PI)[1,2,3]. On mesure alors l'asymétrie avant-arrière dans la distribution angulaire des photoélectrons pour les molécules chirales orientées aléatoirement et ionisées par une lumière polarisée circulairement. L'étude du complexe du méthyloxirane, molécule chirale, avec du phénol, molécule non chirale, a montré un transfert de chiralité original[4,5]. La micro-solvatation du 1-phényléthanol avec de l'eau ou chaque énantiomère du 2-butanol montre un changement de son PECD suite à la modification du potentiel chiral lors de la diffusion de l'électron.

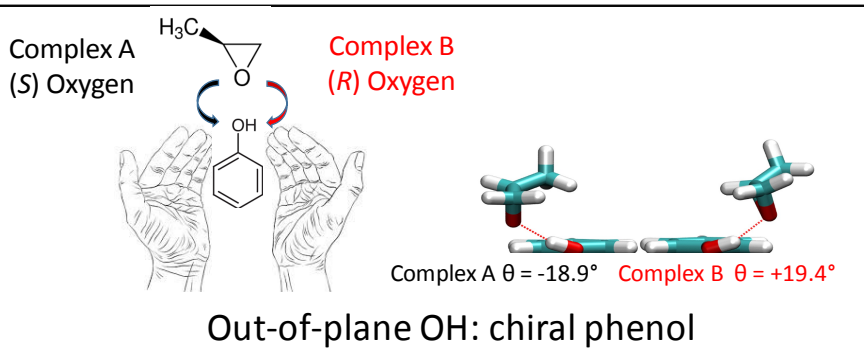

Figure 1 : Complexe entre méthyloxirane et le phénol. Le phénol devient chiral en ayant un groupe OH hors du plan du cycle.

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Chirality and molecular flexibility probed using circularly polarized light

Etienne Rouquet[1], Darius Lebeau[1], Sanket Sen[1,2], Valéria Lepère[1*], Anne Zehnacker[1]

[1] *Institut de Sciences Moléculaires d'Orsay (ISMO), CNRS-Université Paris Saclay, Orsay, France*
[2] *Synchrotron SOLEIL, L'Orme des Merisiers, Gif sur Yvette, France*

Chirality, the property of a molecule that cannot not be superimposed onto its mirror image, is ubiquitous in living organisms, such as in peptides, and in the pharmaceutical industry, particularly in drugs. Studying their structure and flexibility are therefore a key challenge for understanding how such molecular structures interact with their environment (complexation or solvation) or their target.

We have recently developed an experimental set-up that enables the measurement of photoelectron circular dichroism (PECD) via a conformer-selective resonant ionization scheme (RE2PI)[1,2,3]. We then measure the forward-backward asymmetry in the angular distribution of photoelectrons for randomly oriented chiral molecules ionized by circularly polarized light. The study of the complex of methyloxirane, a chiral molecule, with phenol, a non-chiral molecule, revealed chirality transfer from the former to the latter[4,5]. Microsolvation of 1-phenylethanol with water or each enantiomer of 2-butanol shows a change in PECD resulting from the modification of the chiral potential during electron scattering.

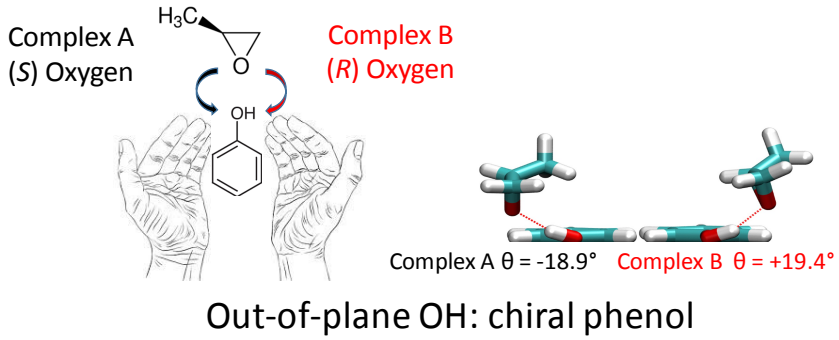

Figure 1 : Complex between methyloxirane and phenol. The phenol becomes chiral with its OH group out of the plane of the ring.

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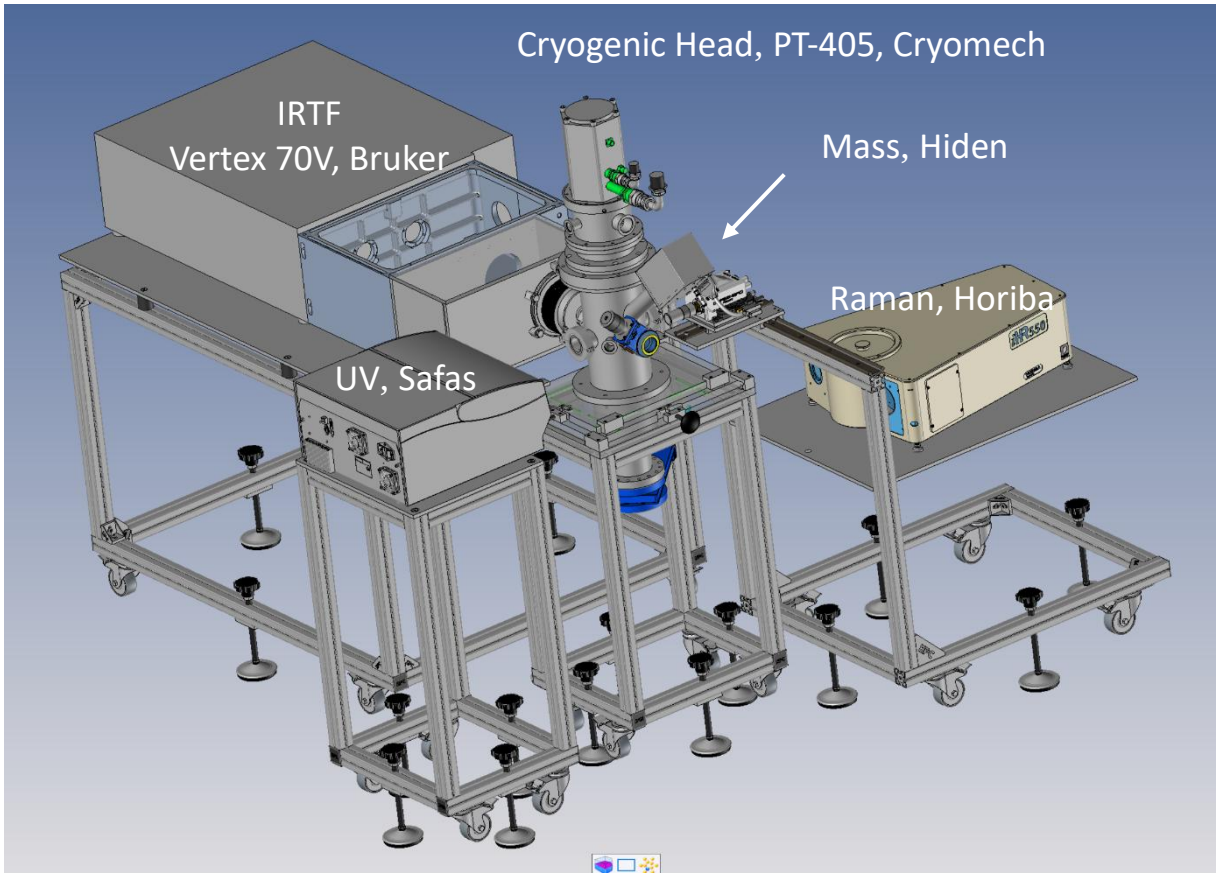
CRIUM (Cryogénie, Raman, Infrarouge, UV, Masse, pour des études en volume et surface). Une nouvelle instrumentation cryogénique

Stéphane Coussan[1],

[1] *Aix-Marseille Univ, CNRS, PIIM, Marseille, France*

Le nouvel ensemble cryostatique, CRIUM, sera opérationnel d'ici la fin avril 2026. Il regroupera, autour d'une seule tête cryogénique (4 K), un spectromètre IRTF, un spectromètre Raman, un spectromètre UV-visible, un spectromètre de masse et des sources de rayonnement accordables allant de l'UV au MIR ou large bande (lampe UV et penray). Cet ensemble sera sous vide primaire (FTIR) afin d'éviter toute contamination atmosphérique. Deux défis majeurs devront être relevés : la spectroscopie UV-visible par fibre et par réflexion, et la capacité à se placer à 1.5 cm du dépôt cryogénique à 4 K pour la spectroscopie Raman. Un autre défi concerne le Raman, car cette spectroscopie n'est pas très sensible (un photon sur un million est un photon « Raman », et les échantillons cryogéniques sont généralement très dilués (concentrations comprises entre 1/200 et 1/2000). Les résultats attendus seront discutés en termes d'applications atmosphériques, astrochimiques et énergétiques (tokamak, matériaux faisant face au plasma).



Photolysis of cis-pinonic acid particles at the single-particle scale

Gwendoline Bourdon[1*], Pierre-Marie Flaud[2], Emilie Perraudin[2], Eric Villenave[2], Sophie Sobanska[1]

[1] *Institut des Sciences Moléculaires, UMR 5255 CNRS, Univ. Bordeaux, Talence, France*
[2] *EPOC, UMR 5805 CNRS, Univ. Bordeaux, Pessac, France*

At the global scale, biogenic volatile organic compounds (BVOCs) are predominantly emitted by vegetation (e.g., monoterpenes such as α- and β-pinene) and lead to the formation of biogenic secondary organic aerosols (BSOAs), which are estimated to account for 30–50% of the global organic aerosol budget1. Once formed, BSOAs can undergo further transformations through multiphase aging processes. These reactions modify both the chemical composition and physico-chemical properties of aerosols, such as hygroscopicity, viscosity, and gas–particle partitioning, thereby influencing their atmospheric fate, air quality, and climate impacts. Cis-pinonic acid (CPA) is a key compound in the formation of biogenic secondary organic aerosols originating from the photo-oxidation of α-pinene2,3. Owing to its low vapor pressure (~7 × 10^{-5} Pa) and its Henry's law constant, the CPA, in the atmosphere, can be presence both in the gas phase and in particle. Despite the proven role of CPA in SOA formation and aging, unknowledges gaps remain regarding the photo-oxidative mechanisms involved. The few mechanisms proposed so far are mainly based on studies conducted in bulk aqueous solutions or flow reactors4,5. Investigations at the single-particle scale are still lacking, even though it is known that reactivity in bulk systems can differ from that at the gas–particle interface due to effects related to particle curvature and exchange surface area. At the single-particle level, levitation techniques provide unique advantages for studying aerosol physico-chemical properties and processes, notably by eliminating substrate-induced artifacts and while controlling environmental parameters (e.g. temperature and relative humidity)6. In this context, the present study aims to elucidate the photo-oxidative aging mechanisms of CPA particles, used as a model for BSOAs generated from α-pinene photo-oxidation, in order to improve our understanding of the atmospheric fate and impact of BSOAs.

To achieve these objectives, an original experimental set up coupling acoustic levitation with high-resolution proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS) was developed. This approach enables real-time observation of volatile compound exchanges between a single particle and the surrounding gas phase during physico-chemical processes. Comparison between bulk and single-particle experiments reveals the emission of methyl vinyl ketone from the particle, produced via a Norrish type II pathway during CPA photolysis. This innovative methodology opens new perspectives for investigating dynamic gas–particle exchanges at the single-particle scale and for a more comprehensive understanding of atmospheric aerosol aging mechanisms.

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* correspondant : gwendoline.bourdon@u-bordeaux.fr

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Exploring Structure and Dynamics of Large PAHs clusters using Deep Neural Network Potentials

Antoine Laurens[a*], Maïa Courtiel[a], Jérôme Cuny[a], Aude Simon[a]

a. Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, Toulouse, France

Email : antoine.laurens1@utoulouse.fr

Abstract:

Since the 1970s, characteristic emission features known as Aromatic Infrared Bands (AIBs) have been observed throughout the Interstellar Medium (ISM). These bands are widely attributed to Polycyclic Aromatic Hydrocarbons (PAHs), which are now estimated to account for 10% to 20% of the galactic carbon. Consequently, PAHs play a fundamental role in key astrophysical processes, such as the formation of molecular hydrogen (H_2) or the photoelectric heating of interstellar gases. In the ISM, these molecules exist in various forms, notably as pure or mixed clusters (incorporating different PAH species or other molecules like water). To study these systems theoretically, density functional based tight binding (DFTB), a semi-empirical formulation of DFT, has emerged as a method of choice, particularly for clusters containing around a hundred atoms[1]. However, DFTB alone remains insufficient to fully characterize the thermodynamic and structural properties of larger and more realistic clusters that can reach up to a thousand atoms.

To overcome this limitation, deep neural network potentials (DNNPs) have emerged as a promising approach to achieve both high accuracy and low computational cost[2]. By implementing an efficient active learning procedure, we have developed DNNPs that maintain DFTB level quality for clusters of several hundred atoms as illustrated in Figure 1. This approach enables a complete description of these complex systems, bridging the gap between molecular scales and "very small grains". We will present preliminary results. The challenge for these systems is the transferability of the DNNP with size and the good description of anisotropic interactions of various nature.

Keywords: Polycyclic Aromatic Hydrocarbons, Clusters, Deep Neural Network Potentials

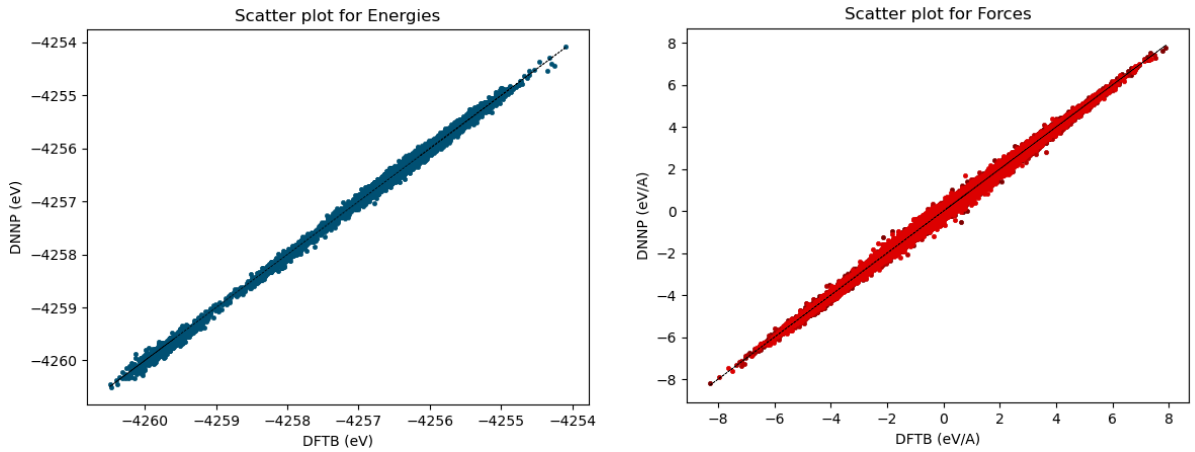

Figure 1. Correlation plots of energies and forces for $(C_{16}H_{10})_5$.

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Density-dependent intensity in CO_2 absorption spectra from requantized molecular dynamics simulations

E. Ducreux*, H. Tran

Laboratoire de Météorologie Dynamique/IPSL, CNRS, Sorbonne Université, École normale supérieure, PSL Research University, École Polytechnique, Institut Polytechnique de Paris, F-75005, Paris, France

Intensity depletion, defined as the decrease of experimentally retrieved line intensities with gas density, is a significant non-impact effect in high-resolution molecular spectroscopy. Although the true line intensity is an intrinsic molecular property, experimentally determined values can be biased when standard line-shape profiles based on the impact approximation are used. This bias arises from the finite duration of intermolecular collisions, which redistributes part of the absorption from the line center to a broad underlying contribution, leading to an apparent reduction of the fitted intensity with density.

For carbon dioxide (CO_2), a major atmospheric greenhouse gas, accurately characterizing this effect is essential for applications such as atmospheric remote sensing and precision gas metrology. Recent experimental studies have reported measurable intensity depletion in self-broadened CO_2 spectra in the near-infrared region, with typical values around 1% per atmosphere at room temperature and stronger effects at lower temperatures. These observations emphasize the need for a detailed physical understanding of density-dependent effects.

In this work, we investigate intensity depletion in self-broadened CO_2 spectra using requantized classical molecular dynamics simulations (rCMDS). This approach combines classical dynamics calculations based on accurate intermolecular potentials with a requantization procedure to generate absorption spectra for various pressure and temperature conditions. By analyzing these spectra using the Hartmann–Tran profile, we quantify the dependence of retrieved line intensities on gas density and temperature.

The simulations reproduce the main experimental trends, including the increase of depletion at lower temperatures and its dependence on rotational quantum number. The analysis provides insight into the underlying mechanisms, including the role of finite collision durations and the possible contribution of metastable dimers. Furthermore, the associated continuum absorption is characterized, and its evolution with temperature is determined and compared with available experimental data. Overall, these results highlight the limitations of impact-based line-shape models and the necessity of incorporating non-impact effects for accurate spectroscopic applications.

* correspondant : emile.ducreux@lmd.ipsl.fr

Caractérisation du transfert d'énergie dans la dissociation induite par collision (CID) ; cas du cation n-butylbenzène avec le xénon

Roland Thissen[1,2*], Nicolas Solem[1,2], Christian Alcaraz[1,2], Nandana Pattathadathil[1,3], Kinga Nagy[4], Ágnes Révész[4], György Lendvay[4], Károly Vékey[4], László Drahos[4]

[1] CNRS, Institut de Chimie Physique, Université Paris-Saclay, UMR 8000, Orsay 91405, France;
[2] Synchrotron SOLEIL, L'Orme des Merisiers, Gif-sur-Yvette 91192, France
[3] Department of Physics, University of Trento, 38123 Trento, Italy
[4] HUN-REN Research Centre for Natural Sciences, H-1117 Budapest, Magyar Tudósok krt. 2

La dissociation induite par collision (CID) est une méthode d'activation clé en spectrométrie de masse tandem. Cependant, les mécanismes régissant le transfert d'énergie lors des collisions ion-neutre restent encore mal compris [1]. Nous avons abordé cette problématique à l'aide du dispositif expérimental CERISES [2] couplé à la ligne de lumière DESIRS [3] du synchrotron SOLEIL, qui permet un excellent contrôle de l'énergie impartie à l'ion avant et pendant la collision. En utilisant le cation radical n-butylbenzène comme sonde, nous avons réalisé des expériences de CID à collision unique avec du xénon [4] sur une large gamme d'énergies de collision, combinées à des mesures de coïncidence photoélectron-photoion au seuil (TPEPICO) [5] afin de calibrer le comportement de fragmentation. Nous montrons que le transfert d'énergie lors du processus CID se décrit très bien par une fonction bimodale (figure 1) : il comprend des collisions rasantes avec un transfert d'énergie minimal et des supercollisions avec une conversion d'énergie translationnelle en énergie interne quasi complète aux énergies de collision faibles à modérées. La proportion de supercollisions augmente avec l'énergie de collision, devenant prédominante au-dessus de ~6 eV, tandis que l'efficacité du transfert d'énergie diminue aux très hautes énergies. Ces résultats affinent la compréhension de la dynamique de la CID, expliquant les divergences observées dans les études précédentes et soulignant que la fragmentation aux énergies de collision analytiques typiques est principalement due à une minorité de collisions hautement inélastiques. Ce modèle bimodal offre un pouvoir prédictif amélioré pour l'interprétation des spectres de fragmentation en spectrométrie de masse.

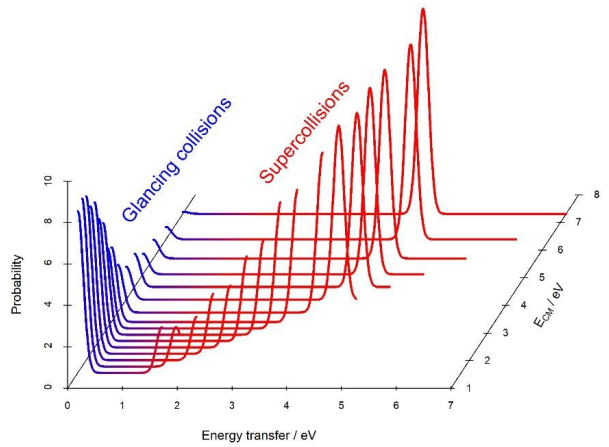

Figure 1 : *représentation de la distribution bimodale de transfert entre énergie cinétique et énergie interne, qui permet de décrire l'évolution de la fragmentation du butylbenzene après collision avec le xenon.*

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* correspondant : roland.thissen@cnrs.fr

Probing Environment-Induced Vibrational Stark Effects in Benzyl Alcohol Derivatives in Gas Phase

Fernando Torres-Hernández, Satchin Soorkia, Michel Broquier, Gilles Grégoire, Eric Gloaguen

Institut des Sciences Moléculaires d'Orsay ISMO, Université Paris-Saclay, UMR CNRS 8214, F-91405 Orsay, France.

Understanding how local electric fields influence molecular systems and their spectroscopy provides a valuable approach for characterizing chemical systems. The Stark effect describes the modification of a molecule's spectroscopic properties under the influence of an electric field, whether externally applied or generated by its surrounding environment [1]. Such fields can arise in both gas-phase and condensed-phase systems, leading to spectral changes such as shifts or broadening.

This phenomenon can be explored in electronic transitions (referred to as the electronic Stark effect (ESE)) which is particularly valuable for studying UV–Vis chromophores. ESE has been widely used to probe charge migration processes [1], guide the design of fluorescent sensors [2], and, more recently, enable detailed conformational analysis through field-induced shifts in electronic transitions [3]. Complementarily, the vibrational Stark effect (VSE), defined as the shift in vibrational frequencies of a molecular probe in response to an electric field, provides a highly sensitive measure of the local chemical environment [4]. As such, VSE offers a powerful route to elucidate conformational preferences by correlating structure-dependent electric fields with vibrational frequency shifts.

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

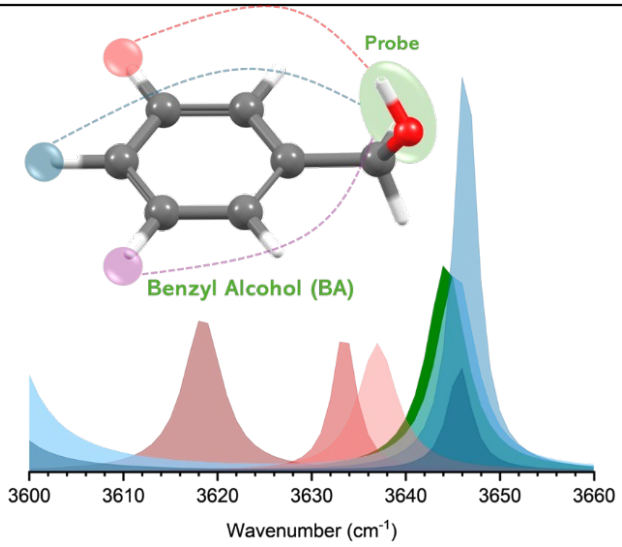

Figure 1 : Vibrational shifts of Benzyl Alcohol (BA) derivatives.

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Photodissociation et photodétachement : cas des anions de la famille du méta nitrophénolate

Satchin Soorkia[1*], Franco L. Molina[1,2], Michel Broquier[1] et G. Grégoire[1]

[1] *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, 91405 Orsay, France*
[2] *Department of Physics and Astronomy, University of Aarhus, Danmark*

L'anion méta-nitrophénolate (mNP^-) est un système modèle de photodonneur du radical NO après excitation électronique dans le domaine visible, présentant une bande origine $S_0 \rightarrow S_1$ située à 625 nm (2,0 eV). Nous avons étudié l'effet sur l'absorption électronique de l'ajout de substituants électrodonneurs (groupement méthyl, $-CH_3$, et groupement amino, $-NH_2$) en position ortho du groupement nitro ($-NO_2$). Tous les composés substitués présentent un spectre d'absorption élargi, signature d'un changement structurel important entre l'état fondamental et le premier état excité.[1]

Si la méthylation induit un déplacement de l'absorption dans le bleu, la substitution amino provoque d'importants déplacements vers le rouge (voir Figure 1). Pour le $4NH_2mNP^-$, l'absorption débute en dessous de 800 nm, la libération de NO demeurant la voie de fragmentation principale. Ces déplacements sont analysés par des calculs *coupled cluster* (CC2/aug-cc-pVDZ) qui mettent en évidence la compétition entre les effets stériques et électrostatiques des groupements donneurs en ortho du groupement $-NO_2$.

Nous avons également étudié le photodétachement de ces systèmes. Dans le cas du mNP^-, nous avons mis en évidence l'existence d'un état excité de l'anion de type état lié par dipôle (DBS, Dipole Bound State ou Anion Dipolaire), où l'électron est stabilisé par une interaction charge-dipôle avec une énergie de liaison d'environ 150 cm^{-1}. La présence d'états excités au voisinage du seuil de photodétachement induit une compétition entre le photodétachement et la photodissociation, un phénomène notamment observé pour l'anion $2CH_3mNP^-$.

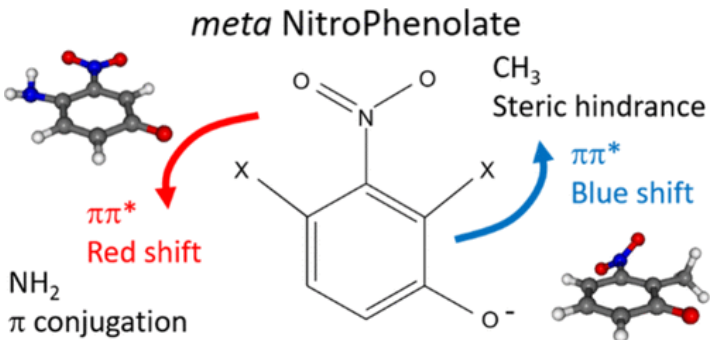

Figure 1 : Effets stériques et électrostatiques des substituants sur l'absorption du méta-nitrophénolate.

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* correspondant : satchin.soorkia@universite-paris-saclay.fr

Étude par isolation en matrice cryogénique des voies de photolyse et des réactions radicalaires de molécules organiques d'intérêt atmosphérique

Alejandro Gutiérrez-Quintanilla*, Daniel E. Camacho Granados, Anjali Mahadevan, Karinne Miqueu

[1] *IPREM UMR 5254 – Université de Pau et des Pays de l'Adour – France*

La photolyse et les réactions chimiques avec des oxydants constituent les deux voies principales de dégradation moléculaire en phase gazeuse dans l'atmosphère. L'étude de la structure, des propriétés électroniques et des signatures vibrationnelles des espèces réactives (radicaux, carbènes, etc.) formées à la suite de ces processus est importante non seulement pour la chimie atmosphérique, mais aussi pour de nombreux autres domaines de la chimie, tels que la combustion et l'astrochimie.

Ces derniers temps, nous avons appliqué la technique d'isolation en matrice afin d'étudier les premières étapes de la photolyse des dérivés du phénol. Dans cette présentation, nous mettrons d'abord en évidence certains des résultats les plus importants obtenus sous irradiation UV large bande (lampe Hg + filtres) de 4-méthoxyphénol, 4-nitroguaiacol et 1,2,3-benzènetriol piégés dans des matrices d'Ar et de N_2. La photodissociation, avec des voies de formation de CO et de CO_2, est majoritairement observée dans ces systèmes, accompagné de la formation des ketenes dans le cas particulier du 4-methoxyphénol. Par ailleurs, la photoisomérisation est également observée et discutée dans le cas du 1,2,3-benzènetriol.

Enfin, nous présenterons les premiers résultats d'une étude collaborative avec des collègues taïwanais (P. Joshi & Y.P. Lee) portant sur la réactivité de la méthylvinylcétone (hémiterpénoïde) avec des radicaux chlore ($Cl^{\bullet}$) générés in situ dans des matrices de para-hydrogène. Des produits radicalaires issus de l'addition du chlore sur la double liaison, ainsi que de l'abstraction d'hydrogène, ont été observés, permettant leur caractérisation par spectroscopie vibrationnelle pour la première fois.

Temperature Programmed Desorption of SO_2 from Water Ice Surfaces: Adsorption Energy Distributions

Ferdinand Benoit[1*], Antoine Hacquard[1], Jean-Hugues Fillion[1], Mathieu Bertin[1]

[1] *Sorbonne Université, CNRS, De la Molécule aux Nano-Objets : Réactivité, Interactions et Spectroscopies, MONARIS, 75005, Paris, France*

Sulfur-bearing species play a key role in the chemical evolution of the interstellar medium and icy bodies in the Solar System, such as the surface of Jovian moons. Yet the sulfur budget remains poorly constrained. Sulfur dioxide (SO_2) is considered one of the main sulfur reservoirs in icy environments, making its interaction with water ice surfaces highly relevant for the understanding and modelling of the S-based astrochemistry [1].

We performed experiments to extract adsorption energy distributions of SO_2 on water ice substrates as a model for astrophysical environments, in order to better constrain its thermal behavior and solid–gas exchange processes for astrochemical simulations. To achieve this, we conducted a systematic experimental study of temperature-programmed desorption (TPD) of SO_2 deposited on three types of surfaces: polycrystalline gold, compact amorphous solid water, and crystalline water ice (see Fig. 1).

Experiments were carried out under ultra-high vacuum conditions using the SPICES (Surface Processes and ICES) setup at Sorbonne Université (MONARIS). By analyzing the different desorption flux profiles, we highlight distinct desorption regimes associated with multiple implantations of the SO_2 molecule within the different solid water films [2]. In this presentation, I will demonstrate how TPD measurements reveal the complex desorption behavior of SO_2 on water ice and provide quantitative adsorption energy distributions, offering new constraints for modeling sulfur chemistry in astrophysical icy environments.

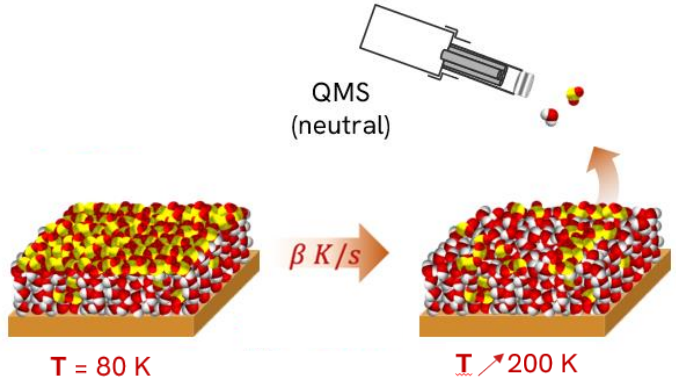

Figure 1: Concept of a TPD experiment with SO_2 (red and yellow) deposited at 80 K on compact amorphous solid H_2O (white and red) grown at 100 K on polycrystalline Au substrate. The substrate is heated with a linear temperature ramp (β = 12 K/min) up to 200 K. During heating, molecules desorb from the surface, creating a desorption flux that is detected by a quadrupole mass spectrometer.

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High resolution infrared measurements of dioxane isomers using Fourier transform and quantum cascade laser spectroscopies coupled to supersonic jet and long path cell

Pierre Asselin[a], Olivier Pirali[b], Manuel Goubet[c], Robert Georges[d], Anthony Roucou[e], Colwyn Bracquart[e] , Alaa Houwayji[e] and Arnaud Cuisset[e]

[a]*Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, Paris, F-75005 France.*
[b]*Université de Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, F-91405 Orsay, France,*
[c]*Université de Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France.*
[d]*Université de Rennes, CNRS, IPR (Institut de Physique de Rennes)—UMR 6251, F-35000 Rennes, France*
[e]*Université du Littoral Côte d'Opale, UR4493, Laboratoire de Physico-Chimie de l'Atmosphère, F-59140 Dunkerque, France*

Dioxines are volatile organic compounds considered as atmospheric pollutants. Among them, 1,4-dioxane ($C_4H_8O_2$) is extensively released in the environment.[1] The spectroscopic detection and quantification of 1,4-dioxane in sub ppbv levels is still a challenge to analytical methods and generate concerns that 1,4-dioxane in the environment has mostly gone undetected. There is also a fundamental interest in monitoring these molecules in simulation chambers (CHARME at LPCA) to study their reactivity with major oxidants but it requires knowledge of their rovibrational signatures through high-resolution experiments over a broad spectral range.

We report here a high resolution study of dioxane isomers on a wide infrared range (IR) combining the Jet-AILES set-up implemented at SOLEIL, and a room temperature long path cell, both coupled to a Fourier Transform Spectrometer (FTS), and the SPIRALES set-up available at MONARIS laboratory, a pulsed supersonic jet coupled to mid-IR quantum cascade lasers (QCL).[2]

In the case of 1,4 dioxane, high resolution IR spectroscopy turns to be the best alternative to determine ground state molecular parameters in the absence of permanent dipole moment.[3] In the fingerprint region, several bands of 1,4-dioxane were analyzed using mainly both jet-cooled spectroscopic set-ups. Reliable ground and excited-state (ES) molecular parameters could be derived from global rovibrational fits distributed over 4 vibrational excited states including all possible projections of the vibrational dipole moment with different selection rules, which strongly reduces the correlations between molecular parameters. Last, a combined HR millimeter-wave and jet-cooled-QCL and cell-FT IR spectroscopic study of the very expensive 1,3 dioxane isomer enabled to derive precise molecular parameters for the ground state and 6 vibrational states in the 950-1250 cm^{-1} range.

This present work focused about rovibrational analyses of dioxane isomers highlights the complementarity between supersonic jet set-ups and room temperature long path cells coupled to broadband FT and/or narrow band QCL infrared spectroscopies to characterize large molecules relevant for atmosphere science. [4]

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Simulating steady state spectra of acrolein while accounting Nuclear Quantum Effects

Mukul Dhiman[1*], Simon Huppert[2], Isabelle Navizet[1], Etienne Mangaud[1]
[1] *MSME CT, Université Gustave Eiffel, Marne la Vallée, France*
[2] *INSP, Sorbonne Université, Paris, France*

This study investigates the photoabsorption cross-section spectra of the atmospheric volatile organic compound acrolein in both gas and aqueous phases by incorporating Nuclear Quantum Effects (NQE) at the cost of classical molecular dynamics. Using adaptive Quantum Thermal Bath (adQTB) method the zero point energy leakage (ZPEL) is treated, which has plagued standard Quantum Thermal Bath (QTB) dynamics. The spectroscopic results obtained are in excellent agreement with quantum molecular dynamics (Path Integral MD) method, experimental observation and previous works on photoabsorption spectrum of acrolein molecule. The adQTB approach was able to capture weak $n \rightarrow \pi^*$ transitions and broadening in the gas phase, as well as the blue shift and reduced peak intensity due to solvent effects in the aqueous phase. The adQTB method is shown to perform - if not better - at par with PIMD in gas and solvent phase while being much superior to classical MD and standard QTB method particularly for solvated systems. This work shows that using adQTB method, it is possible to overcome the ZPEL and use QTB based method to study spectroscopic properties.

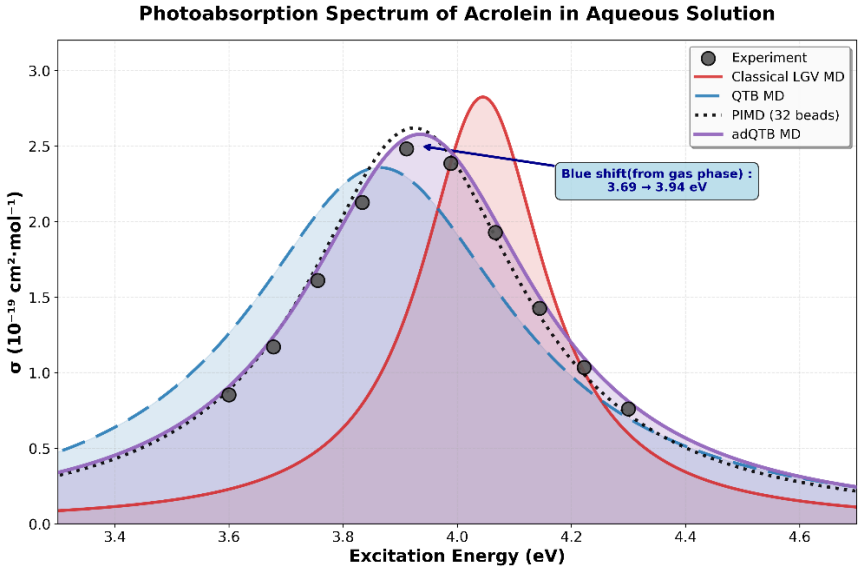

Figure: The figure represents the adQTB spectrum as captured for the acrolein in solvent phase. We see the blue shift captured compared to gas phase calculations and the solvent spectral properties captured by adQTB method which agrees with experimental and PIMD calculations.

[1] M. Dhiman *et al* JPCA (In Review)
* correspondent: mukul.dhiman@univ-eiffel.fr

Modeling the DABCO molecule in various environments (Ar, H_2O, CO_2, NH_3) with extended Density Functional Tight Binding schemes

P. Guibourg[1], F. Spiegelman[1] and M. Rapacioli[1]

[1] Laboratoire de Chimie et Physique Quantiques - Université Paul Sabatier, Toulouse

It is often challenging to model the evolution of properties of molecular compounds when they interact with an environment. One may cite the trapping of species in rare gas matrices or the deposition of molecules at the surface or in the volume of finite size clusters. We will present the combination of the Density Functional Tight Binding (DFTB) scheme [1], to describe molecules, with a Force-Field (FF) approach, to describe Rare gas (Rg) atoms. We have extended a former model [2] by introducing an atomic-population-dependent correction to a repulsion term between the DFTB atoms and Rg atoms. In this new model, the dispersion contribution also depends on the atomic populations. This model allows, in particular, to describe neutral and ionic systems and has been applied to simulate clusters of argon atoms and a 1,4-diazabicyclo[2.2.2]octan (DABCO) molecule. New reference calculations (MP2, CCSD(T)-F12) on small $DABCO^{0/+}$-Ar_n clusters will be presented. We show that the new DFTB-FF model performances are significantly improved with respect the former model for small aggregates, in particular with regard to cohesive energies. Finally, by coupling the new DFTB-FF model with a minima global search algorithm, namely a combination of Parallel Tempering Monte Carlo (PTMC) explorations and quenches [3], we provide a set of stable structures for $DABCO^{0/+}$-Ar_n clusters in the range n=1-50 atoms pointing out the size-evolution of geometric features and energetic properties. Ionization potentials are shown to decrease with size, consistently with new experimental measurements. Similar global research was performed to obtain structural and energetic properties of DABCO surrounded by other solvents like H_2O, CO_2 and NH_3.

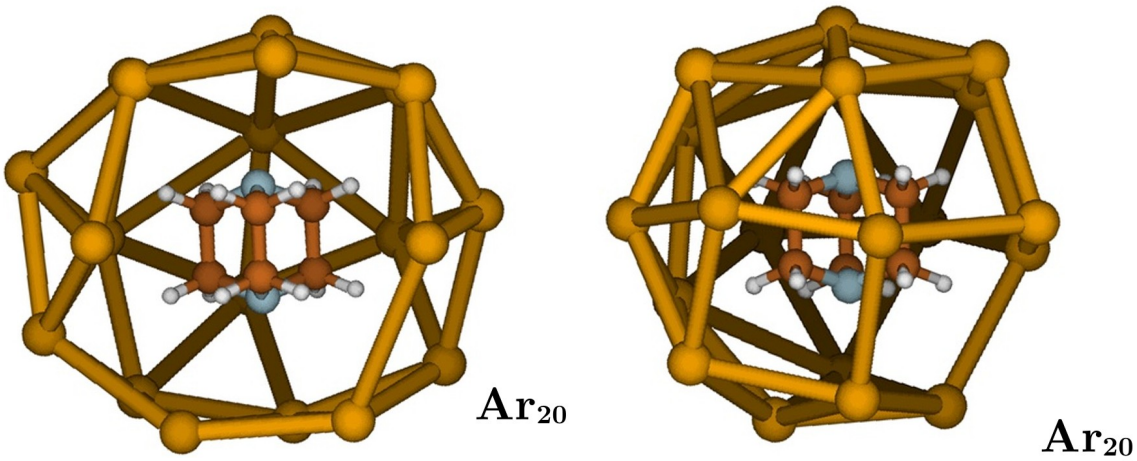

Figure 1 : Relaxed structures for DABCO-$Ar^{o/+}$ 20. Structure on the left are quenched with neutral DABCO and with ionic DABCO on the right.

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Spectroscopie Rotationnelle des Isomères du Cyanocyclopentadiène et du Diazocyclopentadiène pour la Recherche Astronomique dans les Milieux Interstellaires Chauds et Froids

Noé Gallifa[1*], Brett A. McGuire[2,3], Jerôme Loreau[4], Roman Motiyenko[1], J.-C. Guillemin[5], et Laurent Margulès[1]

[1] Univ. Lille, CNRS, UMR 8523 - PhLAM, Physique des Lasers Atomes et Molécules, F-59000 Lille, France
[2] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[3] National Radio Astronomy Observatory, Charlottesville, VA 22903, USA
[4] Katholieke Universiteit Leuven, Department of Chemistry, Belgium
[5]Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR UMR6226, F-35000 Rennes, France

La détection de molécules cycliques dans le milieu interstellaire a considérablement progressé au cours de la dernière décennie, TMC-1 s'imposant comme la source de référence pour les espèces azotées [1]. Parmi celles-ci, les deux isomères du cyanocyclopentadiène (1- et 2-cyano-CPD), détectés dans le cadre du programme GOTHAM ([2-3]), représentent des espèces d'intérêt astrochimique majeur. Les composés diazotés associés, notamment le diazocyclopentadiène (diazo-CPD, analogue des cyclopentadiényles détectés), et le diazométhane (CH_2N_2, la plus simple molécule de ce groupe), constituent quant à eux une famille chimique complémentaire tout aussi intéressante. Cependant, les données spectroscopiques de laboratoire de ces espèces sont jusqu'ici limitées au domaine des ondes centimétriques, rendant les extrapolations vers les domaines (sub)millimétriques peu fiables. Ce manque de données à plus haute fréquence est critique pour les cœurs chauds, où les températures plus élevées peuplent des niveaux rotationnels supérieurs. En effet, les prévisions fondées seulement sur les données centimétriques présentent des écarts allant de quelques kHz à plusieurs dizaines de MHz en raison de la distorsion centrifuge (DC).

Nous présentons donc une extension de l'analyse rotationnelle du 1- et 2-cyano-CPD dans la gamme 75-500 GHz, et du diazo-CPD dans la gamme 150-400 GHz. Les spectres ont été enregistrés avec le spectromètre FLASH de l'Université de Lille [4]. Leur analyse comprend plusieurs milliers de transitions simulées à la précision instrumentale (50 kHz). Les ajustements réalisés avec le programme ASFIT ont permis de déterminer 12 nouveaux paramètres DC (sextiques et octiques) pour les isomères du cyano-CPD, et 6 nouveaux paramètres (quartiques et sextiques) pour le diazo-CPD, améliorant la précision de toutes les constantes rotationnelles par rapport aux travaux antérieurs. Les fonctions de partition ont été calculées pour chacune des molécules en intégrant les contributions vibrationnelles, fournissant ainsi une correction indispensable à l'estimation des densités de colonne dans les milieux chauds. Ces nouvelles données ont permis d'engager des recherches pour le diazo-CPD vers TMC-1, NGC 6334I, ainsi que dans les relevés PILS et EMoCA, sans détection à ce stade. En revanche, la recherche préliminaire des isomères cyano-CPD vers NGC 6334I révèle quelques coïncidences spectrales prometteuses. Les travaux futurs cibleront les états vibrationnels excités de ces molécules et d'autres sources de type cœur chaud.

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* correspondant : *noe.gallifa@univ-lille.fr*

Ecoulements hypersoniques et atmosphères exoplanétaires

Lyam Rolland Roignant[1], Solène Perot[1], Julien Lecomte[1], Nicolas Suas-David[1], Lucile Rutkowski[1], Michaël Rey[2], Eszter Dudás[3], Robert Georges[1*]

[1] Institut de physique de Rennes, UMR CNRS 6251, Université de Rennes, Rennes, France
[2] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR CNRS 6303, Université de Bourgogne Europe, Dijon, France
[3] Laboratoire Collisions Agrégats Réactivité, UMR CNRS 5589, Université de Toulouse, Toulouse, France

Les moyens d'observation modernes, tels que le télescope spatial James Webb, fournissent des spectres infrarouges haute résolution d'atmosphères d'exoplanètes d'une qualité inédite. Ils révèlent sans ambiguïté la présence d'espèces moléculaires - CO, CO_2, H_2O, CH_4 - dans l'atmosphère de « jupiters chauds » dont la température peut dépasser 1000 K. Les codes de transfert radiatif, utilisés pour extraire des profils de concentration et de température des atmosphères sondées, s'appuient sur des modèles théoriques simulant les signatures spectrales de ces molécules à haute température. Des données expérimentales infrarouges mesurées en laboratoire à haute température sont donc indispensables pour construire et valider en amont ces modèles théoriques.

Le dispositif SMAUG [1], développé à Rennes, produit des écoulements hypersoniques présentant une température rotationnelle très basse (inférieure à 40 K) et une température vibrationnelle très élevée (typiquement 1000 K). La grande sensibilité de la technique CRDS (cavity ringdown spectroscopy) s'avère idéale pour sonder ces écoulements et identifier les bandes vibrationnelles de molécules clés dans la gamme 1,5 – 1,7 µm. Ce dispositif a été intensivement employé pour produire les spectres infrarouges du méthane [2,3] et, plus récemment, de l'éthylène [4,5]. La basse température rotationnelle simplifie la structure des bandes et leur analyse, tandis que la température vibrationnelle élevée permet d'accéder à des états vibrationnels excités.

Parallèlement, une approche expérimentale complémentaire est en cours de développement : sonder, par CRDS, une couche de choc stationnaire où les degrés de liberté rotationnels et vibrationnels s'équilibrent, afin d'obtenir des spectres haute température cette fois à l'équilibre thermodynamique.

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[4] S. Perot, J. Lecomte, N. Suas-David, L. Rutkowski, M. Rey, S. Kassi, A. V. Nikitin, R. Georges, *JQSRT*, **324**, 109065 (2024). https://doi.org/10.1016/j.jqsrt.2024.109065
[5] S. Perot, J. Lecomte, N. Suas-David[a], L. Rutkowski, M. Rey, E. Dudás, R. Georges, *Analysis of a non-LTE hypersonic spectrum of ethylene between 5880 and 6200 cm^{-1},* soumis à *J. Chem. Phys.*
* correspondant : robert.georges@univ-rennes.fr

Sub-Doppler Spectroscopy of Methane in the THz range

Anđela Zarin, Luan Juppet, Naveed Ahmed Chishti, Olivier Pirali

Institut des Sciences Molécularies d'Orsay (ISMO), France

Methane plays a crucial role in atmospheric and planetary sciences, as one of the primary anthropogenic greenhouse gases. [1] Its accurate spectroscopic characterization is essential for climate modeling and improvement of databases. Over the past decades, extensive spectroscopic studies have been carried out in the mid-infrared and visible regions, providing large datasets of transition frequencies, intensities and pressure broadening coefficients. [2-4] However, in the THz domain, experimental data remain deficient and no sub-Doppler measurements have been reported in the THz range so far. This lack of high-precision data limits the refinement of spectroscopic model and datasets.

Methane as a spherical top molecule, has no permanent dipole moment. As a result, pure rotational transitions are electric-dipole forbidden, making conventional microwave and terahertz spectroscopy very challenging. However, weak transitions can arise through different mechanism that induce a dipole moment. [5] Such mechanisms are centrifugal distortion and vibration-rotation interaction. These effects relax the strict selection rules and enable otherwise forbidden transition to be observed. In the 100-1000 GHz range, the most intense transitions observed at the room temperature are pure rotational transitions in the v_4 vibrational mode. In this work, we present sub-Doppler double-resonance (DR) measurements of methane in the v_4 vibrational band allowing for first Sub-Doppler measurements of these lines. Our DR scheme, exploit a MIR pump radiation that selectively pump molecules into v_4 state while THz radiation probe pure rotational transitions in this state. Resolving pure rotational transitions in 300-1100 GHz in the sub-Doppler regime enables improvement of frequency accuracy for refining effective Hamiltonian models and spectroscopic databases.

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andela.zarin@universite-paris-saclay.fr

High-resolution study of the spectrum of allene around 11 µm

Solène Perot[1*], Athéna Rizopoulos[1] and Jean Vander Auwera[1]

[1] *SQUARES, C.P.160/09, BLU-ULB Brussels Laboratory of the Universe, Université libre de Bruxelles, Brussels, Belgium*

Allene (propadiene, C_3H_4) was detected in Titan's atmosphere [1] together with its isomer, propyne [2]. Interconversion between these two species can be induced by collisions with atomic hydrogen. The abundance of atomic hydrogen in Titan's atmosphere could therefore be inferred from the ratio of the abundances of allene and propyne [3]. To precisely determine the abundances of allene and propyne, as well as their seasonal and spatial variations, new measurements are required. To do so, high-resolution infrared measurements from ground- and space-based instruments are available. The interpretation of these observations relies on the availability of reference spectroscopic data. The present work aims to improve the description of line positions and intensities in the ν_{10} and ν_9 bands of allene, located respectively near 841 and 999 cm^{-1}. High resolution Fourier transform spectra of pure allene at room temperature were recorded between 600 and 1200 cm^{-1} using a Bruker IFS 125HR spectrometer under various pressure conditions. An effective Hamiltonian model was developed based on a previous work [4]. It led to the identification of more than 5800 transitions in the recorded spectra. The spectroscopic constants are currently being refined. The results of this ongoing study will be presented.

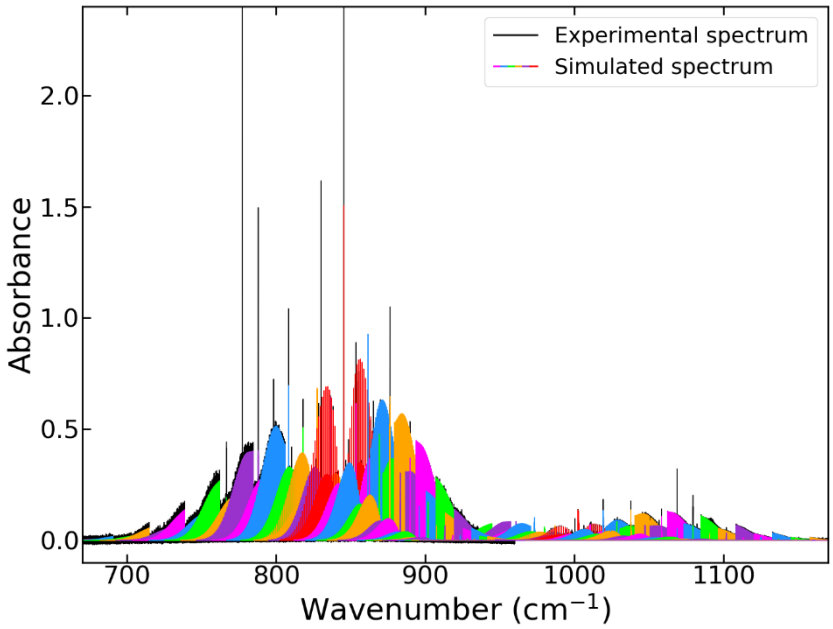

Figure 1 : Experimental and simulated spectra of allene around 11 µm, corresponding to absorption resulting from the excitation of the ν_{10} and ν_9 vibrational modes.

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* correspondant : solene.perot@ulb.be

Experimental state-to-state rate coefficients of gas-phase inelastic molecular collisions

Chinmai Sai Jureddy,[1] Brian Hays,[2*] Alberto Macario[3], Ian Sims[1]

[1] Institut de Physique de Rennes (IPR), UMR 6251 CNRS, Université de Rennes, Rennes, France
[2] Université de Lille, CNRS, UMR 8523 – PhLAM, Laboratoire de Physique des Lasers, Atomes et Molécules, Lille, France
[3] Laboratoire de Physique des Lasers (LPL), UMR 7538 CNRS, Université Sorbonne Paris Nord, Villetaneuse, France

Reliable data on state-to-state rate coefficients are essential for accurately modelling rarefied gases. In fact, the necessity of this information has been claimed in order to develop chemical models of gas phase environments, such as the interstellar medium or the planetary atmospheres. Thus, from the over 300 of molecules already observed in the interstellar medium, the study of rotational collisional energy transfer processes has been only theoretically calculated for over 60 species. In the case of the experimental studies this amount is dramatically lower, counting only a few of specific studies, such as ammonia, because they are quite limited and remained sometimes unaffordable.

Thus, one example is the experimental method proposed to measure state-to-state rate coefficients of rotational inelastic ammonia collisions [1]. This method is based on pump-probe experiments using Fourier transform rotational spectroscopy techniques. They used the inversion doublets of the ammonia molecule to pump the system and so alter the thermal equilibrium population of these levels, and then probe how collisional relaxation processes affect to different transitions by means of chirp-pulses of the correlated transitions. After changing the timing between the pump and probe pulses, the state-to-state rate coefficients were determined, and thanks to the chirped pulse technique the propensity rules associated to these collisional processes were also characterized. Nevertheless, the high specificity of the method means that only a few of laboratories around the world can use it.

Here we present the first steps in the development of a pump-probe procedure for general molecular systems, based on the previous mentioned one, to obtain experimental state-to-state rate coefficients for inelastic rotational energy transfer of molecules of astrochemical interest by the use of the rotational spectroscopy setup in Rennes. This procedure aims to unravel the propensity rules for inelastic energy transfer of polyatomic molecules such as acrylonitrile and propose experimental measurements of state-to-state collisional rate coefficients in order to do comparison with theory. The first results obtained from acrylonitrile and methyl cyanide collisional relaxations with Argon will be also displayed.

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* correspondant : brian.hays@univ-lille.fr

Measurements of dissociation rates of naphthalene and azulene cations close to threshold energy.

J Bernard[1], S Indrajith[2*], G Montagne[1], S Martin[1], and U Kadhane[3]

[1]*Institut Lumière Matière (iLM), UMR5306, Université Lyon 1-CNRS, Villeurbanne, France*
[2]*Institut de la Matière Condensée et des Nanosciences (IMCN), Université Catholique de Louvain, Louvain-la-Neuve, Belgique*
[3]*Indian Institute of Space Science and Technology, Thiruvananthapuram, Kerala 695547, India*

There is broad consensus that some midinfrared fluorescence emissions observed in the photodissociation regions (PDRs) of interstellar clouds originate from polycyclic aromatic hydrocarbons (PAH). In PDRs, molecules are ionized and energized by intense radiation fields emitted from nearby stars. Astrophysical models describing PAH evolution require precise evaluation of the competition between dissociation and radiative stabilization as a function of internal energy. Depending on internal energy, isomerization may also play a key role in both the nature of dissociation processes and their lifetimes. Most recent studies [1] rely on statistical models that require input parameters such as dissociation energy, transition state energy, and the preexponential factor, which are often poorly constrained for complex PAHs. In the present work, we performed measurements of the dissociation rates of the naphthalene and azulene cations at internal energy. They were produced at a temperature close to ambient, stored in the Mini-Ring electrostatic storage ring [2], and irradiated with an OPO laser at various near-UV wavelengths. Two-photon absorption is needed to dissociate these molecular ions at ambient temperature and in this photon energy range (3.3 to 4.6 eV). Three-photon absorption could be excluded as the subsequent dissociation would be too fast. Therefore, after two photon absorption, the internal energy distribution was expected to peak close to two-photon energy, leading to exponential decay from which it would be easy to extract dissociation rates. However, as shown in Figure 1, the observed decay contained several contributions (up to four) that could be attributed to the presence of both naphthalene and azulene isomers in the stored beam and to fast radiative cooling by recurrent fluorescence (RF) that can shift the internal energy by a fixed amount. By scanning the photon energy, we could measure dissociation rates k_d as a function of internal energy and compare these $k_d(E)$ curves with statistical models (RRKM or Arrhenius) over a 2.5 eV energy range starting from ~6.6 eV. The results show a good agreement at high energy, while an observed deviation at low energy is attributed to RF. RF is found to be competitive and to quench dissociation at internal energy below ~7.2 eV.

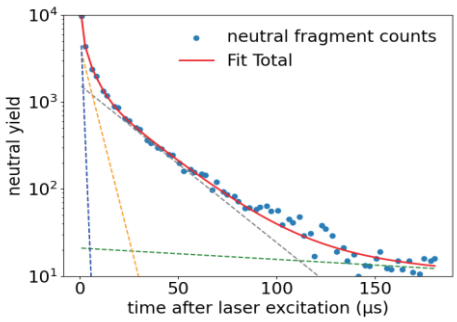

Figure 1. dots: Neutral yield resulting from two photon (340 nm) absorption in naphthalene cations stored in Mini-Ring. full line: Fit by a sum of four exponential decays.

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* correspondant: suvasthika.indrajith@uclouvain.be

7 Posters

Contents

The MetCTG Project: Metrology for comparable and trustworthy greenhouse gas remote sensing datasets

E. Ducreux[1*], H. Tran[1] and the MetCTG Team[2]

[1] Laboratoire de Météorologie Dynamique/IPSL, CNRS, Sorbonne Université, École normale supérieure, PSL Research University, École Polytechnique, Institut Polytechnique de Paris, F-75005, Paris, France
[2] https://www.metctg.ptb.de/home

Satellite remote sensing of atmospheric greenhouse gases (GHGs), including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), provides essential information on their sources, transport, and sinks, supporting climate monitoring and mitigation policies. As current and upcoming satellite missions face increasingly stringent accuracy requirements, ensuring the comparability, traceability, and reliability of retrieved datasets has become a key scientific and metrological challenge.

The MetCTG project aims to address this challenge by developing a robust metrological framework for GHG observations. Central to the project is the improvement of spectroscopic parameters that underpin satellite retrievals. High accuracy laboratory measurements are combined with advanced theoretical calculations and molecular simulations to refine spectral line data for key atmospheric species and their isotopologues across relevant spectral bands. Particular attention is given to effects such as spectral interference from water vapor and line intensity depletion, which can impact retrieval accuracy.

To ensure consistency and reproducibility, inter laboratory comparisons are conducted using multiple state of the art spectroscopic techniques. These efforts enable the establishment of spectroscopic equivalence and support the development of improved line shape models for next generation retrieval algorithms. The enhanced datasets are then implemented in satellite retrievals and validated through coordinated campaigns combining ground based, airborne, and satellite observations.

A major outcome of the project is the establishment of traceability to the International System of Units (SI), allowing rigorous uncertainty assessment and improved comparability between datasets. By strengthening the reliability of GHG observations, MetCTG contributes to more accurate emission estimates and supports informed decision making in climate policy.

* correspondant : emile.ducreux@lmd.ipsl.fr

Caractériser l'influence des interactions non covalente sur la réactivité. Application à la réaction d'agrégats d'acide acétique avec la méthylamine

Emilie-Laure Zins[1*], Lucas Albouy[1], Roland Thissen[2,3], Claire Romanzin[2,3], Christian Alcaraz[2,3], Olivier Aroule[4]

[1] : Laboratoire MONARIS, De la Molécule aux Nanos-objets : Réactivité, Interactions et Spectroscopies, Sorbonne Université, CNRS, UMR 8233
[2] : Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay
[3] Synchrotron SOLEIL, L'Orme des Merisiers, 91192 Saint Aubin, Gif-sur-Yvette
[4] : Institut des Sciences Analytiques, Université Lyon 1, CNRS, UMR 5280

Les interactions non covalentes modifient localement la densité électronique des partenaires. Cette redistribution de la densité électronique peut affecter directement la réactivité des espèces [1]. Les outils interprétatifs de la chimie quantique nous permettent de quantifier cette modification de densité électronique. Ainsi, la théorie quantique des atomes dans la molécule permet ainsi de quantifier l'affaiblissement ou le renforcement d'une liaison, à partir de l'analyse topologique de la densité électronique [2]. Par ailleurs, la fonction de localisation électronique (ELF) permet de déterminer la population des bassins de paires électroniques [3]. Avec ces outils, nous nous sommes intéressés à la réaction de formation d'une liaison de type peptidique entre l'acide acétique et la méthylamine, et à l'influence d'interactions non covalentes entre des molécules d'acide acétique sur cette réactivité [4].

D'un point de vue expérimental, les agrégats d'acide acétique sont formés dans un jet moléculaire, puis ionisés par des photons VUV sur la ligne DESIRS du synchrotron SOLEIL. Dans ces conditions, il se forme des agrégats protonés d'acide acétique [5]. Le montage CERISES [6] permet ensuite l'identification de ces agrégats et leur sélection en masse dans un premier quadrupôle. La méthylamine est ensuite ajoutée dans un octopole, et les produits de la réaction sont analysés à l'aide d'un second quadrupôle.

La complémentarité théorie – expérience permet d'identifier les produits de la réaction, et de comprendre l'influence de la taille des agrégats sur leur réactivité en termes de perturbation de la densité électronique locale dans les agrégats.

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* correspondant : emilie-laure.zins@sorbonne-universite.fr

Caractérisation en temps réel de particules ultrafines atmosphériques

Ioana Bena[1], Marc Briant[1*], François Gaie-Levrel[2], Olivier Sublemontier[1], Jean-Baptiste Sirven[3], Ronald Berger-Lefébure[4]

[1] NIMBE, Université Paris-Saclay, CEA, CNRS, 91191, Gif sur Yvette
[2] Airparif, 7 rue Crillon, 75004 Paris
[3] SPC, Université Paris-Saclay, CEA, 91191, Gif sur Yvette
[4] iUMTEK, 503 rue du Belvédère, Institut d'Optique Graduate School, 91400 Orsay,

La surveillance de la qualité de l'air est un enjeu majeur de ces dernières décennies. L'une des questions importante et complexe concerne la surveillance des particules fines (1 µm <) et en particulier ultrafines (0.1 µm <) que l'Anses a recommandé de contrôler dès 2018 [1]. Un point délicat de ce contrôle est la mesure de la concentration en nombre de Particules UltraFines (PUF) d'une composition élémentaire donnée. Cette mesure est cruciale car :

- Les PUF représentent moins d'1 % de la masse des aérosols, mais plus de 80 % de leur nombre total.
- Les PUF restent en suspension dans l'air plusieurs heures, voire quelques jours, en fonction des conditions environnementales.
- Les risques sanitaires dus à l'inhalation des PUF sont liés non seulement à leur composition chimique, mais aussi à leur taille qui leur permet de pénétrer profondément dans les voies respiratoires et de passer dans la circulation sanguine.

L'objectif de nos travaux est d'obtenir, en temps réel et in situ, les concentrations en nombre et en masse d'aérosols d'une composition élémentaire donnée. La gamme de tailles considérée s'étend de quelques dizaines de nm à 1 µm, couvrant au maximum le domaine des particules submicrométriques et ultrafines [2, 3, 4].

Pour atteindre ces objectifs, un nouveau dispositif expérimental basé sur le couplage d'un système de lentilles aérodynamiques (SLA) [5] et de la LIBS (Laser Induced Breakdown Spectroscopy) est en cours de développement. Le SLA permet de produire sous vide un jet d'aérosols fin, collimaté et dense, tout en évitant la contamination des éléments optiques par leur dépôt. Un laser pulsé à haute cadence (qq dizaines de kHz) est focalisé sur le jet d'aérosols et permet leur analyse élémentaire via la spectroscopie LIBS. Les avantages de la technique présentée par rapport aux techniques conventionnelles à pression ambiante sont :

- l'absence de bruit de fond dû au gaz environnant;
- une sensibilité accrue grâce à l'effet de concentration du SLA;
- la possibilité de détecter les particules individuellement, permettant ainsi leur comptage;
- la détection plus efficace des éléments émettant dans l'UV lointain, même jusqu'au VUV.

Les premiers résultats obtenus sur ce nouveau dispositif seront présentés et commentés..

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* correspondant : marc.briant@cea.fr

Spectroscopie résolue en temps sur des acènes isolés en phase gazeuse pour l'étude du processus de Fission de Singulet

O.Shviro[1*], A.Scognamiglio[2], L.Barreau[3], C.Schouder[4], M.Ha-Thi[5], L.Poisson[6]

[1,2,3,4,5] *Institut de Sciences Moléculaires d'Orsay, Université Paris-Saclay, France*

La photophysique moléculaire permet de comprendre la structure énergétique des molécules et les couplages intra- et inter-moléculaires existants, ce qui constitue une connaissance nécessaire pour le développement de futures applications. En particulier, les dimères de certains acènes, qui sont les molécules étudiées ici, présentent une propriété spécifique dite de fission de singulet, un processus particulièrement pertinent pour le progrès des cellules photovoltaiques. En effet, ce phénomène permet la création de deux molécules excitées à partir de l'absorption d'un photon unique par le dimère, augmentant ainsi le rendement quantique.

Des études récentes [1] ont montré que le rendement quantique, défini comme le ratio entre les excitations produites et les photons absorbés, dépasse les 100% pour des cellules photovoltaiques organiques dont le fonctionnement repose sur la fission de singulet d'acènes. Bien que le processus de fission de singulet se produise dans des complexes moléculaires, dont la forme la plus simple est le dimère, l'étude de systèmes isolés en phase gazeuse constitue une étape cruciale pour comprendre les interactions et les processus mis en œuvre dans des systèmes complexes. Dans cette étude, nous nous concentrons sur la dynamique ultrarapide de molécules isolées en phase gazeuse à l'aide d'un dispositif pompe-sonde utilisant un laser femtoseconde. Nous présentons les résultats obtenus pour de bons candidats au processus de fission singulet tels que le tétracène et le pentacène. Les molécules isolées sont d'abord étudiées, puis des agrégats d'argon sont utilisés pour contrôler la stœchiométrie des complexes moléculaires et former des dimères.

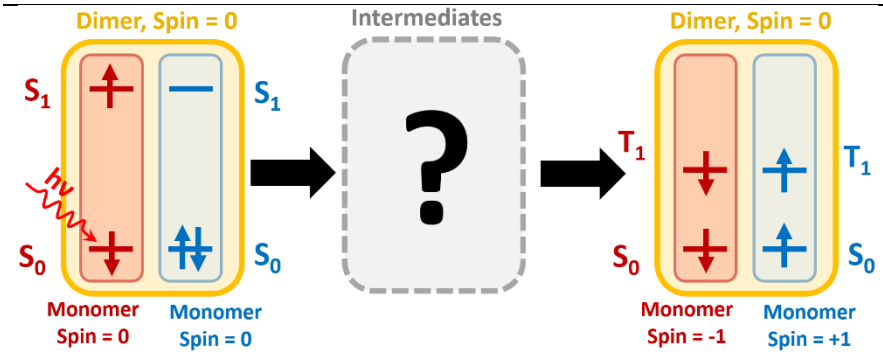

Figure 1 : Schéma du principe de Fission de Singulet. Le spin total du dimère est conservé, et permet d'atteindre un état final de deux monomères excités.

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* correspondant : oriane.shviro@universite-paris-saclay.fr

Conformer-specific spectroscopy of a photosensitizer model and its complexes with water in the gas phase

Arsène Kossov,[1*] Christine Le Narvor[2], David Bonnaffé[2], Pierre Çarçabal[3]

[1] *ISMO, Université Paris-Saclay, UMR 8214, Bât. 520, rue André Rivière, 91400 Orsay, France*
[2] *ICMMO, Université Paris-Saclay, UMR 8182, Bât. 670, 17 Avenue des Sciences, 91400 Orsay, France*
[3] *LCAR, Université de Toulouse, Bât. 3R4, 118 route de Narbonne, 31062 Toulouse Cedex 09, France*

New photosensitizer drugs that use mannose to detect retinoblastoma cancer and treat it through photodynamic therapy are being developed [1]. We studied a custom-made photosensitizer model with double resonance conformer-selective spectroscopies to find the geometries of the most stable jet-cooled conformers. Complexes of the model with up to three water molecules have also been observed.

The complex conformational space of this highly flexible model gave us the opportunity to test different computational tools for conformational exploration before optimization at DFT level of theory. The isolated model has shown a preference for folded geometries. The possibility for water to unfold the model and to ease further molecular recognition is studied. Experiments with heavy water allow unambiguous assignment of the monohydrated complex. For dihydrated and trihydrated complexes, no assignment has yet been made.

The great diversity of non-covalent interactions stabilizing this model in the gas phase has been highlighted by NCI Plot electronic density topology method. This is the beginning of a great multidisciplinary project between physics, chemistry and pharmaceutical sciences.

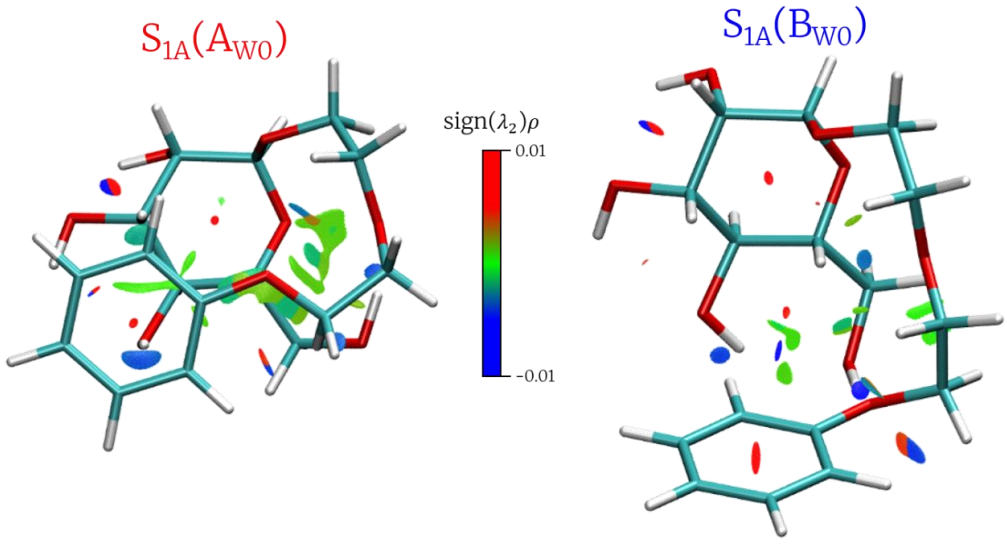

Figure 1 :Geometries of the most stable conformers of the photosensitizer model observed in the gas phase and NCI Plot surfaces that show the great diversity of non-covalent interactions governing the folding of the conformers

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* correspondant : arsene.kossov@universite-paris-saclay.fr

Role of Local vs Non-local Terms in VCD and IR Spectra of Polymorphs by using polarizable force field and molecular dynamics

Ernesto Garcia Alfonso[1*], Carine Clavaguera[2], Ke Lin[3] and Anne Zehnacker[1]

[1] Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS UMR8214, 91405 Orsay, France
[2] Université Paris Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay, France
[3] School of Physics, Xidian University, Xi'an 710071, China.

Phenylalanine (**Phe:** $C_9H_{11}NO_2$) is a fundamental building block for protein synthesis and neurotransmitter precursors, serving as a versatile scaffold for advanced supramolecular engineering [1]. In its crystalline and gel states, Phe organizes into complex tetramers stabilized by a network of intermolecular hydrogen bonds between deprotonated carboxyl groups ($-COO^-$) and protonated amine groups ($-NH_3^+$). Infrared (IR) spectroscopy is a method of identifying vibrational signatures of specific functional groups. In contrast, vibrational circular dichroism (VCD) provides a unique "chiral fingerprint", which is essential for determining absolute configuration and conformation in environments where traditional *X*-ray diffraction (XRD) may be limited. The present study investigates the role of **local** *vs* **non-local** terms within the VCD and IR spectra of solid-state-like phenylalanine assemblies. Utilising the AMOEBA polarizable atomic multipole force field in Tinker [2,3] and **ChirPy** [4,5] spectrum calculation, we conducted a comprehensive analysis of global dihedral free energy and implemented a sophisticated spectral decomposition method that incorporated direct coupling and gauge transport. The methodology employed is outlined as follows: (1) Experimental structures: The extraction of Fibre and Powder experimental information was conducted from the Cambridge Crystallography Database. In addition, the orthorhombic unit cell was replicated (a/=b/=c; α=γ=β=90°). Thirdly, the Tinker-HP [2] AMOEBA polarizable atomic multipole force field is initiated for an *NVT* ensemble, with a duration of 7 ns. In order to calculate the dipole and magnetic moments of the molecules, a Tinker-VCD [3] is employed for a range of different trajectories (40) in an *NVE* ensemble, extending up to 50 ps. Finally, the VCD/IR spectrum is obtained through a ChirPy Python-based code. For further comparison, please refer to Figure 1. This approach provides a robust framework for examining molecular arrangements and their direct impact on the chiroptical response, offering a roadmap for designing responsive biomaterials for drug delivery, sensing, and catalysis.

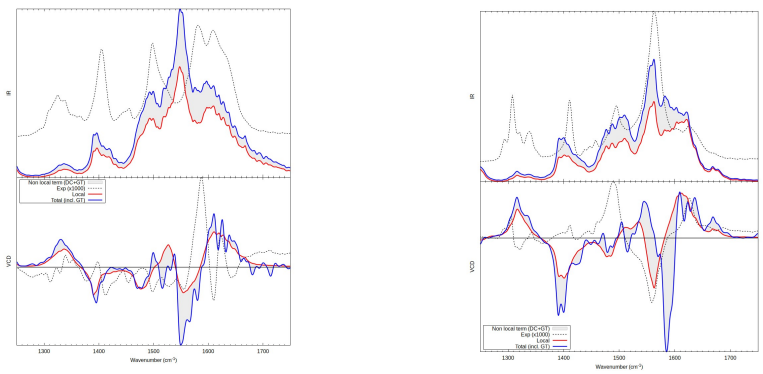

Figure 1: Infrared (top panel) and VCD (bottom panel) for Fibre (on the left) and Powder (on the right). The dashed lines show the experimental data, while the red and blue solid lines show the local and non-local contributions.

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* correspondant : ernesto.garcia-alfonso@universite-paris-saclay.fr

Photographic Visualization of Laser Evaporation Techniques

Anna Elisabeth Holz[1*], Léo Lavy[1], Arsène Kossov[2], Pierre Çarçabal[1]

[1] *Univ Toulouse, CNRS, LCAR, Toulouse, France*
[2] *Univ Paris Saclay, CNRS, ISMO, Orsay, France*

Several laser evaporation techniques can be used to introduce intact biomolecules into gas phase analyzing tools such as spectrometers. The evaporation process can in some cases be visualized using a commercial camera. In our work, we visualized a plume as found on graphite when evaporated with an Nd:YAG laser (1064nm), as well as a plume found on a liquid micro-jet of water when evaporated with an IR laser (2.74-3.23µm). In both cases, the camera is synchronized with a pulsed laser (10Hz) to capture one picture of the evaporation process at each pulse. The delay between camera and laser can be varied to visualize the evolution of the process. For the liquid micro-jet, we also explore the influence of laser intensity and wavelength on the resulting pictures. We are able to take pictures and videos of the evaporation processes on graphite and water, and analyze the impact of delay, wavelength and laser intensity. The results of this ongoing work will facilitate the connection and synchronization of the liquid micro-jet evaporation with a supersonic expansion of a laser spectroscopy and mass spectrometry experiment designed to interrogate the structure of biomolecules in interaction with several molecules.

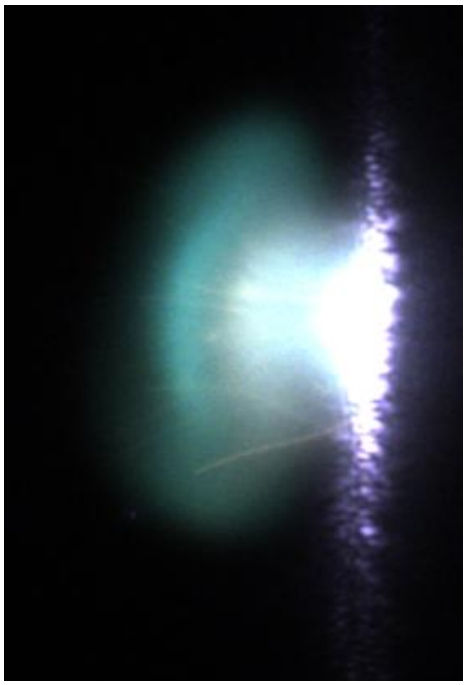

Figure 1

Figure 2

Figure 1: Laser evaporation of graphite with λ=1064nm
Figure 2: Laser evaporation of the liquid jet with λ=2.86µm
In both cases the laser arrives from the left.

* correspondant : anna.holz@utoulouse.fr

Tailoring Attosecond Charge Migration in Native Molecular Ions

Evan Munaro-Langloÿs[1], Franck Lépine[1], and Victor Despré[1]

[1] *Universite Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622 Villeurbanne, France*

Attosecond XUV pulses provide a powerful means of triggering pure electron dynamics in molecules, such as the phenomenon known as hole migration [1,2]. While hole migration has been extensively studied in neutral molecules following ionization [3], its counterpart in pre-charged systems, specifically molecular ions, remains largely unexplored. These systems are ubiquitous in chemical and biochemical environments, and understanding their intrinsic electron dynamics offers new opportunities to control and probe electron correlation effects in realistic conditions.

In this work, we investigate correlation-driven hole migration in molecular ions using non-Dyson algebraic diagrammatic construction [4] combined with multi-electronic wave-packet propagation [5]. We consider a series of systems with different native charges by examining protonated and deprotonated derivatives of molecules exhibiting strong outer-valence electron correlation.

Our findings reveal that protonation and deprotonation affect outer-valence electronic structure and dynamics in markedly different ways. Protonation suppresses correlated dynamics by strongly altering the preferred ionization sites, whereas deprotonation reduces correlation strength while significantly accelerating hole migration. In both cases, these effects are rationalized in terms of the spatial distribution of the excess charge prior to ionization. Furthermore, comparison across different molecules suggests that systems with similar structures respond consistently to the added charge.

These findings highlight how molecular charge state can be used to tailor electron correlation and ultrafast charge dynamics, opening new perspectives for the design of systems with desired electronic behavior.

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Molecular spectroscopy in the 8 – 10 THz region using a nonlinear metasurface source

N. A. Chishti[1], A. Zarin[1], J. H. Krakofsky[2], M.A. Belkin[2], M. Rieder[2], M.H. Mammez[3], J.F. Lampin[3], M.A.M. Dumel[1], O. Pirali[1*]

[1]*Institute of Molecular Sciences of Orsay (ISMO), University of Paris Saclay, France.*

[2] *Walter Schottky Institute, Technical University of Munich, Garching, Germany.*

[3]*Institute of Electronics, Microelectronics and Nanotechnology (IEMN), University of Lille, France.*

The terahertz (THz) spectral region is rich in molecular ro-vibrational transitions. However, improving the precision of molecular spectroscopy measurements performed above 1 THz requires the development of continuous-wave (CW), narrow linewidth, sufficiently powerful sources. While some solutions exist in specialized labs to cover the 1-5 THz range, the Reststrahlen band (5 – 10 THz) has remained out of reach. We present here preliminary high resolution spectroscopy measurements performed in this frequency range by utilizing tunable THz radiation with power upto 24 µW, generated by the Difference-Frequency Generation (DFG) in a nonlinear metasurface. This non-linear metasurface is fabricated and provided by collaborators at the Technical University of Munich (TUM), Germany [1].

In our experiment at the Institute of Molecular Sciences of Orsay (ISMO), two continuous-wave mid-infrared lasers, a tunable CO_2 laser operating on several lines around 10.6 µm with a power of about 1 W and a mid-infrared tunable quantum-cascade laser (QCL) near 8.3 µm with a power of about 300 mW, were superimposed on the metasurface to generate THz radiation in the 8 -10 THz region. We developed and optimized the full spectroscopic chain, including laser beams combining and focusing onto the metasurface, collection of generated THz with an off-axis parabolic mirror, coupling into a gas cell for a double pass experiment and then detection on bolometer.

Using this THz radiation source, we recorded the spectra of different molecules in the targeted spectral window, including H_2O and HDO in 8 – 10 THz region. The initial spectroscopy results are quite promising and demonstrate that metasurface enabled THz generation is a practical route toward molecular spectroscopy in the 5–10 THz region. These encouraging results motivate further improvements in alignment, filtering and frequency stability of lasers to move towards THz precision spectroscopy.

In addition, the generated THz radiation was examined with a THz camera after appropriate MIR filtering. Camera images revealed a focused THz mode, and tuning the QCL to a water absorption line caused the THz spot to disappear and reappear outside the line, providing an additional confirmation of the THz nature of the detected signal.

References:

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corresponding author: Olivier.pirali@cnrs.fr*

$[Mo_6X_{14}]^{2-}$ cluster complexes (X, halogen) as a molecular platform for photochemistry: ligand exchange, bond activation and photo-products

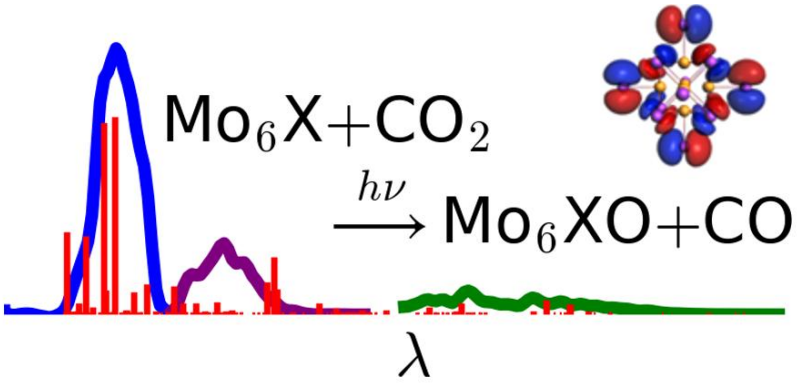
Aikaterini Tsirkou[1], Nina Tyminska[2, 3], Nicolas Vannier[3], Fabien Grasset[3, 4], Yann Molard[3], Richard A. J. O'Hair[5], Karine Costuas[3], Stéphane Cordier[3], Luke MacAleese[1]

[1] *Institut Lumière Matière (iLM) - CNRS & Université Claude Bernard Lyon 1, Villeurbanne, France;*
[2] *University Paris-Saclay, Institute for the Sciences of Light, Saclay, France;*
[3] *Institut des Sciences Chimiques de Rennes (ISCR) - UMR6226, CNRS & Université de Rennes, Rennes, France;*
[4] *LINK, National Institute for Materials Science - IRL3629, CNRS–Saint-Gobain–NIMS, Ibara, Japan*
[5] *University of Melbourne, Victoria, Australia*

Atomically precise metal nanoclusters display unique reactivity that cannot be inferred from either atomic nor bulk matter. Among them, hexanuclear Mo6 clusters are promising photocatalysts, reported for hydrogen evolution reaction (HER) and CO2 photo-reduction.[1,2] However, their precise reaction mechanisms remain poorly understood. Only few gas-phase studies were performed to date.[3,4,5] Here the focus is set on the conditions of ligand exchange reaction (X/O2 or X-/HO-), and on the intramolecular reactivity of the exchanged species upon collisional heating or photoactivation.

Ion trap mass spectrometry offers a complementary approach to solution studies by generating, isolating, and probing reactive intermediates at the molecular scale. Collision induced dissociation (CID), Laser induced dissociation (LID), action spectroscopy and Ion-molecules reactions in the ion trap probe precursors structure, optical properties, energetics and reactivity. Experiments are complemented by quantum-chemical (QC) simulations to characterize excitations, photofragment structures, stabilities, and reactivity.

This work provides the first molecularly resolved UV–visible absorption properties of Mo_6 clusters, together with the comprehensive characterization of the wavelength dependence of photoproducts, fully supported by QC calculations. Alternative photo-specific reactive pathways were identified compared to CID, including the first observation of photo-oxidized species, demonstrating the reducer character of the photoexcited state. Furthermore, we present the first experimental evidence of several key photoinduced processes: (i) photo-enhanced CO_2 dissociation on dehalogenated Mo_6 clusters, leading to the formation of metal–oxo species and the release of CO, in agreement with QC-predicted structures and energetics; (ii) activation of the O–H bond on the Mo_6 cluster, yielding recombination products such as HX and H_2O; and (iii) photo-specific neutral losses of H_2 from hydroxylated cluster complexes, providing initial mechanistic insight into the photocatalytic HER.



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Modulation of Molecular Fluorescence through Controlled Access to Conical Intersections

Martial Boggio-Pasqua[1*], V. Adebayo[1], L. Wang[2], J. Gierschner[2], M. Stolte[3], F. Würthner[3], Y. Feng[4], H. Gao[4], J. Zhou[4], H. Qiu[4], L Liu[4], Z. Xie[4], Suzanne Fery-Forgues[5]

[1] *Université de Toulouse, CNRS, Laboratoire de Chimie et Physique Quantiques, Toulouse, France*
[2] *Madrid Institute for Advanced Studies, IMDEA Nanoscience, Madrid, Spain*
[3] *Institute für Organische Chemie & Center for Nanosystems, Würzburg, Germany*
[4] *State Key Laboratory of Luminescent Materials and Devices, SCUT, Guangzhou, P. R. China*
[5] *Université de Toulouse, CNRS, SPCMIB, Toulouse, France*

Once a molecule is excited by absorption of a photon, it can return to the ground state by fluorescence (emission of a photon), but many other pathways for de-excitation are possible such as internal conversion (direct non-radiative decay to the ground state), intersystem crossing (possibly followed by phosphorescence emission), intramolecular charge transfer, conformational changes, etc. These de-excitation pathways may compete with fluorescence emission if they take place on a timescale comparable with the average time (lifetime) during which the molecules stay in the excited state. If they take place on a much shorter timescale than fluorescence (i.e., ns timescale), then fluorescence can be completely quenched [1].

I will illustrate how computational chemistry can help understanding the competition between radiative (e.g., fluorescence) and non-radiative decays (e.g., internal conversion) in two examples. The first one deals with the fluorescence modulation in heterocyclic BN-based triazine derivatives (see Fig. 1a) displaying an unusual 'inverted energy gap law' behaviour [2]. The second one is an investigation of fluorescence enhancement through aggregation-induced emission in benzodiazepine derivatives (see Fig. 1b). In the first case, the fluorescence modulation is achieved through chemical substitution independently of the environment, while in the second case it is the environment that controls the molecular fluorescence. The theoretical results presented herein shed light on the mechanistic picture accounting for these different photophysical behaviours.

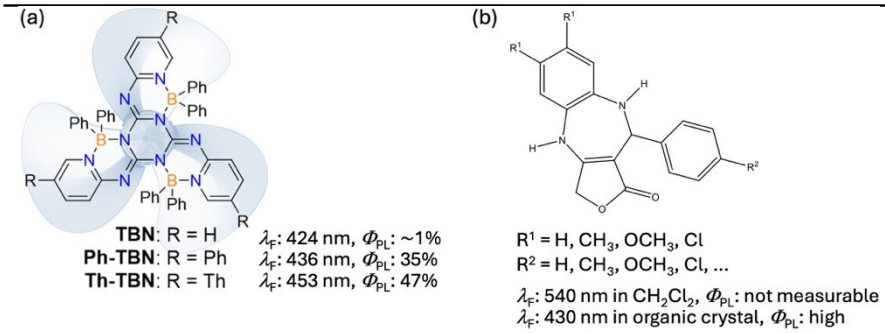

Figure 1 : Tunable fluorescence in a) heterocyclic BN-based triazine derivatives through chemical substitution, and in b) benzodiazepine derivatives through environment effects.

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* correspondant : martial.boggio@irsamc.ups-tlse.fr

Coincidence-Resolved Ionisation Studies of Astrophysically Relevant Molecules

Eszter Dudás[1*], Patrick Moretto-Capelle[1], Stéphane Faure[1], Anthony Bonnamy[1], Jean-Philippe Champeaux[1]

[1]*Laboratoire Collisions Agrégats Réactivité - UMR5589, Toulouse, France*

Understanding how electronic excitation drives ionisation and fragmentation in molecules exposed to cosmic radiation and stellar wind is essential for describing chemical evolution in the interstellar medium,[1] cometary comae,[2] and planetary atmospheres.[3] In these environments, dissociative ionisation induced by low-energy secondary electrons generated by cosmic rays, X-rays, or stellar wind particles represents a major pathway for molecular destruction and radical formation. Despite its importance, the microscopic mechanisms linking deposited electronic energy to specific bond-cleavage processes remain poorly understood, largely due to the absence of coincidence-resolved laboratory measurements capable of directly correlating the ionisation process with the resulting fragmentation channels.

This presentation focuses on the dissociation dynamics of 1-methylpyrene (MP), investigated using the SWEET experimental setup under electron-induced collision conditions to probe the fragmentation behaviour of polycyclic aromatic hydrocarbon (PAH) ions. Interaction with 200 eV electrons initiates multiple ionisation and fragmentation pathways leading to the production of molecular cations and fragment species.[4] In parallel, ongoing studies examine collisions between neutral MP and ionic projectiles such as C^+, O^+, CO^+, O_2^+, and CO_2^+ in order to investigate ionisation via electron capture processes.

The talk will present the experimental methodology, recently published results on electron-impact ionisation, and current investigations into electron-capture-induced ionisation.

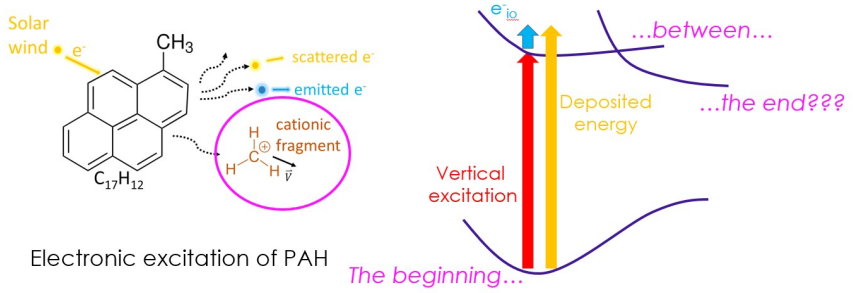

Figure 1: Ionisation Studies of Astrophysically Relevant Molecules.

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

Réseaux de liaisons hydrogène dans les sucres fluorés étudiés par spectroscopie vibrationnelle

Léo Lavy[1*], Ihssane Nait-El-Kouri[1], Arsène Kossov[1,2], Jean-Philippe Loisel[1], Matthias Büchner[1], Mrinal Naskar[3], Bruno Linclau[3], Pierre Çarçabal[1].

[1] Laboratoire Collisions Agrégats Réactivité, CNRS, Université de Toulouse, France
[2] Institut des Sciences d'Orsay, CNRS, Université d'Orsay, France
[3] Organic and Medicinal Chemistry Group, Chemistry Department, Ghent University, Belgique

Dans les systèmes biologiques, les molécules de sucre sont capables de former plusieurs liaisons hydrogène qui sont à l'origine de leur interaction avec les récepteurs moléculaires ou l'activation d'enzymes. L'ajout de fluor dans ces sucres modifie leur capacité à former les liaisons hydrogène, conduisant parfois à une meilleure efficacité thérapeutique [1,2]. Ici, l'étude spectroscopique en phase gazeuse de molécules de sucre avec ou sans atome de fluor en interaction avec une ou plusieurs molécules d'eau est présentée. Ces systèmes moléculaires sont produits et refroidis en phase gazeuse grâce à une désorption laser couplée à une détente adiabatique d'un gaz de néon. Le spectre infrarouge dans la région d'élongation OH est mesuré avec une méthode sélective en conformère et résolue en masse déjà utilisée pour étudier les sucres et leurs complexes avec l'eau [3]. Les molécules étudiées sont des sucres fonctionnalisés d'un groupement phényle dans lesquels un seul groupement OH donneur de liaisons hydrogène est présent - les autres étant remplacés par des groupes méthyles (OCH_3). Ces systèmes étant disponibles en faibles quantités uniquement, une méthode économe de préparation des échantillons est utilisée dans ce travail [4]. Tandis qu'un unique conformère du sucre sans fluor (P1, voir Fig. 1) est observé, le sucre contenant un atome de fluor (P9, voir Fig. 1) présente deux conformères qui diffèrent de la rotation du groupe contenant le fluor. En interaction avec l'eau, le réseau de liaisons hydrogène peut interagir avec le fluor produisant une signature spécifique dans le spectre infrarouge.

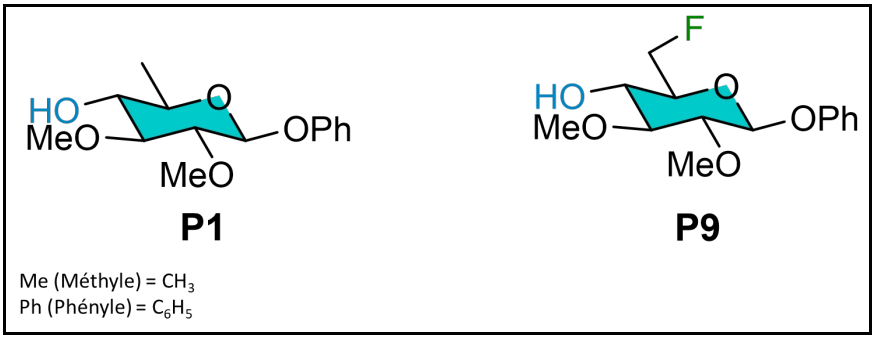

Figure 1 : P1 et P9, deux molécules analogues de sucre étudiées dans ce travail.

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* correspondant : leo.lavy@gmail.com

Formation and transfer of HCl in a macromolecular noncovalent complex: details of a presumably roaming mechanism

Vincent Bouthier[1*], Alexandre Giuliani[2,3], Laurent Nahon[2], Jean-Christophe Poully[1]

[1] *CIMAP UMR 6252 Université Caen Normandie, ENSICAEN, CNRS, CEA, Normandie Univ, 14070 Caen, France*
[2] *Synchrotron SOLEIL, 91190 Saint Aubin, France*
[3] *INRAE, UAR1008, Transform Department, Rue de la Géraudière, 44316 Nantes, France*

In the last twenty years, the “roaming atom” mechanism emerged and gained enormous interest thanks to its success in explaining experimental results that are not accounted for by the widely accepted statistical transition state theory.[1] In the roaming atom mechanism, on the pathway from reactants to products of a given chemical reaction, there is no tight transition state, defined as a saddle point on the potential-energy surface (PES) of the system. Instead, the roaming atom (or group of atoms) explores large and relatively flat regions of the PES, bypassing saddle points. Along its trajectory, “frustrated bonds” between the roaming species and other atoms of the system are successively formed and cleaved.[2] A crucial characteristic is the low total energy required for the roaming atom mechanism to play a major role, once the roaming radical is formed. Another characteristic of the roaming atom mechanism is the asymmetric energy partitioning between the reaction products.

Despite the numerous studies devoted to the roaming atom mechanism, its involvement in large molecular systems, particularly those of interest in biology and pharmacology, is unknown. In a recently-published work, we reported HCl formation and transfer within gas-phase non-covalent complexes involving vancomycin, a glycopeptide antibiotic containing more than 170 atoms, and the Ac_2-^{L}Lys-^{D}Ala-^{D}Ala peptide receptor, following UV-VUV photo-excitation.[3] Our experimental results suggest an unusual reaction mechanism, potentially involving abstraction of H by a “roaming chlorine atom” radical reaction, notably because of the energetics obtained from photon energy thresholds of the fragment ions formed after photoexcitation. However, details of this mechanism are still missing.

The aim of a very recent beamtime at the SOLEIL synchrotron was to study HCl transfer within non-covalent complexes involving chemical derivatives of vancomycin and the peptide receptor. More specifically, our results should allow to determine whether the sugar moieties of vancomycin play a role in HCl formation and transfer, to identify which chlorine atom is involved, and to evaluate the nature of the abstracted H atom (labile or not). Particular attention is also devoted to identify the HCl transfer site on the receptor, and to determine whether it specifically involves the lysine residue of Ac_2-^{L}Lys-^{D}Ala-^{D}Ala. Preliminary results suggest that a single chlorine atom is predominantly involved, while the observation of HCl transfer to Ac-^{D}Ala-^{D}Ala shows that the lysine residue is not required for the transfer process. Moreover, several groups contribute as sources of the H atom in HCl: both sugar groups, but not only. In addition, labile but also non-labile H atoms can be abstracted by chlorine.

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* correspondant: vincent.bouthier@ganil.fr

Gas Phase Structural Analysis of Microsolvated Biomolecules

Alper Laçin[1], Colwyn Bracquart[1], Sarra Kilani[1], Charles Desfrançois[1], Alberto Macario Farto[1], Bruno Manil[1], Frederic Lecomte[1], and Nicolas Nieuwjaer[1]
[1] *Laboratoire de Physique des Lasers – Université Sorbonne Paris nord, Centre National de la Recherche Scientifique, Villetaneuse – France*

The introduction of large biomolecules into the gas phase has become possible thanks to the development of ”soft” ionization sources, such as electrospray or matrix-assisted laser desorption. Although these sources are able to preserve weak interactions during the gas-phase transfer, the desorption process can induce structural changes, and the biological relevance of the resulting studies is not always ensured. In this context, the ”Biomolecules and Spectroscopies” team is developing a laser induced liquid bead ionization desorption [1], a new laser-desorption source based on micro-droplets : liquid microdroplets (50 µm diameter), containing the biomolecules of interest are irradiated under vacuum with an infrared laser. This innovative approach combines the advantage of the gas phase (stoichiometric control, ion manipulation and trapping) with the potential to preserve the native structure of biomolecules.

A primary challenge in the field lies in the detailed characterization of the desorption process to optimize the analysis of hydrated biomolecules. The present study utilizes a microdrop dispenser to generate a stable droplet stream, ensuring consistent spatial overlap with the focal point of a Q-switched Nd:YAG laser. We investigate the influence of laser wavelength and irradiance on droplet fragmentation and the resulting desorption mechanisms. The desorbed ionic species are subsequently extracted via electrostatic acceleration and analyzed by Time-of-Flight Mass Spectrometry (ToF-MS). Preliminary results indicate that the detected signals are strongly dependent on both explosion dynamics and extraction parameters.

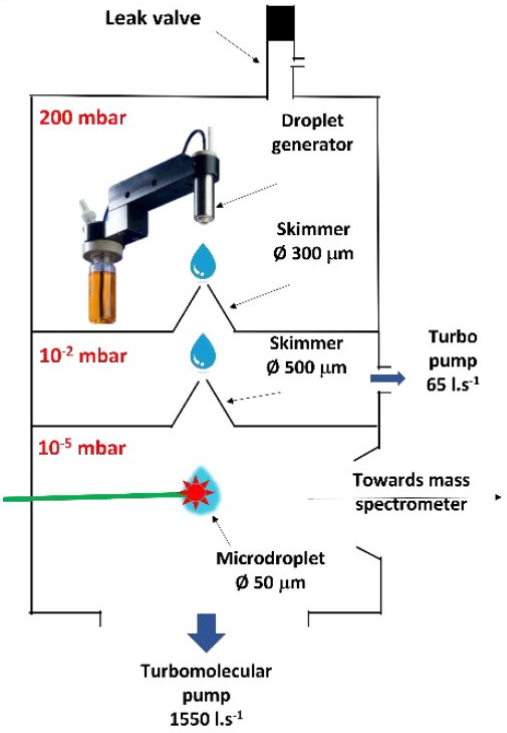

Figure 1: Scheme of the desorption source housed in a primary vacuum chamber. The droplets are introduced by differential pumping stages into a low-pressure chamber through two skimmers. The droplets are irradiated in the desorption chamber by an IR laser tuned on the absorption band of the solvent.

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Refinement of a solution-seeded supercritical fluid pulsed expansion: Optimizing vaporization and molecular cooling

Joulanda Taha[1], Jean-Xavier Bardaud[1,2], Eric Gloaguen[1]*

[1] *CNRS, Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, Orsay, France*
[2] *Present address : Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay, France*

Introducing molecules into the gas phase as neutrals is a critical challenge in various analytical techniques enabling advanced spectroscopic characterization. Our current molecular jet source coupled with a supercritical CO_2 fluid chromatography (SFC) setup [1] introduces analytes that are detected after expansion by resonant two-photon ionization (R2PI), yet, its molecular expansion stage only achieves partial vaporization generating by that molecular clusters. To maximize the efficiency of sample vaporization, the source should be improved to achieve complete cluster vaporization and enhanced molecular cooling through multiple modifications including the addition of a heated channel downstream the expansion stage to break down clusters. Therefore, the design variables of the source (Figure 1) influencing the expansion profile are being explored to optimize both vaporization and cooling, in order to produce isolated analytes suitable for conformer-resolved laser spectroscopy experiments. Solution of Caffeine dissolved in Acetonitrile is used as a model sample injected into CO_2 to assess these changes.

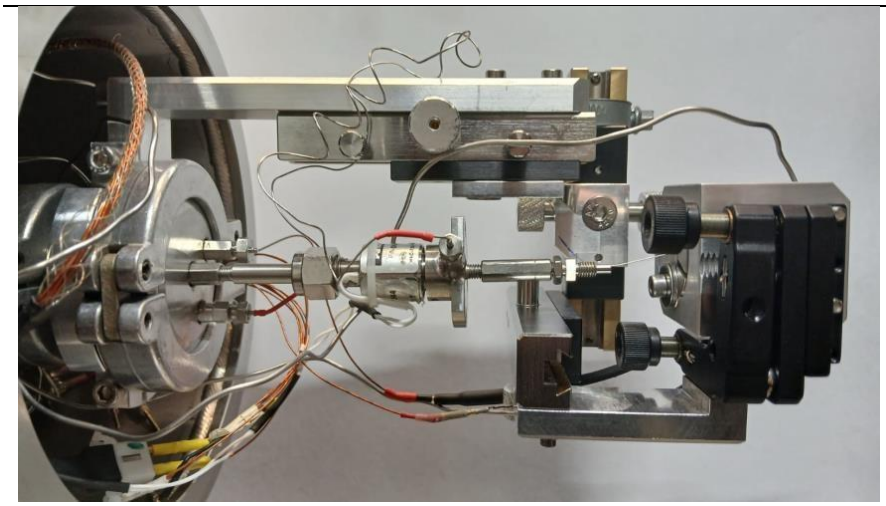

Figure 1: Photograph of the pulsed vaporization source assembly in its current design.

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* correspondant : eric.gloaguen@cnrs.fr

Investigating Water–organic Particle Properties Relevant to the Atmosphere Using Contact-Free Levitation Techniques

Gwendoline Bourdon[1,2], Pierre-Marie Flaud[2], Frederic Adamietz[1], David Talaga[1], Emilie Perraudin[2], Eric Villenave[2], Sophie Sobanska[1*]

[1]Univ. Bordeaux, CNRS, ISM, UMR 5255, F-33400 Talence, France
[2]Univ. Bordeaux, CNRS, EPOC, UMR 5805, F-33600 Pessac, France

**sophie.sobanska@u-bordeaux.fr*

It is now well known that atmospheric aerosols have significant impacts on air quality and climate change[1]. Among these, secondary organic aerosols (SOA) are formed in situ in the atmosphere through the gas-phase oxidation of volatile organic compounds (of anthropogenic and biogenic origins) by major atmospheric oxidants such as ozone, hydroxyl radicals, and nitrate radicals. Secondary organic aerosols can then undergo changes during their transport through the atmosphere due to various physicochemical and/or photochemical processes. These physical and chemical transformations reactions may affect both the chemical composition and the physical properties of aerosols and, in fine, influence their impacts.
By absorbing water, which is ubiquitous in the atmosphere, aerosols can act as cloud condensation nuclei (CCN) and induce cloud formation, thereby affecting the Earth's radiative balance. The liquid water content of aerosols, which varies with the relative humidity of the surrounding gas phase, governs phase transitions, liquid-gas partitioning, the absorption of trace gases (reactive or otherwise), multiphase reactions, and the microphysical properties of the particles. The surface properties of atmospheric particles, such as surface tension, can directly affect a particle's interactions with water vapor and thus its activation into cloud droplets. However, the complexity of aerosol aging processes occurring at the gas/particle interface is not yet well understood, especially for SOA.
Recent developments using single-particle approaches allow for the study of various chemical processes and microphysical properties at the particle scale [2]. Indeed, a single particle can act as a single reactor, resulting in a large chemical heterogeneity within the particle [3]. Moreover, it has been demonstrated that the air-aqueous droplet interface is favorable to interfacial reactions [4], which can lead to the acceleration of chemical reactions and initiate spontaneous reductions of organic compounds for example [5,6].
Here, we have carried out single particle studies using acoustic levitation to characterize the physico chemical properties of individual particles containing organic substances in various humidity conditions. Interactions between atmospheric water vapor and aerosols will be presented, as water plays a key role in determining the observed microphysical properties of aerosols in the atmosphere.

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[4] Wang, Y.; et al., *Chemosphere*, **289**, p. 133127 (2022)
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Étude de potentiels intermoléculaires ab initio pour des clathrates hydrates d'hydrogène

Mathéo Segaud[†1], David Lauvergnat[†], Yohann Scribano[*]

[†] *Institut de Chimie Physique UMR CNRS 8000 - Université Paris-Saclay, Orsay F-91405, France*
[*] *Laboratoire Univers et Particules de Montpellier, UMR CNRS 5299 - Université de Montpellier, Place Eugene Bataillon 34095 Cedex, France*

Les clathrates hydrates sont des composés inorganiques formés de molécules d'eau, cristallisées autour d'une ou plusieurs petites molécules hôtes (H_2, CO, CO_2, CH_4) et maintenues par un réseau de liaisons hydrogènes. Leur présence est avérée dans des milieux naturels comme les fonds océaniques ou les permafrosts, où les conditions de température et pression exercées à un environnement aqueux permettent leur formation, et soupçonnée dans des comètes et certains satellites naturels [1]. Comprendre leur structure relève donc d'un intérêt en astrochimie, environnemental, ainsi qu'énergétique puisque ces composés sont aussi étudiés comme potentiels moyen de stockage d'hydrogène [2].

Néanmoins, encore bien peu de données de référence sont disponibles quant à l'influence du confinement sur les propriétés spectroscopiques des molécules piégées dans des clathrates hydrates. Cela est notamment dû à la très petite échelle du confinement de l'hôte, dont les mouvements de translation, rotation et vibration sont quantifiés, de grande amplitude et fortement couplés entre eux. La complexité de ce système nous conduit à recourir à des méthodes efficaces (représentation de Smolyak) capables de simuler les états propres de translation-rotation (calculs 5D) à l'aide d'un potentiel ab initio[3][4].

Les résultats présentés illustreront l'influence du choix du potentiel d'interaction molécule-hôte considéré et de la complexité de son expansion. Nos calculs (*Figure 1, droite*) ont été réalisés avec une décomposition à n-corps du potentiel, tronquée à deux ou trois corps, sur le système $H_2 + 40.H_2O$ (*Figure 1, gauche*). Une investigation autour de la question de la validité de ce type de décomposition à n-corps du potentiel sera également discutée sur la base de résultats préliminaires au moyen d'un nouveau potentiel.

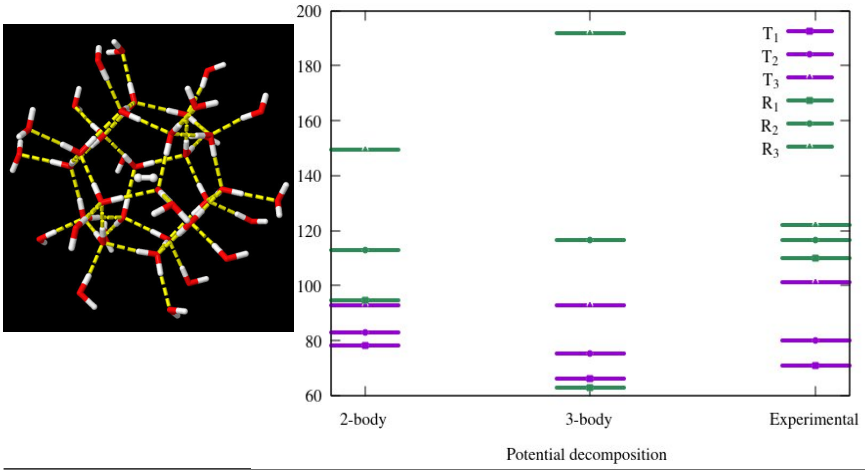

Figure 1 : (gauche) Clathrate de dihydrogène avec une cage de 40 molécules d'eau. (droite) Énergies de transition des premiers niveaux de translation ($T_{1,\,2,\,3}$) et de rotation ($R_{1,\,2,\,3}$) en fonction du niveau de description du potentiel, et comparaison avec des valeurs expérimentales [5]. En abscisse, de gauche à droite : décomposition jusqu'aux interactions à 2 corps pour le calcul des états TR, jusqu'aux interactions à 3 corps, et les valeurs expérimentales [5].

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[1] correspondant : matheo.segaud@universite-paris-saclay.fr

Du faisceau d'ions à l'image : vers le séquençage du glycome par ESIBD+SPM

Olivier Durif [1], Myriam Wadsack [1], Claudia Leticia Gomez Flores [1], Rebecca Forth [1], Jimin Ham [1], Shengpeng Huang [1], Dhaneesh Kumar Gopalakrishnan [1], Kelvin Anggara [1]

[1] *Max Planck Institute for Solid State Research, Stuttgart, Germany*

Le séquençage des glycanes - le « code sucre » - est l'un des défis majeurs de la biologie structurale, en raison de l'extraordinaire diversité isomérique et de la fragilité de ces biomolécules. Nous présentons le développement d'un instrument de nouvelle génération, conçu pour générer, préserver et déposer sur surface des ions moléculaires intacts, en vue de leur imagerie par microscopie à sonde locale à l'échelle de la molécule unique.

L'instrument combine une source électrospray, une optique ionique pour la sélection des molécules, et un étage de dépôt sous ultra-vide permettant l'atterrissage doux (soft landing) d'ions fragiles sans fragmentation. À terme, cette plateforme vise le séquençage complet du glycome par imagerie directe de glycanes individuels, ouvrant la voie à une lecture optique du « code sucre » molécule par molécule.

[1] Wu X, Kumar D, Ham J, Huang S, Anggara K. Soft Landing Mass-Selected Ions for Single Molecule Imaging. *ACS In Focus*; 2025. doi:10.1021/acsinfocus.7e9004

correspondant : o.durif@fkf.mpg.de

Stability and electronic structure of aromatic neutral radicals

Jordan Dezalay[1], Jennifer A. Noble[1*]

[1] Laboratoire PIIM, CNRS/Aix-Marseille Univ. 13013 Marseille

Aromatic molecules are ubiquitous across many environments, playing key roles in combustion, atmospheric science, food/flavouring, pharmaceuticals and astrophysics. Aromatics are chromophores, allowing easy access to electronically excited states for their characterisation and the study of their subsequent photoreactivity. The spectroscopy of some charge states, notably neutral molecules, protonated and deprotonated ions, and radical cations, has been relatively well studied due to a combination of high relevance for the applications detailed above and ease of access to the charge state, experimentally and theoretically. The neutral charge states of hydrogenated and dehydrogenated radicals, however, are almost completely unknown, despite their key role in hydrogen transfer processes (whether concerted Proton Coupled Electron Transfer (PCET) processes, which are the basis of many critical biological reactions, or as intermediates in the formation of molecular hydrogen from atomic hydrogen in the interstellar medium). Via an experimental approach employing, respectively, a molecular beam and an ion trap, we generate neutral hydrogenated and dehydrogenated aromatic radicals and test both their intrinsic- and photo-stability. Coupling these experiments to quantum chemical calculations, we describe the geometry and electronic structure of previously uncharacterised neutral radicals. We will illustrate the approach via recent spectroscopic studies of molecules of interest in biophysics, such as nucleobases,[1] and in astrophysics, including cyano-bearing aromatics [2] observed in the interstellar medium.

[1] A. Hacquard, J. Dezalay, J. A. Noble et al., in preparation
[2] Z. Efthymiou, J. Dezalay, J. A. Noble et al., in preparation
* correspondant: jennifer.noble@univ-amu.fr

Liste des participants

- Abdoul-Carime Hassan
- Asselin Pierre
- Attal Loïse
- Büchner Matthias
- Baaden Marc
- Benoit Ferdinand
- Bernard Jérôme
- Bessac Fabienne
- Boggio-Pasqua Martial
- Borja Damien
- Bourdon Gwendoline
- Bouthier Vincent
- Bracquart Colwyn
- Briant Marc
- Calvo Florent
- Chambres Pantxika
- Chin Wutharath
- Chirot Fabien
- Chishti Naveed Ahmed
- Courtiel Maia
- Coussan Stéphane
- Crépin Claudine
- Cuisset Arnaud
- Desfrancois Charles
- Dhiman Mukul
- Ducreux Emile
- Dudás Eszter
- Durif Olivier
- Falvo Cyril
- Gallifa Noé
- Garcia Alfonso Ernesto
- Georges Robert
- Gloaguen Eric
- Godard Palluet Amélie
- Goubet Manuel
- Guibourg Paul
- Gutiérrez Quintanilla Alejandro
- Halberstadt Nadine
- Hindle Francis
- Holz Anna Elisabeth
- Hoyau Sophie
- Indrajith Suvasthika
- Joblin Christine
- Kossov Arsène
- L'hermite Jean-Marc
- Labet Vanessa
- Laçin Alper
- Laliotis Athanasios
- Laurens Antoine
- Lavy Léo
- Lepere Valeria
- Macaleese Luke
- Macario Farto Alberto
- Manil Bruno
- Marciniak Alexandre
- Moretto-Capelle Patrick
- Munaro Langloys Evan
- Nieuwjaer Nicolas
- Noble Jennifer
- Perot Solène
- Pirim Claire
- Poully Jean-Christophe
- Quéméner Goulven
- Rabilloud Franck
- Rapacioli Mathias

- Romanias Manolis
- Segaud Mathéo
- Shviro Oriane
- Simon Aude
- Sobanska Sophie
- Soorkia Satchin
- Spiegelman Fernand
- Tarrat Nathalie
- Thissen Roland
- Torres Hernandez Fernando
- Toubin Céline
- Tsybizova Alexandra
- Yalouz Saad
- Zamith Sébastien
- Zarin Andjela
- Zins Emilie-Laure

Liste des auteurs