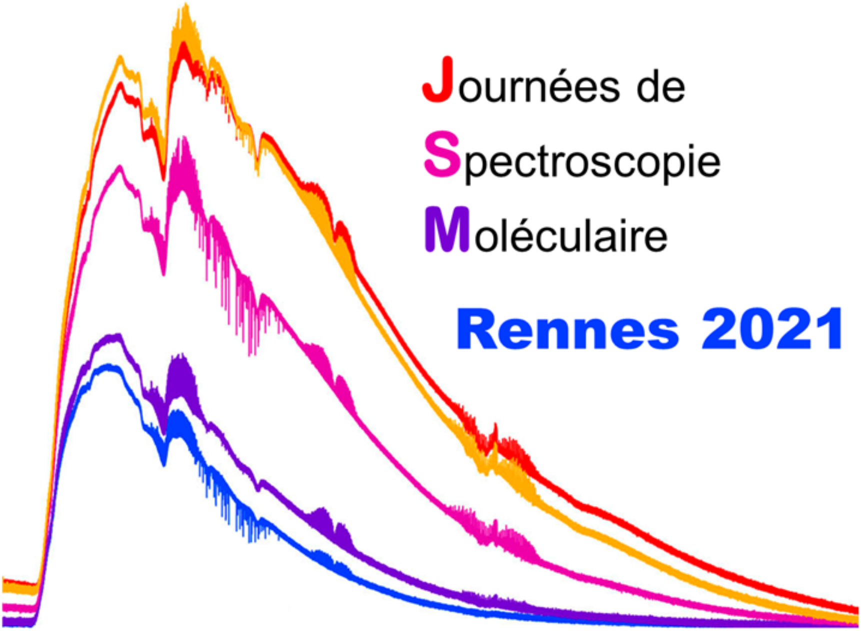

Journées de Spectroscopie Moléculaire

Rennes 2021

Lundi 28 Juin

13^{30} - 13^{45}	Mot de bienvenue
13^{45} - 14^{00} 14^{00} - 14^{15}	**Marie-Aline Martin**, ISMO
14^{15} - 14^{30}	**Eszter Dudás**, IPR
14^{30} - 14^{45}	**Helgi Hróðmarsson**, Univ. Leiden
14^{45} - 15^{00}	**Romain Basalgète**, LERMA
15^{00} - 15^{15}	**Pierre Çarçabal**, ISMO
15^{15} - - 16^{00}	**Café & Posters**
16^{00} - 16^{15}	**Jennifer Noble**, PIIM
16^{15} - 16^{30}	**Raghed Bejjani**, IPR/ Univ Louvain
16^{30} - 16^{45}	**Sebastian Hartweg**, SOLEIL
16^{45} - 17^{00}	**Ugo Jacovella**, ISMO
17^{00} - - 18^{30}	**Session Posters**

Mardi 29 Juin - matinée

9^{00} - 9^{15} 9^{15} - 9^{30}	**Jean-François Lampin**, IEMN
9^{30} - 9^{45}	**Luyao Zou**, PhLAM
9^{45} - 10^{00}	**Gaël Mouret**, LPCA
10^{00} - 10^{15}	**Noureddin Osseiran**, PhLAM
10^{15} - - 11^{00}	**Café & Posters**
11^{00} - 11^{15} 11^{15} - 11^{30}	**Jean-Paul Booth**, LPP
11^{30} - 11^{45}	**Jonas Bruickhausen**, LPCA
11^{45} - 12^{00}	**David Bonhommeau**, GSMA

Mardi 29 Juin - après midi

14^{00} - 14^{15}	**Jean-Michel Hartmann**, LMD
14^{15} - 14^{30}	
14^{30} - 14^{45}	**Safa Khemissi**, LISA
14^{45} - 15^{00}	**Oznur Yeni**, ILM
15^{00} - 15^{15}	**Gildas Goldsztejn**, ISMO
15^{15} -	**Café & Posters**
- 16^{00}	
16^{00} - 16^{15}	**Christof Janssen**, LERMA
16^{15} - 16^{30}	
16^{30} - 16^{45}	**Anusanth Anantharajah**, LISA
16^{45} - 17^{00}	**Justin Chaillot**, LIPhy
17^{00} -	**Session Posters**
- 18^{30}	

Mercredi 30 Juin

Atelier spectroscopie en milieux extrêmes

Cet atelier a vocation à servir d'espace d'échange technologique. Chaque présentation durera en moyenne 30 min pour laisser place à la discussion.

9^{00} - - 9^{45}	**Robert Georges, IPR** – *Spectroscopie en milieux extrêmes*
9^{45} - - 10^{30}	**Ian Sims & Brian Hays, IPR** – *Spectroscopie millimétrique appliquée à la cinétique basse température*
10^{30} - - 11^{15}	**Sophie Carles, IPR** – *Spectrométrie d'ions en écoulements supersoniques*
11^{15} - - 12^{00}	**Lucile Rutkowski, IPR** – *Spectroscopie par peignes de fréquence*

Après-midi: Visite des labos du département de physique moléculaire à l'IPR.

Laboratory rotational spectroscopy of reactive interstellar species in the terahertz domain

Marie-Aline Martin[1]*

[1] Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique : UMR8214 – France

The identification of new molecules in the interstellar medium (ISM) is intrinsically linked to their prior study in the laboratory, especially at centimeter to submillimeter wavelengths where the recorded spectra act as identity cards. Although reactive species represent a significant amount of the known interstellar species (more than 50%), the astronomical detection of relatively large ones (5 atoms and more) remains hindered by the lack of available laboratory data. Indeed, these species are often challenging to produce and characterize in the laboratory compared to their stable, often commercially available, counterparts. It is also interesting to note than even for already known reactive species, laboratory data are often limited to the centimeter and millimeter-wave region ($f <$ 300-400 GHz) while observatories such as ALMA can operate up to about 1 THz. New laboratory data on a wide range of reactive species are thus more than ever needed. At ISMO, we are exploiting chirped-pulse millimeter-wave and frequency-multiplication-based (sub)millimeter spectroscopy to record the rotational spectrum of known or postulated astronomical species. Several set-ups (H-abstraction by F atoms, RF and DC discharges) can be coupled to our two spectrometers allowing to produce radicals and reactive species. In this talk, I will present an overview of our experimental capabilities illustrated by recent results on several radicals.

High-Temperature Non-LTE Cavity Ring-down Spectroscopy using SMAUG experimental setup

Eszter Dudás[1]*, Abdessamad Benidar[1], Samir Kassi[2], Michael Rey[3], Vinayak Narayan Kulkarni[4], Christine Charles[5], Robert Gamache[6], Robert Georges[1]

[1] Institut de Physique de Rennes – CNRS UMR 6251 – Université Rennes1 – France
[2] Université Grenoble Alpes, LIPhy, F-38000 Grenoble and CNRS, LIPhy, F38000, Grenoble – France
[3] Université de Reims Champagne-Ardenne : UMR7331, Reims – France
[4] Indian Institute of Technology, Guwahati – Inde
[5] Australian National University – SP3 lab, Mills Road, Blg 60, Canberra, ACT 2601, Australie
[6] Dep. of Environmental, Earth, and Atmospheric Sciences, Univ. of Massachusetts – États-Unis

The SMAUG apparatus was developed to produce high-resolution IR spectra of polyatomic molecules of interest for hot astrophysical atmospheres, such as those that surround hot Jupiters which can reach up to 2500K. High-temperature IR spectroscopic data is needed to retrieve temperature and concentration profiles of these atmospheres. SMAUG can operate according to two complementary working regimes: in heavily non-LTE (vibrationally hot and rotationally cold) conditions and in close to LTE conditions, to help interpret the complex patterns of highly excited vibrational states. Two different gases, CO and CH_4, were used. In non-LTE conditions, a rotational temperature of 39K was measured for CH_4, while multiple vibrational temperatures were necessary to reproduce the observed intensities. Two types of vibrational relaxations were identified, which evidenced a more rapid vibrational relaxation between the vibrational energy levels constituting a polyad than was observed for relaxations from one polyad to another. Using a novel post-shock CRDS technique, CO and CH_4 spectra were also recorded at high temperature in close to LTE conditions.

Much ado about symmetry? - C_{60} ionization in space

Helgi Hróðmarsson[1*]
[1] Universiteit Leiden [Leiden] – Pays-Bas

The presence of the ${C_{60}}^+$ cation in the diffuse interstellar medium is a testament to the robustness of C_{60} and infers a cosmic importance to the molecule's photoionization process. Now with four of the Diffuse Interstellar Bands (DIBs) having been assigned to transitions in ${C_{60}}^+$, the dynamic nature of the photoionization of C_{60} needs to be understood, as many symmetry-related complexities arise upon the loss of an electron in neutral C_{60}. We inspected the photoionization dynamics of the C_{60} buckminsterfullerene with VUV synchrotron radiation using a double-imaging photoelectron photoion coincidence spectrometer and we present the data as a 2D photoelectron matrix which contains a wealth of spectroscopic data. The most pertinent is the threshold photoelectron spectrum (TPES), which is compared to data relevant to the DIBs. Our analysis reveals the importance of symmetry in the ground state and excited states of ${C_{60}}^+$ and gives us hope that more DIBs may be assigned to ${C_{60}}^+$ in the near future.

Experimental study of X ray photon-induced desorption from methanol containing ices and its astrophysical implications

Romain Basalgète[1]*, Rémi Dupuy[1], Géraldine Féraud[1], Xavier Michaut[1], Laurent Philippe[1], Lionel Amiaud[2], Anne Lafosse[2], Jean-Hugues Fillion[1], Mathieu Bertin[1]

[1] Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères – Paris VI, Observatoire de Paris, Université de Cergy Pontoise, Université Pierre et Marie Curie (UPMC) - Paris VI, INSU, CNRS : UMR8112, École normale supérieure [ENS] – France

[2] Université Paris-Sud 11 - UFR Sciences – Université Paris XI - Paris Sud – Faculté des Sciences - 91405 Orsay cedex, France

Methanol CH_3OH is a small organic molecule of particular importance in astrophysics. It has recently been detected in its gaseous form in protoplanetary disks. Its presence in these star forming regions is still not fully understood. It is generally believed to form on the surface of cold (T $<$ 100 K) dust grains, in condensed phase. As it cannot thermally desorb from these ices, a non thermal process should explain its gas phase presence. In protoplanetary disks, it is expected that X-rays emitted by the central young stellar object could trigger CH_3OH ejection from the ices into the gas phase, hence explaining the detections. This process, known as X-ray photodesorption can participate to the overall gas to ice ratio of methanol in these regions. Experimental study of X-ray photodesorption from methanol containing ices has been achieved by coupling the Ultrahigh Vacuum SPICES setup to the SEXTANTS beamline of the SOLEIL synchrotron facility. The desorbing molecules are probed by mass spectrometry and quantitative X-ray photodesorption yields are derived. I will present the main findings of these experiments and I will discuss their astrophysical implications.

Vibrational spectroscopy of sugars in the gas phase.

Ander Camiruaga[1], Nathan Chapelle[1], Adrien Piqot Lescop[1], Pierre Çarçabal[1]*

[1] Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique : UMR8214 – France

Sugars are complex flexible biomolecules that can adopt multiple conformations influenced by the interactions with surrounding molecular partner such as solvent molecules or other biomolecules. The bioactive forms of such assemblies are governed by the combination of intrinsic properties of each molecular components as well as by their intermolecular arrangement. Monitoring the intermolecular interactions at play and their balance with intramolecular preferences provides key information on affinity and selectivity, the key ingredients for efficient biological activity.

Gas phase conformer selective and vibrationally resolved spectroscopic methods, complemented by computational conformational landscapes exploration, uniquely probe local molecular interactions. In the near infrared, between 3.5 and 4 mm, we interrogate intramolecular stretching modes of O-H and N-H groups, which are directly involved in the intra- and intermolecular interactions as donors and acceptors.

The presentation will focus on our most recent studies of conformations and interactions in neutral sugar containing assemblies such as glycoplipids, sugar-peptide complexes and hydrated complexes by means of gas phase IR spectroscopy.

Présentation Lundi 28 Juin 16h00

La spectroscopie électronique des anions déprotonés froids : compétition entre la photodissociation et le photodétachement.

Jennifer Noble[1]*

[1] Physique des interactions ioniques et moléculaires – CNRS : UMR7345, Aix Marseille Univ – France

Un anion déprotoné photoexcité peut subir une désactivation via plusieurs mécanismes concurrents. La fragmentation de l'anion donne lieu à des fragments anioniques (et neutres), tandis que la photodissociation de l'électron forme un radical neutre déshydrogéné qui peut être stable ou non. Nous avons récemment modifié notre dispositif expérimental - basé sur un piège de Paul refroidi par cryogénie - pour permettre la mesure de tous ces produits de photoexcitation. L'étude des spectres UV-visible d'une multitude d'anions aromatiques déprotonés - avec différents groupes fonctionnels et hétéroatomes - nous a permis de tirer quelques conclusions générales sur la stabilité de l'anion déprotoné et du radical déshydrogéné. Nous discuterons de nos résultats récents sur des molécules aromatiques simples. Nous montrerons, par exemple, que le site de déprotonation détermine la stabilité des radicaux déshydrogénés dans les acides aminés.

Photodissociation spectroscopy of ionic species produced in a pulsed free jet expansion

Raghed Bejjani[1,2*], Anthony Roucou[2], Xavier Urbain[2], Clément Lauzin[2]

[1] Institut de Physique de Rennes – CNRS UMR 6251 – Université Rennes1 – France
[2] Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain – Belgique

We will present 'Stargate', an instrument developed in house able to produce cold molecular ions and ionic van der Waals complexes. The aim of this instrument is to study such species by high-resolution photodissociation spectroscopy. Its main components are (i) a pulsed supersonic expansion plasma source, to produce the desired species at relatively low rotational temperature (50-70K), (ii) a time of flight mass spectrometer which includes a single unit able to perform acceleration, bunching and gating, and (iii) a photodissociation laser followed by a second mass selection of the fragmented ion. We will be presenting the first results obtained with this apparatus, (i) the first mass spectra of cationic and anionic species, formed from different gas mixtures and (ii) the first photodissociation spectra of the rovibronic overtones of N_2O^+ using a dye laser. Finally, future improvements, in terms of clusters production, spectral resolution and sensitivity will be discussed.

Photoelectron spectroscopy of the water dimer: a complex vibrational landscape?

Sebastian Hartweg[1*], Gustavo Garcia[1], Laurent Nahon[1]

[1] Synchrotron SOLEIL – CNRS : UR1 – France

Hydrogen bonds and proton transfer reactions can be considered as being at the very heart of aqueous chemistry and of utmost importance for many processes of biological relevance. Nevertheless, these processes are not yet well understood, even in seemingly simple model systems. Here we probe the vibronic structure of the water dimer via transitions to the electronic ground state of the cation by means of mass-tagged photoelectron spectroscopy. Our work reveals previously unresolved vibrational structure with 10-30 meV (80-242 cm-1) typical splitting, in disagreement with a previous theoretical photoionization study predicting an apparent main vibrational progression with approximately a 130 meV spacing. Deviations from the theoretically predicted structure are discussed in terms of known difficulties with calculations of strongly coupled anharmonic systems involving large amplitude motions and potential contributions of the non-zero vibrational energy of the neutral water dimer at a finite experimental internal temperature.

UV-FUV photo-processing of molecular cationic species of potential astrophysical importance

Ugo Jacovella[1*]

[1] Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, CNRS UMR 8214 – France

The recent detections in pre-stellar sources of cyano substituted and pure hydrocarbon cycles have emphasized the importance of aromatic chemistry in earliest stages of star formation. Ultraviolet (UV) and far-UV (FUV) radiations are ubiquitous in Space and thus the photo-processing of one or two-membered ring ions may open chemical networks, leading to the formation of larger aromatics. We investigated the fate of positively charged ring structures after UV and FUV photoexcitation and its potential impact on stellar and interstellar chemistry. Cations were trapped in a linear ion trap prior to light interrogation using the UV and FUV radiations (4.5 – 13.6 eV) from the DESIRS beamline at the synchrotron SOLEIL. Action photodissociation spectra were obtained by monitoring the photofragment yields as a function of photon energy. These spectra are used to discuss the photostability in different Space regions and to propose potential important top-down mechanisms for astrochemistry.

Présentation Mardi 29 Juin 9h00

Un laser moléculaire térahertz pour la spectroscopie à haute résolution

Marie-Hélène Mammez[1], Zachary Buchanan[2,3], Olivier Pirali[3,4], Marie-Aline Martin[3], Joan Turut[5], Guillaume Ducournau[5], Sophie Eliet[5], Francis Hindle[1], Stefano Barbieri[5], Pascale Roy[4], Gaël Mouret[1], and Jean-Francois Lampin[5*]

[1] Laboratoire de Physico-Chimie de l'Atmosphère – Université Littoral Côte d'Opale – France
[2]Department of Chemistry, University of California, Davis, CA – United States
[3] Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, CNRS UMR 8214 – France
[4] SOLEIL synchrotron, AILES beamline, Gif-sur-Yvette, France
[5] Institut d'Électronique, de Microélectronique et de Nanotechnologie - CNRS UMR 8520 – Université de Lille, Université Polytechnique Hauts-de-France, Ecole Centrale de Lille – France

Les lasers moléculaires térahertz (THz) pompés optiquement par laser à cascade quantique (quantum cascade lasers ou QCL) sont de nouvelles sources dans ce domaine de fréquences où des sources puissantes ont longtemps manqué. Nous avons établi un catalogue des raies les plus intenses de l'ammoniac et nous avons développé un laser pouvant générer plus de 50 raies dans la gamme 0.7-5.5 THz. L'accordabilité fréquentielle autour de chaque raie est très limitée mais nous montrerons qu'il est néanmoins possible d'utiliser ces sources comme oscillateur local dans un spectromètre hétérodyne THz à haute résolution.

Millimeter-wave emission spectrometer based on direct digital synthesis and zero-biased detectors

Luyao Zou[1]*, Roman Motiyenko[1], Eugen Alekseev[2], Laurent Margulès[1]

[1] Laboratoire de Physique des Lasers, Atomes et Molécules - CNRS UMR 8523 – Université de Lille – France

[2] Institute of Radio Astronomy of NASU – Kharkiv, Ukraine

Spectral acquisition speed and sensitivity are essential for studying meta-stable molecular species. Chirped-pulse spectroscopy has been demonstrated in the past decade to be an efficient technique to achieve rapid spectral acquisition with decent sensitivity. In the millimeter-wave regime, chirped pulse spectrometers working under specific frequency range can be constructed using commercially available microwave and millimeter wave electronics, among which the arbitrary waveform generator (AWG) is usually the key instrument to produce chirp excitation. At Lille, however, we build our millimeter-wave emission spectrometer based on direct digital synthesizer (DDS) and zero-biased detectors (ZBD). The spectrometer's design is simpler and more portable than the AWG-based spectrometers, without lossing speed, phase stability, and sensitivity. By choosing appropriate Schottky multiplier chain and ZBD, the spectrometer can sample spectra from 50 to 500 GHz. We also developed specific window functions to further exploit the SnR of the frequency-domain spectra. The performance of the spectrometer and the concept of windowing will be presented.

Spectroscopie THz et cavités de haute finesse

Coralie Elmaleh[1], Francis Hindle[1], Robin Bocquet[1], Arnaud Cuisset[1], Gaël Mouret[1]*

[1] Laboratoire de Physico-Chimie de l'Atmosphère – Université de Lille, Université Littoral Côte d'Opale – France

Les spectromètres submillimétriques ou THz présentent souvent une sensibilité limitée par le manque de maturité de cette zone spectrale. En tirant profit d'une nouvelle approche, nous avons réalisé une expérience de " Cavity Enhanced Absorption Spectroscopy (CEAS) " et de " Ring down cavity " encore inédites autour de 600 GHz. Il s'agit pourtant de techniques de routines dans l'Infra Rouge permettant d'atteindre des sensibilités record. Le défi consiste à adapter cette approche aux grandes longueurs d'ondes. Nous présenterons une solution qui permet d'atteindre des longueurs d'interactions kilométriques en tirant profit de guides d'ondes surdimensionnés à très faible perte et de miroirs de Bragg de bonne réflectivité.

Combined spectroscopic and theoretical investigation of Limona ketone, a key oxidation product of limonene

Noureddin Osseiran[1*], Nunzia Savoia[1], Pascal Drean[1], Thérèse Huet[1], Manuel Goubet[1]

[1] Physique des Lasers Atomes et Molécules – CNRS UMR 8523, Unversité de Lille – France

Vegetation is a major source of emission of Biogenic Volatile Organic Compounds (BVOCs) which play an important role in atmospheric chemistry. In particular, monoterpenes ($C_{10}H_{16}$) are emitted in important amounts by plants. Among these, α-pinene, β-pinene and limonene are the most predominant species. These BVOCs as well as their oxidation products are considered as precursors of Secondary Organic Aerosol (SOA) formation, and thus have considerable impact on numerous environmental processes as well as on human health. It is important, in this regard, to determine their gas phase structure which permits to predict interactions sites and patterns with surrounding molecular systems. Within this context, the rotational spectrum of Limona ketone ($C_9H_{14}O$), a major oxidation product of limonene, was recorded and analyzed over the 4 - 20 GHz centimeter-wave range. The rotational spectrum analysis was supported by quantum chemical calculations and observed transitions were assigned to the most stable equatorial conformer. The spectrum clearly shows lines splitting due to internal rotation of a methyl group. Transitions were assigned and fitted at instrumental accuracy using a torsion-rotation Hamiltonian and the experimental barrier of the methyl torsion was determined and discussed. The relative stabilities and interconversion barriers between conformers were also explored.

Présentation Mardi 29 Juin 11h00

A new look at oxygen plasmas - Quantitative VUV and IR absorption spectroscopy of reactive intermediates

Jean-Paul Booth[1]*

[1] Laboratoire de Physique des Plasmas – Ecole Polytechnique – Palaiseau, France

Despite many decades of study, models of discharges in molecular gases still lack accurate data on many key collisional processes, even for such "simple" and ubiquitous gases as O_2. Good data is lacking for near-threshold electron-impact dissociation, surface recombination, the role of metastables, of gas heating, of vibrational excitation, of energy transfer and surface thermal accommodation. We present measurement in a DC positive column discharge in pure O2. Although it has been studied for a very long time, new experimental methods, including synchrotron Vacuum ultraviolet absorption spectroscopy and laser cavity ringdown absorption spectroscopy (CRDS), allow the densities of all the major species (atomic, molecular, in ground and excited states), as well as the gas translational temperature to be measured, with much-improved absolute accuracy, and with time resolution. Applied to (partially- and fully-) modulated discharges, these measurements provide unprecedented insight into the kinetic processes occurring (in the gas phase and at surfaces), and a profound test of the models.

High-resolution gas phase THz spectroscopy of the catechol low frequency modes involving an intramolecular hydrogen bond

Jonas Bruckhuisen[1*], Guillaume Dhont[1], Anthony Roucou[1], Atef Jabri[2], Hamdi Bayoudh[2], Thi Thanh Tran, Manuel Goubet[3], Marie-Aline Martin-Drumel[4], Arnaud Cuisset[1]

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[2] Laboratoire Interuniversitaire des Systèmes Atmosphériques – Université Paris-Est Créteil Val-de-Marne, CNRS UMR7583, Université Paris VII - Paris Diderot – France
[3] Physique des Lasers Atomes et Molécules – Université de Lille, CNRS UMR 8523 – France
[4] Institut des Sciences Moléculaires d'Orsay – CNRS UMR 8214, Université Paris-Sud, Orsay – France

Catechol, was investigated, an ortho substituted aromatic volatile organic compound (VOC) with two hydroxy groups which, due to tunneling between two symmetrically equivalent structures, can interchangeably act as donor and acceptor in a weak hydrogen bond. We performed a rotationally resolved analysis of the "free" and "bonded" –OH torsion modes of the intramolecular H-bond using synchrotron-based FT-Far-IR spectroscopy at the AILES beamline of SOLEIL. Numerous series of hot bands involving the lowest vibrational energy modes are observed and a set of anharmonic parameters is proposed. Finally, using a millimeter-wave spectrometer, the room temperature Doppler limited rotational spectrum of catechol has been measured in the 70-220 GHz frequency range. Pure rotational lines belonging to the ground and the four lowest energy vibrationally excited states have been assigned. Splitting due to the tunneling were resolved for the free –OH torsion state and a global fit gathering the far-IR and millimeter-wave data provides the rotational parameters of the low-energy far-IR modes, especially those involving the intramolecular hydrogen bond.

Carbon dioxide diffusion in sparkling beverages by molecular dynamics simulations

Mohamed Ahmed Khaireh[1], Marie Angot[1], Clara Cilindre[1], Gérard Liger Belair[1], David Bonhommeau[1]*

[1] Groupe de spectrométrie moléculaire et atmosphérique – Université de Reims - Champagne Ardenne, CNRS UMR 7331 – France

Sparkling beverages like champagnes are multicomponent mixtures supersaturated with carbon dioxide (CO_2). When such a liquid is poured in a glass, CO_2 bubbles can form by heterogeneous nucleation inside cellulose fibers, grow in the bulk before exploding at the free surface of the liquid, then releasing organoleptic compounds. At the very origin of this life cycle of CO_2 bubbles is CO_2 diffusion. By modeling brut champagnes as carbonated hydroalcoholic solutions, molecular dynamics simulations were recently carried out for 6 water models and 3 CO_2 models in an attempt to identify the optimal molecular model to describe Champagne wines. Several physical quantities were discussed like the number of hydrogen bonds or water multipole moments to get a more precise understanding of the quality of each model. To extend our analysis beyond the scope of champagnes, the alcoholic degree has also been varied to evaluate its influence on CO_2 diffusion coefficients. The presentation will summarize the main results of these recent works and emphasize the incoming challenges to describe more finely the diffusion of species in multicomponent systems like sparkling beverages.

De l'importance de l'absorption induite par collision pour le sondage de notre atmosphère

Jean-Michel Hartmann[1*]
[1] Laboratoire de Météorologie Dynamique – CNRS UMR 8539 – France

Le but principal de cet exposé est de fournir quelques éléments de base sur l'Absorption Induite par Collision dans les spectres infrarouge de molécules gazeuses à celles et ceux qui ne sont pas familier(s)s avec ce phénomène.
Pour cela, j'expliquerai dans un premier temps ce qu'est l'Absorption Induite par Collision (AIC) en décrivant le mécanisme responsable et les principales caractéristiques de l'AIC.

Je décrirai ensuite quelles sont les contraintes associées aux mesures en laboratoire des AIC et comment on peut les calculer à l'aide de modèles quantiques et classiques.

Enfin, je présenterai quelques exemples d'AIC dans les spectres de l'atmosphère de la Terre et expliquerai comment elles peuvent être utilisées et interviennent dans la télédétection de paramètres atmosphériques tels que la pression et/ou la température de la surface.
Je conclurai avec un exemple montrant le rôle important de l'AIC dans les spectres d'autres planètes

Effets stériques sur la rotation interne de deux groupes méthyle du 2,6- et 3,4-diméthylfluorobenzène

Safa Khemissi[1*], Julie Mélan[1], Ha Vinh Lam Nguyen[1]

[1] Laboratoire Interuniversitaire des Systèmes Atmosphériques – CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris – France

Les spectres micro-ondes des deux isomères 2,6 et 3,4-diméthylfluorobenzène ont été mesurés à l'aide de deux spectromètres micro-ondes à transformée de Fourier et jet moléculaire pulsé dans la gamme de fréquences de 2.0 à 40.0 GHz. En raison des rotations internes de deux groupes méthyle équivalents dans le 2,6-diméthylfluorobenzène (26DMFB), toutes les transitions de rotation se divisent en quadruplet, tandis que des quintuplets apparaissent pour le 3,4-diméthylfluorobenzène (34DMFB) à cause de ses deux groupes méthyle inéquivalents. Ces divisions ont été analysées et modélisées pour en déduire une barrière de torsion de 236,7922(21) cm–1 pour les deux groupes méthyle dans 26DMFB et de 456,20(13) cm–1 et 489,78(15) cm–1 pour les groupes méthyle en position méta et para, respectivement, dans 34DMFB. Pour les deux isomères, une modélisation obtenue avec le programme *XIAM* a atteint une déviation standard proche la précision de mesure. Les résultats expérimentaux sont comparés aux valeurs prédites obtenues par des calculs de chimie quantique et à celles d'autres dérivés du toluène.

Présentation Mardi 29 Juin 14h45

Analyse par spectroscopie d'ions IRMPD de polysaccharides de lichen contenant des unités galactofuranose

Oznur Yeni[1*], Isabelle Compagnon[1]
[1] Institut Lumière Matière – CNRS, Université de Lyon – France

La complexité structurale des glycanes rend leur séquençage difficile. Parmi les nombreuses différences structurales, la taille du cycle peut induire des propriétés biologique et physico-chimique différentes. A l'inverse des mammifères, certains organismes comme les lichens possèdent des unités galactofuranose dans leurs polysaccharides.
La spectroscopie d'ions IRMPD est une méthode prometteuse pour identifier la taille du cycle et est utilisée dans le cadre du projet ALGAIMS pour détecter du galactofuranose dans les polysaccharides de lichen[1].

Dans ce contexte, je présenterai mon projet de thèse qui consiste en l'application de l'approche MS-IR pour la détermination de la taille du cycle du galactose. Des signatures MS-IR ont été obtenues sur des échantillons synthétiques de saccharides[2,3]. Des études théoriques ont été réalisées pour expliquer ces signatures. L'application de l'approche MS-IR sur des extraits de lichen sera discutée.

Références :

1. ANR-18-CE29-0006
2. B. Schindler *et al.*, Physical Chemistry Chemical Physics., 2019, 21, 12460–12467
3. B. Favreau *et al.*, *JOC.*, 2021, 86, 6390–6405.

Présentation Mardi 29 Juin 15h00

Un laser moléculaire térahertz pour la spectroscopie à haute résolution

Gildas Goldsztejn[1]*

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Grâce à un rayonnement synchrotron X, nous avons photoexcité la phtalocyanine de fer au seuil 1s de l'azote (approx. 400 eV) et mesuré les électrons émis sur une large gamme d'énergie. Nous avons fait varier l'énergie incidente autour des résonances électroniques N 1s Ⓡ OM* (Orbitale moléculaire non occupée) et observons, à l'énergie de liaison correspondant à un photoélectron 3p du fer, une augmentation de la section efficace au passage de ces résonances. Nous l'interprétons en terme de transfert d'excitation entre l'azote et le fer.

Precision spectroscopy for atmospheric remote sensing with and without isotopes

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Using the ozone molecule as an example, we present the quest for accurate and consistent molecular spectroscopic data over several spectral ranges from the UV to the microwave region. The fragility of the ozone molecule makes experimental determination of absolute values difficult and desired uncertainties better than 1% are reached only in exceptional cases. We present measurements in the UV, visible and mid-infrared ranges with a thorough discussion of uncertainty sources. The new data shows agreement within 1% uncertainty, but indicates that the current database recommendations suffer from systematic biases in the UV and IR spectral regions exceeding 1% levels. Isotopologues of ozone and other molecules are interesting targets for atmospheric research, but the study of isotopic fractionation by remote sensing in the mid-infrared requires accuracies well beyond the 1% limit. Tackling this issue requires spectral resolution and frequency control exceeding the performance of standard FTIR spectrometers. We present work in progress on a frequency stabilised QCL at 10 μm which will allow measuring absorption lines without compromising on line shapes.

Étude des positions de raies dans les spectres infrarouges de $ClNO_2$, molécule d'intérêt atmosphérique

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Le chlorure de nitryle ($ClNO_2$) est un composé produit par des réactions hétérogènes dans la troposphère marine entre les aérosols de NaCl et N_2O_5, et probablement dans la stratosphère entre N_2O_5 et HCl. Malgré son intérêt atmosphérique, $ClNO_2$ n'a encore jamais été détecté par spectroscopie infrarouge (IR) à transformée de Fourier (TF). Dans ce contexte, la région de 12.6 μm peut être exploitée pour une future détection avec l'instrument IASI-NG, qui aura deux fois plus de résolution et de rapport signal-sur-bruit. Aussi, cet instrument (645-2760 cm-1) pourra voler avec le futur instrument FORUM (150-1400 cm-1), et permettre ainsi des observations en synergie dans l'IR lointain et moyen, seulement si les données spectroscopiques existent.

Pour $ClNO_2$, des spectres IRTF des régions de 12.6 et 27 μm ont été enregistrés à SOLEIL avec de meilleures conditions expérimentales qui ont permis d'observer des structures bien résolues. Cela a permis des analyses détaillées de ces régions avec des Hamiltoniens effectifs adéquats, et, par suite, de générer des listes de raies précises pour une future télédétection de $ClNO_2$.

Présentation Mardi 29 Juin 16h45

Spectroscopie haute performances: rencontre entre métrologie et géoscience

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D'où vient la vie? Quels étaient les climats du passé et peuvent ils nous aider à prévoir celui du futur? Ces informations sont archivées dans l'évolution des rapports isotopiques que l'on mesure avec des spectromètres de masse qui ont atteint leur maturité technologique. Mais la thermodynamique prévoit que ce sont les molécules doublement substituées (clumped isotopes) qui pourraient contenir les informations les plus pertinentes. A ce niveau les spectromètres de masse sont à leurs limites et le consensus chez les géophysiciens est que la spectroscopie optique, en progrès constants, soit en passe de prendre le relais.Cependant pour relever ce défi il faut mesurer des spectres avec une précision inégalée. L'instrument de VCOF CRDS ayant recourt à des techniques issues de la métrologie nous permet de tester les profils de raie, les modèles théoriques et les constantes fondamentales en se basant sur des spectres d'absorption calibrés de façon absolue. Nous présenterons son principe de fonctionnement et ses performances à travers non seulement des applications de spectroscopie fondamentales mais aussi de géosciences.

Detection of astrochemically relevant reaction products in skimmer sampled uniform supersonic flows using chirped-pulse Fourier transform mm-wave spectroscopy

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In the CRESUCHIRP project, we are combining the CRESU (Reaction Kinetics in Uniform Supersonic Flow) technique to provide low temperature flows with the chirped-pulse Fourier transform mm-wave (CPFTMW) spectroscopy to determine branching ratios of astrochemically relevant bimolecular reactions. Two spectrometers have been built in the Ka band (26.5-40 GHz) and the E-band (60-90 GHz). While we have detected reaction products at temperatures down to 10 K in continuous CRESU flows, the sensitivity of the CPFTMW technique is reduced by collisional broadening. To solve this problem, the CRESU flows are sampled via a skimmer into a higher vacuum environment where the temperature and pressure are lowered further, creating favourable conditions for the detection of the molecular signal. I will present the design and characterization of the skimmer chamber as well as our latest results on detection of reaction products.

POSTER # 2

High resolution infrared jet-cooled spectroscopy of furan compounds

Pierre Asselin[1], Sathapana Chawananon[1]

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Furan compounds are produced through hydrolysis-dehydration of cellulose and are largely used as an intermediate to alkane fuels from biomass, industrial usages and biomass burning. For example, furfural (FF) can be transformed by hydrogenation in 2-methylfuran (2-MF) and both are emitted into the atmosphere where their oxidation may lead to ozone and secondary aerosol formation. Accurate spectroscopic data about these compounds become highly necessary to assess their fate and impact on air quality. In this context, high resolution infrared jet-cooled experiments of FF and 2-MF were realized with the SPIRALES set-up implemented at MONARIS. Three tunable quantum cascade lasers were used to investigate the 980-1030 cm^{-1} and 1580-1720 cm^{-1} ranges of CH in plane bending and CC ring or CO stretch vibrational modes, respectively. Quantum chemistry calculations provided good estimates of anharmonic frequencies and sets of rotational constants to initiate rovibrational analyses. FF spectra were analyzed according to the rigid rotor approximation while 2-MF requires internal rotation treatment with a modest V3 potential barrier (413 cm^{-1} in the ground state).

POSTER # 3

Relations isotopiques pour les molécules tétraédriques et octaédriques

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L'étude et l'analyse des spectres à haute résolution de molécules toupies sphériques lourdes n'est pas toujours aisée. La présence de bandes chaudes et de plusieurs isotopologues peut mener à une forte densité des raies rendant l'attribution difficile.

Dans ce travail, à l'aide d'un modèle limité aux premiers ordres, nous avons déduit des relations isotopiques très simples permettant de déterminer les paramètres initiaux de l'analyse. Nous montrons également qu'une approche identique peut être utilisée pour les molécules de type XY4 et XY6 et les résultats sont illustrés par la comparaison des calculs numériques avec les données expérimentales pour différentes molécules : CH_4, GeH_4, RuO_4 et SF_6.

Référence : 1. M. Loëte, C. Richard and V. Boudon, *J. Mol. Struct.* **1206**, 127729 (2020).

POSTER # 4

Analyse détaillée du spectre infrarouge de SiF_4

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SiF_4 est un composé trace courant des gaz émis par les volcans. Une meilleure connaissance de ses paramètres spectroscopiques est requise pour permettre des mesures de concentration précises.
Nous avons entrepris une étude extensive à haute résolution de ses bandes d'absorption infrarouges, pour les 3 isotopologues présents en abondance naturelle : $^{28}SiF_4$ (92.23 %), $^{29}SiF_4$ (4.67 %) et $^{30}SiF_4$ (3.10 %). Nous présentons ici les résultats d'un ajustement d'un jeu de paramètres cohérent pour les états vibrationnels de base et excités. Toutes les données de rotation pure existantes ont été prises en compte. La bande $2\nu_4$ de $^{28}SiF_4$ a également pu être analysée en détail. Une première estimation de la dérivée du moment dipolaire pour la bande ν_3 a été réalisée, menant à une intensité de bande intégrée comparable aux valeurs de la littérature, environ 680 km/mol. La dépendance isotopique des centres de bande et des paramètres de Coriolis a également été étudiée, grâce au formules présentées dans un autre poster.

Référence : 1. V. Boudon, L. Manceron and C. Richard, *J. Quant. Spectrosc. Radiat. Transfer* **253**, 107114 (2020)

POSTER # 5

High resolution rovibrational spectroscopy of bicyclic aromatic hydrocarbons and their nitrogen-substituted ones.

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Polycyclic aromatic hydrocarbon (PAH) molecules are suspected since 80s to be the carriers of infrared (IR) emission features in the interstellar medium (ISM) which questions how these large molecules were formed. The recent discovery of cyano-naphthalenes by radioastronomy confirms the interstellar PAH hypothesis but high resolution data becomes highly necessary to elaborate chemical models leading to the formation of these molecular bricks. In this context, high resolution IR jet-cooled experiments were realized with the SPIRALES set-up implemented at MONARIS. Three tunable quantum cascade lasers were used to investigate the 980-1030 cm -1 and 1580-1720 cm -1 ranges of CH in plane bending and CC ring stretch vibrational modes, respectively. The present study is firstly dedicated to smallest bicyclic ones, naphthalene and biphenyl. Their centro-symmetry excludes any pure rotation study and IR spectroscopy becomes mandatory to retrieve rotational parameters in both ground and excited vibrational states. Additionally, nitrogen-substituted polycyclic PAHs such as quinoline and isoquinoline have been investigated because of the assumed key role in the interstellar chemistry.

POSTER # 6

Development of a new acquisition and treatment method in PFI-ZEKE photoelectron technique

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Cations of radicals are poorly characterized spectroscopically since the production of neutral radicals in a controlled and abundant way and their selected photoionization represent experimental challenges. Recently, we have proposed a new method to increase the signal to noise ratio of photoelectron spectra and thus reduce the acquisition time, which is a crucial parameter when working with unstable species. This method, based on the normal pulsed-field ionization zero-kinetic energy photoelectron spectroscopy technique, replaces the sequence of pulsed voltages by a cw ramped voltage. This acquisition mode generates 2D matrices (photoelectron signal as a function of photon energy and electron time-of-flight) which can be linearized and rotated to extract a photoelectron spectrum with excellent S/N ratio. This procedure, similar to the one used in Slow PhotoElectron Spectroscopy, has been applied to NO and will later be used to study radicals produced in situ with a pyrolysis source.

POSTER # 7

Extended laboratory investigation of the pure rotational spectra of CH_2CN, CH_3O and CH_2OH radical species in the millimeter-wave region (up to 900 GHz)

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Radical species are suspected to be involved in gas phase reactions occurring in the interstellar medium (ISM) and their detection would give important insights about the chemistry happening in the ISM. To support the search of those molecules, laboratory spectroscopy is essential. We led new high-resolution studies in the (sub)millimeter-wave region on 3 different radicals: the cyanomethyl (CH_2CN), the methoxy (CH_3O), and the hydroxymethyl (CH_2OH) radicals from 140 GHz up to 900 GHz. These species were produced by H abstraction from their precursor (acetonitrile, CH_3CN, and methanol, CH_3OH) using F atoms. Their pure rotational spectra were recorded using a frequency multiplication chain spectrometer. For those three species, the previous investigations which allowed ISM detection of CH_2CN and CH_3O, were limited to frequencies below 400 GHz. We completed the spectroscopic characterization above, and below, 400 GHz yielding to an improvement in their spectroscopic parameters. The interstellar search for these species can now be undertaken in cold to warn environments of the ISM up to 900 GHz.

POSTER # 8

H_2O line shape parameters broadened by CO_2: from the lab to space

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For decades, the composition of planetary atmospheres has been inferred from remote sensing measurements. The candidate mission to Venus, EnVision, with onboard 3 spectrometers known as the VenSpec suite, will aim at probing from the surface to above the cloud decks of Venus, which require new spectroscopic measurements and calculations of H_2O that is a target species of the mission. VenSpec-H is designed with a high-resolution spectrometer and will observe the night side of Venus in nadir, spanning the spectral range between 1 and 2.5 μm and enabling the retrievals of various species between 10 and 40 km of altitude. Considering the high pressure in the lower atmosphere of Venus and the high abundance of CO_2, line-shape parameters of H_2O broadened by CO_2 are required to infer the H_2O abundances with accuracy. In 2019 [1], new experimental line-shape parameters of H_2O broadened by CO_2 around 2.7 and 6 μm and Modified Complex Robert-Bonamy (MCRB) calculations of the half-width, line shift, and their temperature dependence were published. We will present the recently measured spectra at 1.88 μm, the line-shape parameters obtained using a multispectrum fitting procedure and the comparison with the MCRB calculated values.

Référence : 1. Régalia et al., JQSRT **231**,126-135 (2019)

POSTER # 9

Spectroscopie haute résolution dans l'infrarouge lointain et analyse du Trioxane

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Le trioxane, $H_2(CO)_3$, est un toupie symétrique qui appartient au groupe de symétrie C3v. La molécule possède 20 modes fondamentaux qui sont répartis en 7 vibrations symétriques de type A1, 3 vibrations de type A2 et 10 vibrations doublement dégénérées de type E.
Les spectres infrarouges du trioxane ont été enregistrés dans la gamme 50-650 cm-1 à l'aide d'un interféromètre Bruker IFS 125 haute résolution situé sur la ligne AILES du synchrotron SOLEIL. En raison de sa plus grande intensité dans la région infrarouge lointaine, le rayonnement synchrotron SOLEIL a été utilisé pour améliorer le rapport signal sur bruit du spectre à la résolution maximale de 0,001 cm-1.
Nous présentons ici une analyse et modélisation détaillées des modes de déformation OCO, $\nu 7$ et $\nu 19$, ainsi que le mode de torsion CH2, $\nu 20$, plus faible avec sa première harmonique $2\nu 20$. Grâce au formalisme et aux programmes développés à Dijon, nous avons pu déterminer avec précision les paramètres du Hamiltoniens effectifs pour ces 3 modes.

POSTER # 10

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

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The Dunkirk waste recovery center continuously treats all the household waste of the urban community by transforming it into electrical and thermal energy through incineration. These activities are carried out with a control of the environmental impact (ISO 14001 certification), based on the continuous improvement of detection techniques. The TeraWaste project explores the potential of high-resolution TeraHertz spectroscopy for the monitoring of gaseous emissions, by developing an in-situ diagnostic unit. The selectivity as well as the ability to detect in scattering media of THz radiation make it an alternative of choice to current solutions. A multi-species time-resolved mapping and quantification, extended to all polar compounds absorbing submillimeter waves of the pole's gaseous emissions, will allow the operator to better meet current standards and future normative evolutions.

Status of the new GEISA-2020 release

Thibault Delahaye[1]*, Raymond Armante[1], Nicole Jacquinet-Husson[1], Noëlle Scott[1], Alain Chedin[1], Laurent Crépeau[1]

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Since the beginning of the 2000's years, the accuracy of molecular spectroscopy in atmospheric research has entered in a new phase in the frame of remote sensing applications (meteorology, climatology, chemistry) with the advent of highly sophisticated and resolved instrumentations. The previous release of the GEISA spectroscopic database (2015 version), including line parameters, cross-sections as well as aerosols, has been described in Jacquinet et al [1]. For the first time, the corresponding line parameters sub-database has been intensively validated using the powerful approach of the SPARTE chain [2] developed at LMD. This chain had an important impact, particularly is the release of molecules as H_2O, CO_2 and CH_4. GEISA and associated management software facilities are implemented and freely accessible on the AERIS/ESPRI atmospheric data center website *geisa.aeris-data.fr*. It is used on-line in various domains like atmospheric physics, planetology, astronomy and astrophysics. Today, the GEISA database is the reference for current or planned Thermal IR/Near IR space missions, such as for IASI, IASI-NG, MERLIN, Microcarb. We will present the GEISA system and the status of the new release achieved in 2020. Examples of validations for major molecules such as H_2O, CO_2, O_3 and CH_4 will be presented.

Références :

1. N. Jacquinet-Husson, et al. *J. Mol. Spectrosc.*, **327**, 31-72 (2016)
2. R. Armante et al, *J. Mol. Spectrosc.*, **327**, 180-192 (2016)

POSTER # 12

Spectroscopie large bande par temps de déclin de cavité par peigne de fréquence dans le proche infrarouge

Romain Dubroeucq[1], Robert Georges[1], Lucile Rutkowski[1]

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Nous proposons une méthode de *cavity ring down spectroscopy* (CRDS) avec une source peigne de fréquence et un spectromètre à transformée de Fourier résolu en temps. Le peigne de fréquence Eribium fibré est asservi à une cavité optique afin d'assurer une transmission continue de la lumière en sortie de cavité pour l'analyse interférométrique. Nous présentons nos résultats préliminaires obtenus avec une cavité de basse finesse qui nous a permis de détecter le CO_2 présent dans l'atmosphère et de l'acétylène contenu dans une cellule.

Long-pathlength spectroscopy in Atmospheric Simulation Chamber, from near-infrared to terahertz

Eric Fertein[1*], Jean Decker[1*], Pierre Kulinski[1], Nicolas Houzel[1], Jonas Bruckhuisen[1], Frank Hindle[1], Gaël Mouret[1], Robin Bocquet[1], Guillaume Dhont[1], Cécile Coeur[1], Arnaud Cuisset[1]

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An Atmospheric Simulation Chamber, CHARME for "CHamber for the Atmospheric Reactivity and the Metrology of the Environment", has been developed at the LPCA, in order to study atmospheric evolution of Volatile Organic Compounds emitted by natural processes or human activities. The development of a multi-pass "Chernin type" cell operational from the near-IR to THz/submillimeter wavelengths and its coupling to CHARME with pathlengths adjusted from 120 m to 280 m in THz and 480 m in Near-IR allowed to detect and quantify greenhouse gases at trace levels by probing their rotational and rovibrational transitions. Significant absorbances of 400 ppm residual N_2O traces and 200 ppm O_3 traces have been measured around 600 GHz with a path-length adjusted to 200 m.

The use of THz spectroscopy in CHARME opens new possibilities especially for the monitoring of stratospheric reaction processes at submillimeter wavelengths. Moreover, the versatility of the submillimeter electronic sources will allow to perform time-resolved quantitative spectroscopies of reactants, oxidants and products involved in targeted reactions occurring in the high-altitude atmospheric layers.

POSTER # 14

Spectroscopie Dual Comb pour la détection de gaz traces atmosphériques

Sandrine Galtier[1]*, Clément Pivard[1], Jérôme Morville[1], Patrick Rairoux[1]

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Le développement d'instruments de mesure de plus en plus sensibles et robustes est essentiel pour améliorer notre compréhension du climat et de la qualité de l'air. Dans ce contexte, la spectroscopie à double peigne (DCS), basée sur le mélange cohérent de deux trains d'impulsions femtoseconde, apparaît comme une méthode émergente pour la détection in situ des gaz atmosphériques. Elle permet l'acquisition d'un large spectre ($>$ 10 THz) avec une grande cadence d'acquisition (10kHz), ce qui réduit drastiquement l'impact des fluctuations atmosphériques sur la sensibilité de l'instrument. Cette technique a été appliquée avec succès dans le proche IR pour la surveillance des gaz à effet de serre (H_2O, CO_2, CH_4). Sa mise en œuvre dans l'UV offrirait une nouvelle instrumentation spectroscopique pour cibler les espèces les plus réactives de l'atmosphère (OH, HONO, BrO ...), dont les sections efficaces d'absorption les plus grandes sont dans l'UV. La spectroscopie dual comb dans l'UV (UV-DCS) serait donc une réponse au manque d'instruments opérationnels actuels dédiés à la détection d'espèces radicalaires. Nous présenterons une implémentation expérimentale adaptée pour l'UV-DCS et les performances théoriques de cet instrument en termes de limite de détection[1]. Des résultats expérimentaux préliminaires dans l'IR seront présentés.

Référence : 1. Galtier, S. Remote Sens., 12, p.3444 (2020)

POSTER # 15

Probing Low-Temperature Reaction Products Using Chirped-Pulse Fourier Transform Millimeter Wave Spectroscopy

Divita Gupta[1*], Myriam Drissi[1*], Theo Guillaume[1], Brian Hayes[1], Ilsa Cooke[1], Omar Abdelkader Khedaoui[1], Thomas Hearne[1], Ian Sims[1]
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Reaction kinetics parameters specific to the different product channels of gas-phase bimolecular reactions at low temperatures constitute crucial input data for astrochemical modeling. We have coupled the chirped pulse microwave spectroscopy technique to the continuous CRESU (Cinétique de Réaction en Ecoulement Supersonique Unifiorme) flows available in Rennes, and have observed the products of photolysis and chemical reactions using a E-band chirped pulse Fourier transform millimeter wave spectrometer. We have characterized the flow conditions suitable for observing products of reactions and provide limits to the performance of these systems. We also observe the products of chemical reactions, particularly of CN radicals with hydrocarbons. The behavior of these products in CRESU environments as well as the results from these studies will be given and the application to observing the branching ratios of chemical reactions will be shown.

POSTER # 16

The HEROES of terahertz spectroscopy

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Despite recent progress in broadband spectroscopy across much of the electromagnetic spectrum, there remains still a sizeable gap, from around 1 to 10 THz, which lacks bright, broadband light sources and widely tuneable, high-resolution measurement techniques. The HEROES project aims to fill the gap, by combining a new generation of far-IR molecular laser with synchrotron radiation. Our new spectrometer uses heterodyne mixing within a hot electron bolometer of a molecular laser pumped by a quantum cascade laser and broadband far-IR synchrotron radiation to produce spectra from 1 to 5.5 THz with 5 GHz instantaneous bandwidth and 80 kHz resolution. This resolution is about 400 times finer than the ultimate resolution available with the Bruker Fourier-transform infrared (FTIR) spectrometer installed on the AILES beamline at SOLEIL (30 MHz). This allows for far more precise determinations of transition energies, particularly important in the field of astrochemistry, which requires good laboratory data for molecular identification. Recent improvements to the HEROES spectrometer will be presented, along with a demonstration of its ability to resolve complicated spectral features, such as transitions in the rotational-torsional spectrum of methanol and its deuterated isotopologues.

POSTER # 17

Measurement of electronic effects of ligands on organometallic complexes

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Organometallic complexes are frequently used in catalysis, where the ligands bound to the metal centre play an important role on the reactivity through their steric and electronic effects[1, 2]. Our work focuses on the evaluation of these effects using various experimental and theoretical approaches with the final aim of providing rational information to chemists to improve their synthetic developments[3]. We have begun studying tricarbonyl iron complexes of the type ($Fe(CO)_3L$) bound to a series of cyclopentadiene ligands L. These experiments were carried out at the DESIRS beamline of synchrotron SOLEIL, using e-/i+ coincidence techniques to obtain mass-selected PES, which provide access to the ionisation energies and state-selected Fe-CO dissociation energies. Rationalization of the experimental results is further made with theory using DFT and bond description methods to get information on the electronic structure of the complex and on the metal-ligand interaction.

Références :

1. Constable, E.C., *In Metals and Ligand Reactivity.* 2005. 22-45.

2. Zecchina, A., Califano, S., *The Development of Catalysis: A History of Key Processes and Personas in Catalytic Science and Technology.* John Wiley and Sons, 2017.

3. Dossmann, H., Gatineau, D., Clavier, H. Memboeuf, A. Lesage, D. Gimbert, Y., J Phys Chem A, 2020. **124**(42): p. 8753-8765.

Large amplitude torsions in nitrotoluene isomers studied by rotational spectroscopy and quantum chemistry calculations

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The monitoring of gas phase mononitrotoluenes is crucial for defence, civil security and environmental interests since they are used as taggant for TNT detection. Rotational spectra of the three isomers of nitrotoluene have been recorded at low and room temperatures using a supersonic jet Fourier Transform microwave (MW) spectrometer and a millimeterwave frequency multiplier chain, respectively. Supported by quantum chemistry calculations, the spectral analysis of pure rotation lines in the vibrational ground state has allowed to characterise the rotational energy, the hyperfine structure due to the N nucleus and the internal rotation splittings arising from the methyl group. An anisotropic internal rotation of coupled -CH_3 and -NO_2 torsional motions was identified for the ortho isomer by quantum chemistry calculations and discussed from the results of its MW analysis. The study of the internal rotation splittings in the spectra of three NT isomers allowed to characterise the internal rotation potentials of the methyl group and to compare them with other monosubstituted toluene derivatives in order to study the isomeric influence on the internal rotation barrier.

POSTER # 19

High-resolution photodissociation spectroscopy of N_2O^+

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The nitrous oxide cation (N_2O^+) is an important intermediate in the upper atmosphere. The photodissociation spectra of N_2O^+ have been measured in the UV range using the new STARGATE instrument (Spectroscopy of Transient Anions and Radicals by Gated and Accelerated Time-of-flight Experiment) developped in UCLouvain.
This poster will present the rovibronic analysis of the $A^2\Sigma^+(002) \leftarrow X^2\Pi(000)$, $A^2\Sigma^+(101) \leftarrow X^2\Pi(000)$ and $A^2\Sigma^+(003) \leftarrow X^2\Pi(000)$ bands measured at 550 K in the 30500-32500 cm^{-1} range. A global vibronic fit has been performed including these bands, Q-branch head of overtones, combination bands and data from other studies. The Renner-Teller effect involving the $X^2\Pi$ and $A^2\Sigma^+$ states was taken into account in the global fit procedure. The improvement of the description of the vibronic energy level will be discussed.

The rotationally resolved symmetric 2OH excitation in H_2O-CO_2 observed using pulsed supersonic expansion and CW-CRDS

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The rovibrational band corresponding to a double excitation of the OH symmetric stretch of the H_2O unit in the H_2O-CO_2 van der Waals complex has been recorded using CW-CRDS and a pulsed slit expansion seeded in He. The set-up is presented. The rotational analysis of this band is detailed and the results of the global fit of these data with those of the other 2OH excitation band and of the ground vibrational states are reported including data from the literature. The tunneling frequency and the vibrational predissociation lifetime are shown to decrease with vibrational excitation.

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