CNRS GDR EMIE Groupement de recherche

Edifices Moléculaires Isolés et Environnés

Réunion plénière 2024
10-14 juin 2024
Biarritz

Lundi 10 juin 2024		
Heures	**Chair**	**événement**
16:00 - 17:00	**Pierre CARCABAL**	Ouverture
17:00 - 17:30		**KL -Spectroscopy and nuclear spin conversion of hydrogenated molecules confined at low temperatures – astrophysical interest - Xavier Michaut**
17:30 - 17:50		OC1 Sébastien ZAMITH *Properties of mixed water-pyrene molecular clusters explored using CID and H/D isotope exchange*
17:50 - 18:20		OC2 Trung Thibault NGUYEN et Michel DUCHALARD *Collision Nanoparticule - Ion*
18:20 - 19:00		Posters
Mardi 11 juin 2024		
9:10 - 09:40	**Manuel GOUBET**	**KL - Développements récents en spectroscopie Terahertz à haute resolution en phase gaz - Olivier Pirali**
09:40 - 10:00		OC3 Morgane TOUREILLE *Dépendance en température du self-continuum d'absorption de la vapeur d'eau dans la fenètre à 1.6 Âµm*
10:00 - 10:20		OC4 Elias NEEMAN *Inversion motion in the rotational spectrum of tricyclic organic compound xanthene*
10:20 - 10:50		Pause café
10:50 - 11:20	**Alejandro GUTIERERREZ QUINTANILLA**	**KL - Gas-phase reactivity of toxic heavy metals towards model molecules of biological interest: a multi-approach strategy - Jean-Yves Salpin**
11:20 - 11:40		OC5 Gildas GOLDSZTEIN *Excitation transfer in metallophthalocyanines*
11:40 - 12:00		OC Franco Leonardo MOLINA *Selective Tautomer Production and Cryogenic Ion Spectroscopy of Nucleobase Radical Cations*
12:00 - 14:30		Déjeuner
14:30 - 15:00	**Valérie BRENNER**	**KL -Modelling the physico-chemical properties of gold nanoparticles and their environment - Carine Clavaguéra**
15:00 - 15:20		OC7 Camille ALAUZET *Modeling of clusters of silver and hydrocarbon at the SCC-DFTB level: a challenge*
15:20 - 15:40		*OC8* Clément SOEP *Influence du ligand dans l'activité anticancéreuses d'une famille de complexes organométalliques d'Au(III)*
15:40 - 16:10		Pause café
16:10 - 16:40	**Stéphane COUSSAN**	**Diamond nanoparticles : synthesis, properties and energy applications - Jean-Charles Arnault**
16:40 - 17:00		C9 Emile DUCREUX *Laboratory measurements of the H2O-CO2 collision system: beyond-Voigt profiles*
17:00 - 17:20		OC10 Sathapana CHAWANANON *Submillimeter Wave Spectroscopy of Furoic Acid Isomers*
17:20 - 19:00		Posters
Mercredi 12 juin 2024		
09:10 - 09:40	**Gilles GREGOIRE**	**KL - Dynamical interplay between molecular chirality and electrons - Valérie Blanchet**
09:40 - 10:00		OC11 Victor DESPRE *Ultrafast non-adiabatic relaxation in polycyclic aromatic hydrocarbons: Dynamics in correlation bands*
10:00 - 10:20		OC12 Ali MUHIEDDINE *Etude de la structure vibrationnelle des molécules de la famille de la chlorophylle par photodétachement*
10:20 - 10:50		Pause café

10:50 - 11:20	**Ha TRAN**	**KL - High-precision spectroscopic measurements and low-energy tests of fundamental physics using frequency metrology methods in the mid-IR - Benoit Darquié**
11:20 - 11:40		OC13 Alain CAMPARGUE *Le spectre d'absorption infrarouge de H2 révèle des surprises*
11:40 - 12:00		OC14 Adrien GENOUD *A VERNIER-FILTERED FREQUENCY COMB ABSORPTION EXPERIMENT: a new band of CrH?*
12:00 - 14:30		Déjeuner
14:30 - 15:00	**Pierre ASSELIN**	**KL - Reactivity of small aggregates of protonated acetic acid with methylamine - Emilie Laure Zins**
15:00 - 15:20		OC15 Lyna BOUREHIL *Fundamental investigation of peptide fragmentation by collision mass spectrometry: structure/dissociation relationship*
15:20 - 17:00		Table ronde
17:00 - 19:00		Posters
Jeudi 13 juin 2024		
09:10 - 09:40	**Nicolas NIEUJAER**	**KL - Observing collisions using laser-aligned molecules - Jean-Michel Hartmann**
09:40 - 10:00		OC16 Nicolas SOLEM *An innovative method to identify structural change through ion-molecule collision, making use of Time-Of-Flight measurements and SIMION simulations*
10:00 - 10:20		OC17 Sylvain MACLOT *Unexpected and delayed fragmentation dynamics of the organometallic ferrocene induced by ion-collision*
10:20 - 10:50		Pause café
10:50 - 11:20	**Marc BRIANT**	**KL - Acid-base chemistry when a solid surface meets liquid water - Simone Pezzoti**
11:20 - 11:40		OC18 Arsène KOSSOV *Pump-probe spectroscopy of a microhydrated sugar-peptide complex*
11:40 - 12:00		OC19 Armel JOUAN *Comprendre les effets de site en matrice : une nouvelle approche par spectroscopie multidimensionnelle infrarouge (2D-IR)*
12:20 - 14:30		Déjeuner
14:30 - 18:00		Après midi libre - collaborations - discussions
18:00 - 19:30		Conférence et posters ouverts au public
Vendredi 14 juin 2024		
09:10 - 09:40	**Luke MAC ALEESE**	**KL - Increasing specificity of Mass Spectrometry by Laser Induced Dissociation: Application to plasma protein oxidation - Marion Girod**
09:40 - 10:00		OC20 Olivier DURIF *Cinétique chimique en phase gazeuse : défis présents et futurs*
10:00 - 10:20		OC21 Jordan DEZALAY *Photophysical properties of the charged GFP chromophore and its derivated*
10:20 - 10:40		OC22 Sophie SOBANSKA *Molecular-scale view of the interaction of water and ice with organic species of atmospheric interest*
	Pierre CARCABAL et Luke MAC ALEESE	clôture

Communications Orales

Spectroscopy and nuclear spin conversion of hydrogenated molecules confined at low temperatures – astrophysical interest

Xavier Michaut

[1] *MONARIS « De la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies », UMR8233, Sorbonne Université CNRS, F-75005 Paris, France*

Email address of corresponding author: xavier.michaut@sorbonne-universite.fr

Hydrogenated molecules like H_2 and H_2O exist in several nuclear spin configurations due to the Pauli exclusion principle. These configurations are called *ortho* (parallel proton spins) and *para* (antiparallel proton spins). The *ortho* and *para* populations have been regularly determined by observations in different regions of space in far-UV absorption (Copernicus, FUSE) and in IR and sub-mm emission (ISO, Spitzer, Herschel). The *ortho/para ratio* (OPR) depends on physico-chemical processes in these environments, such as chemical formation, physical surface interactions, reactive collisions, adsorption and desorption effects of molecules on ice grains, and could be a tracer of molecular history. In order to interpret astronomical observations [1-3], it is important to compare them with the results of the most comprehensive astrochemical model [1-3]. H_2 is the most abundant molecule in the interstellar medium and is known to be the main reactant involved in the reaction chain to form hydrogenated molecules, so the *ortho/para ratio* of H_2 plays a role in the chemical evolution of molecules such as water [1-3]. It has been shown that the ortho/para ratio of H_2 in the gas phase could be affected by the desorption processes of interstellar grains in cold regions [2].

The influence of gas-grain interactions for molecules such as H_2O or CH_4 remains an open question. It is therefore necessary to know the characteristic nuclear spin conversion (NSC) equilibration time of hydrogenated molecules on solid water and solid environments at low temperatures.

After introducing the astrophysical background [1-3], I will present in situ studies of H_2 on icy surfaces and H_2O and CH_4 in noble gas matrices [4-5] in the temperature range between 4 and 30 K using the COSPINU device developed at LERMA and MONARIS. The very slow processes recently observed for H_2 trapped on icy films by Fourier transform infrared absorption spectroscopy (FTIR) will be compared with measurements made using other methods [6-8].

[1] T. Putaud *et al*, Astronomy & Astrophysics **632**, A8 (2019)
[2] E. Bron *et al*, Astronomy & Astrophysics **588**, A27 (2016)
[3] P. Hily-Blant *et al*, MNRAS **477**, 4454–4472 (2018)
[4] C. Wespiser *et al*, J. Chem. Phys. **156**, A074304 (2022)
[5] T. Putaud *et al*, J. Chem. Phys. **156**, A074305 (2022)
[6] T. Sugimoto and K. Fukutani, Nature Physics **7**, 307 (2011)
[7] H. Ueta *et al*, Physical Review Letters **116**, 253201 (2016)
[8] M. Chehrouri *et al*, Physical Chemistry Chemical Physics **13**, 2172 (2011)

Properties of mixed water-pyrene molecular clusters explored using CID and H/D isotope exchange

Sébastien Zamith*†[1], Arya M Nair[1,2], Alexandre Marciniak[1], Jean-Marc L'hermite[3], and Christine Joblin[4]

[1]Laboratoire Collisions Agrégats Réactivité – Université Toulouse III - Paul Sabatier, Centre National de la Recherche Scientifique, Fédération de recherche Matière et interactions – France
[2]IRAP – Université de Toulouse (UPS), CNRS, CNES – France
[3]Laboratoire Collisions Agrégats Réactivité – LCAR, FeRMI, Université de Toulouse III - Paul Sabatier, CNRS – France
[4]IRAP – Université de Toulouse (UPS), CNRS, CNES – 9 Av. Colonel Roche, F-31028 Toulouse Cedex 4, France, France

Résumé

Polycyclic Aromatic Hydrocarbons (PAHs) and water play a key role in the physics and chemistry of star and planet formation. These species are observed with unprecedented details by the James Webb Space Telescope (e.g., (1-3)). In addition, recent observations with ALMA allow deriving the HDO:H2O ratio in a protoplanetary disk. These results suggest that water molecules in our Solar System were inherited from cold chemistry in the pre-solar nebula (4).
A number of laboratory experiments are devoted to studying the properties of PAHs, and some of them consider the case of PAHs incorporated into water ice (5). None of them has studied mixed water-PAH clusters in the gas phase. Such clusters could form in protoplanetary disks, where the relatively high density and turbulence can lead to coagulation (6).

We present the results of our experimental approach to study the properties of mixed water-PAH clusters. More specifically, mixed water-pyrene (C16H10, Py) cationic clusters, are produced in a gas aggregation source cooled at liquid nitrogen temperature (7) prior to thermalization at 25K. The species of interest are mass selected and undergo collisions with rare gases which induce dissociation. The fragmentation products are analysed by time-of-fight mass spectrometry. Previously, we studied the proton localization from the fragmentation pattern of (Py)m(H2O)nH+ (m=(1-3), n=(1-10)) species (8), which helps to identify the structure of these species and their fragmentation pathways. Further structural information can be obtained from the determination of the dissociation thresholds.

Current experiments focus on (Py)1(D2O)nD+, (Py)1(H2O)nD+, (Py)1(D2O)nH+ and (C16D10)1(H2O)nD+ (n=1-9) in order to characterize H/D exchanges in these systems. Both water (H2O/D2O) loss and pyrene loss channels are observed in the fragmentation pattern. In addition, we observe channels involving HDO loss from which we can derive that H/D exchanges are very efficiently driven by the labile proton/deuteron. Our results

---

*Intervenant

†Auteur correspondant: Sebastien.Zamith@irsamc.ups-tlse.fr

sciencesconf.org:emie2024:554907

indicate that the mobility of the proton is higher than that of the deuteron. We also show how these results can be compared with a simple statistical model describing H/D exchanges.

References

(1) R. Chown, A. Sidhu, E. Peeters, A. G. G. M. Tielens, J. Cami, O. Berné, E. Habart, et al. A&A, Forthcoming article (DOI: 10.1051/0004-6361/202346662)

(2) Andrea Banzatti et al, ApJL 957 L22 (2023)

(3) Danny Gasman et al, A&A, 679, A117 (2023)

(4) J. J. Tobin, M. L. R. van't Hoff, M. Leemker, E. F. van Dishoeck, T. Paneque-Carreno, K. Furuya, D. Harsono, M. V. Persson, L. I. Cleeves, P. D. Sheehan and L. Cieza, Nature 615, 227–230 (2023).

(5) J.A. Noble, E. Michoulier, C. Aupetit, J. and Mascetti, A&A, 644, A22, (2020)

M. P. Bernstein, S. A. Sandford, A. L. Mattioda and L. J. Allamandola, *ApJ* 664 1264 (2007)

J. Bouwman, D. M. Paardekooper, H. M. Cuppen, H. Linnartz and L. J. Allamandola, *ApJ*, 700 56 (2009)

(6) K. Lange, C. Dominik and A. G. G. M. Tielens, A&A, 674, A200, (2023)

(7) I. Braud, S. Zamith and J.-M. L'Hermite, Rev. Sci. Instrum., 88, 043102 (2017).
(8) A.M. Nair, H. Leboucher, L. Toucouere, S. Zamith, C. Joblin, J. M. L'Hermite, A. Marciniak and A. Simon, PCCP 26, 5947–5961 (2024).

Collision Nanoparticule - Ion

Thibault Nguyen Trung[*†1], Michel Duchalard[*‡] , Marin Chabot[§1], Emmanuel Dartois[¶2], Olivier Sublemontier[‖3], Benoit Gervais[**4], Eric Giglio[††] , Thomas Pino[2], and Isabelle Ribaud[1]

[1]Laboratoire de Physique des 2 Infinis Irène Joliot-Curie – Institut National de Physique Nucléaire et de Physique des Particules du CNRS, Université Paris-Saclay, Centre National de la Recherche Scientifique : UMR9012, Centre National de la Recherche Scientifique – France

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

[3]Nanosciences et Innovation pour les Matériaux, la Biomédecine et l'Energie (ex SIS2M) – Institut Rayonnement Matière de Saclay, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France

[4]Centre de recherche sur les Ions, les MAtériaux et la Photonique (CIMAP - UMR 6252) – CEA, CNRS : UMR6252, Université de Caen Basse-Normandie, Ecole Nationale Supérieure d'Ingénieurs de Caen – CIMAP - UMR 6252, Bd H. Becquerel BP 5133 14070 Caen-cedex 5, France

Résumé

La collision entre des particules libres sub-micrométriques et des ions peut se produire dans différents environnements astrophysiques. Les rayons cosmiques irradient de façon homogène toute la galaxie et donc les grains de poussières intimement mélangés à la phase gazeuse du milieu interstellaire (1). Dans les chocs produits par les explosions stellaires, des grains sont accélérés à des vitesses très grandes (> 100 keV/u) et collisionnent les protons et les électrons du plasma qui les contiennent (2). Nous avons entrepris une étude conjointe expérience / simulation sur l'ionisation d'une nanoparticule unique par un ion rapide dans ce cadre.

L'expérience *NanoCR* auprès de l'accélérateur Andromède à IJCLab, consiste à croiser, en condition de collision unique, un faisceau d'ions rapides et un faisceau de nanoparticules monocinétiques (polystyrène, rayon 100nm). Ce dernier est produit par une lentille aérodynamique. Après le point de collision les nanoparticules sont analysées par un champs électrique transverse et collectées sur une lame de microscope. Hors ligne, un comptage sous microscope des nanoparticules est effectué selon l'axe d'analyse. Ainsi la distribution d'états de charges des nanoparticules collisionnées est obtenue. Nous présenterons ces distributions pour les projectiles : proton (600kev), C (1 MeV), Ar (1.5 à 9 MeV).

Nous avons également développé une simulation Monte Carlo pour mieux comprendre le

---

[*]Intervenant

[†]Auteur correspondant: thibault.nguyen@ijclab.in2p3.fr

[‡]Auteur correspondant: michel.duchalard@ganil.fr

[§]Auteur correspondant: marin.chabot@ijclab.in2p3.fr

[¶]Auteur correspondant: emmanuel.dartois@universite-paris-saclay.fr

[‖]Auteur correspondant: olivier.sublemontier@cea.fr

[**]Auteur correspondant: gervais@ganil.fr

[††]Auteur correspondant: eric.giglio@ganil.fr

comportement des projectiles dans la nanoparticule de polystyrène, et avoir une estimation de l'état de charge de la nanoparticule après la collision avec l'ion. Cette simulation est basée sur une description évènement par évènement des collisions de l'ion et des électrons qu'il éjecte dans la particule. Nous présentons les résultats simulés pour différents ions (H, He, C et Ar) pour des énergies allant de 10 keV/uma à 50MeV/uma. Nous avons aussi fait varier le rayon de la nanoparticule de de polystyrène de 1 nm à 100 nm. Ces résultats numériques seront comparés aux données expérimentales.

présentation en binôme

Développements récents en spectroscopie Terahertz à haute resolution en phase gaz

Olivier Pirali*[1]

[1]ISMO, SOLEIL – ISMO, Université Paris-Saclay, CNRS, AILES beamline, Synchrotrone SOLEIL – France

Résumé

Notre compréhension des processus physico-chimiques se produisant dans les divers objets du milieu interstellaire repose fortement sur les observations spectroscopiques. La spectroscopie de laboratoire réalisée à haute résolution spectrale (résolution de la structure rotationnelle) a permis la détection de près de 300 molécules dans le milieu interstellaire (en grande majorité grâce à des données enregistrées dans la gamme des longueurs **d'onde millimétriques et submillimétriques,** f=50-1000 GHz). Parmi la totalité des espèces identifiées, 65 % sont des molécules transitoires (radicaux, ions, molécules carbonées insaturées) détectées dans des environnements variés et impliquées dans un grand nombre de réactions chimiques. Néanmoins, la forte réactivité de ces espèces rend leur caractérisation spectroscopique en laboratoire extrêmement difficile. De manière à étudier les molécules radicalaires issues de molécules organiques complexes déshydrogénées, nous avons développé plusieurs outils permettant de les synthétiser en phase gaz, d'effectuer l'analyse de leur spectre de rotation pure et finalement de modéliser leur spectre à l'aide d'Hamiltonien effectifs adaptés. Parallèlement à ces travaux nous développons actuellement des outils (instrumentaux et d'analyse) permettant d'enregistrer des spectres de différentes espèces moléculaires dans des conditions sub-Doppler dans le but de produire des fréquences de transitions de quelques dizaines de kHz dans la gamme de fréquences THz. Je présenterai ces développements méthodologiques récents et leurs intérêts dans un contexte de support aux observations astrophysiques.

---

*Intervenant

Dépendance en température du self-continuum d'absorption de la vapeur d'eau dans la fenêtre à 1.6 μm

Morgane Toureille*[1]

[1]Laboratoire Interdisciplinaire de Physique [Saint Martin d'Hères] – Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble – France

Résumé

Dépendance en température du self-continuum d'absorption

de la vapeur d'eau dans la fenêtre à 1.6 μm

Morgane Toureille*, Didier Mondelain, Jean-Luc Martin, Samir Kassi, Hélène Fleurbaey, Alain Campargue

Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France

L'eau constitue entre 0.1 et 4 % de l'atmosphère terrestre, mais à elle seule, elle contribue à 90- 95 % de l'effet de serre (1). La connaissance de son spectre d'absorption est donc cruciale pour l'étude de l'atmosphère terrestre et des exoplanètes. Le spectre d'absorption de la vapeur d'eau pure est constitué par de nombreuses raies d'absorption rovibrationnelles (2) et par une absorption évoluant lentement avec la longueur d'onde appelée self-continuum de la vapeur d'eau. Dans l'atmosphère, l'eau est mélangée avec les autres molécules (essentiellement N2 et O2). Cela produit un second continuum appelé " foreign-continuum ".

Les premières études du continuum de la vapeur d'eau remontent aux années 1950 (3). Depuis, de nombreuses mesures ont été réalisées dans les différentes fenêtres de transparence de la vapeur d'eau (notamment dans notre équipe par CRDS : Cavity Ring Down Spectroscopy). Grâce à sa sensibilité et à la grande stabilité de la ligne de base des spectres enregistrés, cette technique permet d'obtenir les sections efficaces du continuum dans différentes fenêtres de transparence de la vapeur d'eau avec une précision inégalée. Les mesures antérieures réalisées dans l'équipe ont servi de base à la dernière version du modèle MT_CKD4.01 (4) qui est le modèle de référence utilisé pour prendre en compte le continuum dans les codes de transfert radiatif.

Le travail présenté ici vise à caractériser la dépendance en température du self-continuum dans la fenêtre centrée à 1.6 μm dont la connaissance précise est nécessaire dans la plage des températures atmosphériques. Le self-continuum de l'eau a été mesuré à une trentaine de longueurs d'onde sélectionnées entre 5700 cm-1 et 7000 cm-1 à 285, 296 et 307.5 K. La figure ci-dessous montre la section efficace du continuum dans la fenêtre à 1.6 μm et son

---

*Intervenant

évolution avec la température. Ces résultats serviront à la caractérisation de la dépendance en température du foreign-continuum qui est bien plus faible que celle du self-continuum.

Inversion motion in the rotational spectrum of tricyclic organic compound xanthene

Elias M. Neeman*†[1], Celina Bermúdez[2], and Manuel Goubet[1]

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

[2]Departamento de Química Física y Química Inorgánica, Facultad de Ciencias—I.U. CINQUIMA Universidad de Valladolid Paseo de Belén 7, 47011 Valladolid, Spain – Espagne

Résumé

Microwave spectroscopy, renowned for its effectiveness in analyzing gas-phase molecular structure, remains one of the most widely used physico-chemical methods. It provides detailed information on molecular structure, large-amplitude motions, hyperfine structures and non-covalent interactions within molecules and molecular complexes in the gas phase. The pure rotational spectrum of xanthene has been studied in the gas phase using a combination of Fourier Transform microwave spectroscopy and theoretical calculations in the 2-20 GHz range. Xanthene is a tricyclic molecule, where the two external cycles are aromatics and the middle one is an aliphatic ring. This distribution favors the presence of an internal motion of the aromatic rings coming out of the plane. The ground state inversion splitting of the butterfly movement has been precisely determined from the experiment. The double-minimum potential has been modeled using of the following form: *V=A(zˆ4+Bzˆ2)*. The barrier of the inversion has been then deduced and has been compared to the ab initio and DFT theoretical calculations results. The results of this study will be presented and discussed in detail.

---

*Intervenant

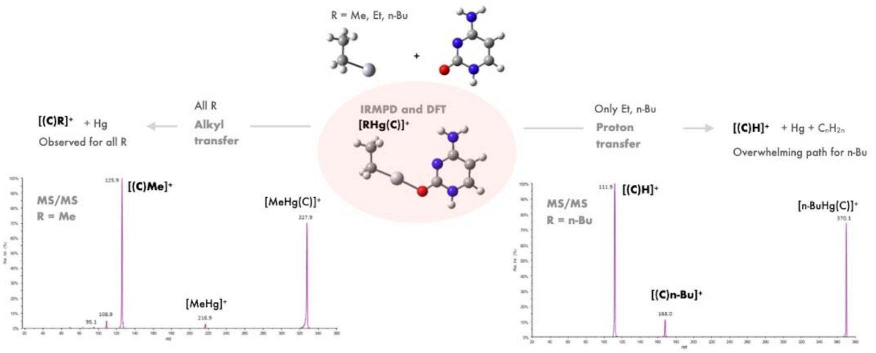
†Auteur correspondant: elias.neeman@univ-lille.fr

Gas-phase reactivity of toxic heavy metals towards model molecules of biological interest: a multi-approach strategy

Jean-Yves SALPIN

Laboratoire Analyse, Modélisation, Matériaux pour la Biologie et l'Environnement (LAMBE), UMR CNRS 8587, Evry-Courcouronnes, France

Among heavy metals, mercury, cadmium and lead have always been in the spotlight, catching the attention of biologists and chemists for their obstinacy in binding biological systems. This well-deserved stardom is associated with the long list of problems derived from their persistence and toxicity, which in the modern world is translated to an omnipresence in environmental and public health policies. Mercury for example, which, unlike many other transition metals, has no known physiological activity as nutrient or in any other natural function [1], may cause both neurological and genetic damages, and may express its genotoxicity by different mechanisms, some implying the direct interaction with DNA.[2] The high toxicity of mercury is also present in its organometallic forms $[RHg]^+$ (R=alkyl or aryl).[3] Among them, the methylmercury cation, CH_3Hg^+, is probably the most ubiquitous, and owing to its enhanced solubility in water, is a dangerous pollutant. Interactions of $[RHg]^+$ ions with DNA double helix have also been hypothesized.[2] However, the detailed mechanisms of the interaction of $[RHg]^+$ ions with DNA building blocks have yet to be clearly characterized. In this context, gas-phase studies may provide useful insights about the mechanisms occurring at the molecular level, especially when these studies combine experimental information and theoretical calculations. This communication will present our results about the interactions of organomercuric ions with different model compounds. To this end, we couple different experimental approaches and more particularly action spectroscopy and/or ion mobility.



Coupled with mass spectrometry, these approaches offer value-added data that cannot be obtained by mass spectrometry alone. The experimental work is systematically combined to theoretical calculations, to characterize the structure of both the complexes and resulting product ions, and to explore the key points of the potential energy surfaces of the associated mechanisms.[4,5] This work is also currently extended to Zn and Cd organometallic complexes (same group), to assess the role of the metal onto the observed reactivity. study the effect of the nature of the metallic center onto the observed reactivity.

References

[1] M. Israr, S. Sahi, R. Datta, D. Sarkar, *Chemosphere* **2006**, *65*, 591-598

[2] I. Onyido, A. R. Norris, E. Buncel, *Chem. Rev.* **2004**, *104*, 5911-5930.

[3] K. A. Graeme, C. V. Pollack, Jr., *J. Emergency Med.* **1998**, *16*, 45-56.

[4] A. Pérez-Barcia, M. Merced Montero Campillo, A. M. Lamsabhi, J-Y. Salpin, M. Yáñez, *PhysChemChemPhys* **2022**, 24, 20624.

[5] J-Y. Salpin, V. Haldys, J-C. Guillemin, O. Mó, M. Yáñez, M. Merced Montero-Campillo, *Isr. J. Chem.* **2023**, e20230014

Excitation transfer in metallophthalocyanines

Ralph Püttner , Manon Carrière , Lou Freschi , Jonathan Laurent , John Bozek[1], Denis Cubaynes , Marc Simon , Niloufar Shafizadeh[2], Benoît Soep[3], Marc Briant , Pierre Carcabal[2], and Gildas Goldsztejn*†2

[1]Synchrotron SOLEIL (SOLEIL) – CNRS : UMRUR1 – L'Orme des Merisiers Saint-Aubin - BP 48 91192 GIF-sur-YVETTE CEDEX, France

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

[3]Institut des sciences moléculaires d'Orsay – CNRS, CNRS : UMR8214 – France

Résumé

Metallophthalocyanines are synthetic molecules closely-related to porphyrin ones. They are widely studied in a vast number of applications in the domains of energy, environment or health. This is mainly due to the rich photophysics and photochemistry they behold. As a showcase, our study of the electronic ground state of iron(II)-phthalocyanine (FePc) shows a strong mixing between the 3d orbitals of the Fe atom and pi orbitals from the phthalocyanine, which underlines strong charge transfer character. Going a step further, we excited locally the N atoms of the ligand and monitored the relaxation pathways involving the metal (Fe or Mn). This study shows a strong interatomic Coulomb decay (ICD) like process where an inner-shell electron from the metal participates in the core-hole relaxation located at the ligand site. With contrast to previous ICD studies that occur after ionization and show a broadening of the peaks, by performing core-excitation at the ligand site, ICD reveals itself by an unambiguous new spectroscopic signature which is an increase of the cross-section of the above-mentioned relaxation pathway across the core-excitation resonant energies. To support our finding, we simulated this cross-section, in case of FePc, which allows us to disentangle all contributions from the different ways to populate the measured electronic final state and even sort out Fano-type interferences terms involved.

---

*Intervenant

†Auteur correspondant: gildas.goldsztejn@universite-paris-saclay.fr

---

Selective Tautomer Production and Cryogenic Ion Spectroscopy of Nucleobase Radical Cations

Franco Leonardo Molina*†[1,2], Michel Broquier*[1], Satchin Soorkia*[1], Gilles Gregoire*‡[1], and Gustavo Pino[2]

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

[2]Instituto de Investigaciones en Físico Química [Córdoba] – Argentine

Résumé

The structure of molecules can be elucidated using cryogenic ion spectroscopy. Cooling enables high-precision IR and UV spectra to be recorded, making it possible to apply IR-UV double resonance methods to determine molecule structures by comparison with quantum chemical calculations
We have introduced a novel approach for the isomer-selective generation of radical cations (R+•) of nucleobases, Cytosine (C), Uracil (U) and Thymine (T), through the photodissociation of cryogenically cooled silver complexes (NB-Ag+) precursors. It is based on a charge transfer state in the NB-Ag+ complex that lies in the vicinity of the locally excited p-p* state and leads to the photochemical production of the radical cation of NB.(1)

The UV-PD spectra of R+• show a broad band in the 15000-20000 cm-1 region and a well-resolved vibronic transitions in the 24000-28000 cm-1 region. Different tautomers were identified using IR-UV and UV-UV Hole-Burning spectroscopy.

The notable outcome is the lack of isomerization during the photodissociation of the silver complex leading to the formation of the DNA radical cations even when the nascent DNA radical is not the lowest energy tautomer. Finally, TD-DFT calculations faithfully reproduce the electronic excitation spectra of highly excited states (D0-D4 transitions), both for the adiabatic energies and vibronic spectra.(2-3)

References

1) Taccone, M. I.; Cruz-Ortiz, A. F.; Dezalay, J.; Soorkia, S.; Broquier, M.; Grégoire, G.; Sánchez, C. G.; Pino, G. A. J. Phys. Chem. A 2019, **123**, 7744–7750.

2) Franco L. Molina, Jordan Dezalay, Satchin Soorkia, Michel Broquier, Majdi Hochlaf, Gustavo Ariel Pino, Gilles Grégoire. Phys. Chem. Chem. Phys. 2022, **24**, 25182.

3) Franco L. Molina, Michel Broquier, Satchin Soorkia, Gilles Grégoire and Gustavo Ariel Pino, J. Phys Chem A. accepted (2024)

---

*Intervenant

†Auteur correspondant: franco.molina@universite-paris-saclay.fr

‡Auteur correspondant: gilles.gregoire@universite-paris-saclay.fr

sciencesconf.org:emie2024:553027

Modelling the physico-chemical properties of gold nanoparticles and their environment

Carine Clavaguéra*[1]

[1]Institut de Chimie Physique – Institut de Chimie du CNRS, Université Paris-Saclay, Centre National de la Recherche Scientifique – France

Résumé

Gold nanoparticles (GNPs) have been demonstrated to be promising nanometric objects thanks to their tunable chemical, physical and optical properties. However, the difficulty in fully understanding these properties can be partly attributed to dynamic interactions with surface ligands and the solvent. In addition to experimental approaches, theoretical chemistry and simulations have been proved to be powerful methods to provide crucial atomistic information. Over the last few years, we have developed a multi-scale simulation strategy to improve our understanding of the GNPs interaction with various chemical environments.

First, the adsorption of various organic molecules, including a number of aromatic compounds, on GNPs was investigated at the DFT level (1). We performed topological analyses to identify the formation of several non-covalent interactions. Interaction energy decomposition analyses revealed that electrostatic and dispersion interactions were the main contributors to these interactions (2). Calculations of vibrational and electronic spectra were used to understand how adsorption on the nanoparticle affects the spectroscopy of the organic compounds, in relation to experimental data from the Institut de Chimie Physique.

Then, the interfacial interaction of water on a series of GNPs of increasing size was systematically studied using classical molecular dynamics (3). As many-body effects play a fundamental role in these interactions, we implemented in the Tinker software the recently developed GAL force field for water-metal interactions (4) to realize the coupling with the polarizable AMOEBA force field. The structural properties of the first solvation shell were investigated, and the re-arrangement of the water network to form an extended 2D hydrogen bond network was observed as the size of GNP increases. Finally, real-time electron dynamics approaches were recently implemented to calculate the electronic stopping power of water molecules irradiated with fast ions, a first step before studying the interface between water and GNP (5).

Mots-Clés: Theoretical chemistry, metal nanoparticles, interfaces, molecular simulation, spectroscopy

---

[*] Intervenant

Modeling of clusters of silver and hydrocarbon at the SCC-DFTB level: a challenge

Camille Alauzet*[1]

[1]Modélisation, Agrégats, Dynamique (LCPQ) – Université Paul Sabatier - Toulouse III – France

Résumé

Le but principal de nos recherches est de comprendre la formation et la richesse des composants des poussières d'étoiles ainsi que le rôle des métaux dans leur croissance. En particulier dans les poussières riches en carbone et notamment en hydrocarbures aromatiques polycycliques (PAHs) pour lesquels les modèles actuels de formation, qui ignorent le rôle des métaux, sont insuffisants. Plus précisément, notre travail est de mener à bien des études théoriques sur systèmes modèles constitués d'agrégats d'argent et d'hydrocarbures pour lesquels des résultats expérimentaux ont été obtenus. En effet, la formation de nanoparticules d'argent et d'une grande variété de molécules, notamment des PAH (and) a été mis en évidence expérimentalement lors d'études visant à former des analogues de poussières par vaporisation laser et en plasma (1). Nous souhaitons donc étudier les structures, la stabilité et la formation d'agrégats de grande taille. L'utilisation de la méthode SCC-DFTB (Self-Consistent Charge Density Functional based Tight Binding) nous est apparue comme une méthode de choix pour décrire la structure électronique. L'efficacité de cette méthode repose sur la paramétrisation de paires atomiques. Des paramètres existent déjà (DFTBhyb) (2) mais ne nous ont pas donné satisfaction car ils ont été créés et optimisés pour des systèmes différents de ceux qui nous intéressent. Nous proposons donc un nouveau jeu de paramètres où la répulsion entre paire d'atomes est obtenue à partir de données MRCI (DFTBγ) (3). Afin de valider ce nouveau jeu de paramètres nous déterminons les structures géométriques et les données énergétiques pour les systèmes modèles AgnC et AgnH, avec DFTBγ et DFTB-hyb et nous les comparons à des résultats DFT déjà connus (4)(5). Des études similaires sont menées pour des systèmes plus complexes possédant des liaisons chimiques de nature différente tels que des agrégats AgnCmHp (m=1-3, n=2, p=0-2) et Agn-C10H8 qui possèdent respectivement des liaisons covalentes et des liaisons faibles métal-ligand. Dans la plupart des cas DFTBγ donne des résultats plus proches des résultats DFT que DFTBhyb. Grâce à cette étude nous appliquons actuellement l'hamiltonien DFTBγ à la détermination des structures les plus stables de complexes AgnC2nH0/n qui se formeraient dans les réacteurs expérimentaux. Ces structures sont déterminées par une méthode d'exploration globale (Parallel Tempering Monte Carlo) effectuée avec le code deMonNano (6). Nous présenterons nos premiers résultats dans cette présentation.
Figure 1: Énergies de liaisons (BEs) et structures des complexes AgnC, AgnCmHp Agn-C10H8 obtenues en DFT avec la fonctionnelle B3LYP-D3BJ (rouge) et en DFTB avec l'hamiltonien DFTBγ (bleu)

(1) Bérard, R.; Makasheva, K.; Demyk, K.; Simon, A.; Nuñez Reyes, D.; Mastrorocco, F.; Sabbah, H.; Joblin, C. Frontiers in Astronomy and Space Sciences 2021, 8, 654879.

---

*Intervenant

(2) https://dftb.org/parameters/download

(3) Alauzet, C.; Spiegelman, F.; Simon A. Computational and Theoretical Chemistry 2024 Submitted

(4)Naumkin, F. Y. Computational and Theoretical Chemistry 2013, 1021, 191–196.
(5) S. Zhao, Z.-P. Liu, Z.-H. Li, W.-N. Wang, K.-N. Fan, Density functional study of small neutral and charged silver cluster hydrides, J. Phys. Chem. A 110 (2006) 11537–11542.
(6) http://demon-nano.ups-tlse.fr/ Rapacioli et al. 2023

Influence du ligand dans l'activité anticancéreuses d'une famille de complexes organométalliques d'Au(III)

Clément Soep*†[1], Yanis Laghsal[2], Marie Chatel Niemann[3], Jean-Louis Hazemann[4,5], Olivier Proux[6], Isabelle Kieffer[7], Murielle Salomé[8], Sylvain Bohic[9], Salmain Michèle[10], Denis Lesage[11], Bertrand Benoît[12], and Héloïse Dossmann[13]

[1]Institut Parisien de Chimie Moléculaire – Université Pierre et Marie Curie - Paris 6, Centre National de la Recherche Scientifique - CNRS – France

[2]Université Paris Cité – Université Paris Cité, Université Paris-Cité – France

[3]Université Paris sciences et lettres – Université Paris sciences et lettres – France

[4]Institut Néel (NEEL) – Centre National de la Recherche Scientifique, Université Grenoble Alpes, Institut polytechnique de Grenoble - Grenoble Institute of Technology, Centre National de la Recherche Scientifique : UPR2940, Institut Polytechnique de Grenoble - Grenoble Institute of Technology – France

[5]Collaborating Research Group beamlines (CRG) – ESRF – France

[6]European Synchrotron Radiation Facility (ESRF) – ESRF – 6 rue Jules Horowitz BP220 38043 GRENOBLE CEDEX, France

[7]Observatoire des Sciences de l'Univers de Grenoble (OSUG) – CNRS : UMS832, INSU, Université Joseph Fourier - Grenoble I – 414 Rue de la piscine - BP 53 38041 GRENOBLE CEDEX 9, France

[8]European Synchrotron Radiation Facility (ESRF) – ESRF – 71, avenue des Martyrs 38000 Grenoble, France

[9]Synchrotron Radiation for Biomedicine (STROBE) – Univ. Grenoble Alpes, Inserm UA07 STROBE, Grenoble, France – France

[10]Institut Parisien de Chimie Moléculaire (IPCM) – Faculté des Sciences et de l'Ingénierie, Institut Parisien de Chimie Moléculaire (IPCM), 75005 Paris, France – France

[11]Institut Parisien de Chimie Moléculaire (IPCM) – Université Pierre et Marie Curie (UPMC) - Paris VI, CNRS : UMR8232 – 4 place Jussieu 75252 Paris Cedex 05 Bâtiment F/74, France

[12]Institut Parisien de Chimie Moléculaire – Chimie Moléculaire de Paris Centre, Institut de Chimie du CNRS, Sorbonne Universite, Centre National de la Recherche Scientifique, Centre National de la Recherche Scientifique : UMR8232 – France

[13]Institut Parisien de Chimie Moléculaire (IPCM) – Chimie Moléculaire de Paris Centre, Institut de Chimie - CNRS Chimie, Sorbonne Universite, Centre National de la Recherche Scientifique – Sorbonne-Université, 4 place Jussieu 75252 Paris Cedex 05 Bâtiment F/74, France

Résumé

Le platine est le métal actuellement le plus utilisé en chimiothérapie. D'autres métaux

---

[*] Intervenant

[†] Auteur correspondant: clement.soep@sorbonne-universite.fr

présentent cependant aussi une toxicité intéressante vis-à-vis des cellules cancéreuses. C'est le cas notamment de l'Au(III) qui est considéré depuis quelques années comme une nouvelle alternative aux agents anticancéreux actuels (1). D'un point de vue mécanistique, deux voies de toxicité sont généralement envisagées : une toxicité structurelle ou une toxicité due à la réactivité du complexe. Dans le premier cas, les complexes présentent une grande stabilité intrinsèque qui empêchent la décoordination d'un ligand et la possibilité d'une nouvelle coordination directe avec le métal (2). Ils interagissent ainsi avec leur cible via des interactions faibles telles que l'empilement π ou les interactions électrostatiques. Dans le second cas, le complexe est capable de libérer un ligand ce qui lui permet de réagir avec sa cible (3). La force de la liaison métal-ligand joue donc un rôle important dans le mode d'action du complexe vis-à-vis des cellules cancéreuses. Son évaluation permet de mieux comprendre les mécanismes impliqués et ainsi d'être en mesure d'améliorer sa toxicité.

Dans ce contexte, nous nous sommes intéressés au rôle joué par différentes phosphines (L) sur l'interaction métal-ligand dans des complexes d'Au(III) (Figure 1). L'effet de la substitution de la phosphine sur la force de liaison AuIII-L a été évalué en déterminant l'énergie de dissociation de cette liaison par spectrométrie de masse (4). Les résultats obtenus ont été ensuite comparés aux données de réactivité et de toxicité des complexes vis-à-vis des biomolécules. Pour cela, la cinétique de la réactivité des complexes avec un acide aminé a été déterminée en phase liquide par RMN 1H. La toxicité des complexes vis-à-vis de cellules cancéreuses a été déterminée par la mesure de la concentration nécessaire pour inhiber la croissance de 50% des cellules. Une relation entre la toxicité du complexe et la force de la liaison métal-ligand a ainsi pu être mise en évidence. Ainsi, les complexes les moins réactifs sont ceux présentant la plus grande toxicité. Des expériences d'imagerie de cellules individuelles utilisant la spectroscopie de fluorescence cryo-micro-X-ray réalisée à l'ESRF ont également été réalisées pour cibler la localisation du complexe dans la cellule et ont permis de mieux comprendre la cible des complexes dans la cellule.

- Awuah, Sci. Rep, 2019. 9 (1).
- Bochmann, Inorg. Chem., 2017. 56, 5728-5740.
- Ott, Chem. Med. Chem., 2014. 9 (6), 1205–1210.
- Dossmann, Inorg. Chem., 2023. 62 (33) 13304-13314.

* correspondant : clement.soep@sorbonne-universite.fr

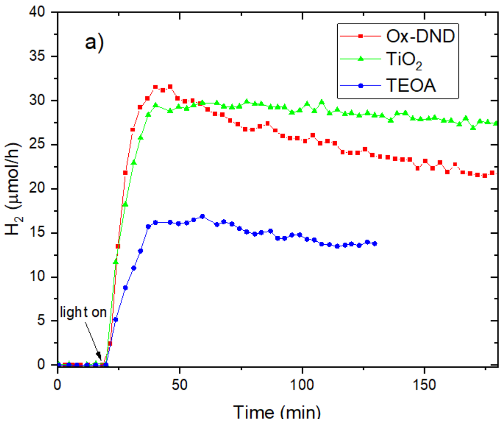
Diamond nanoparticles : synthesis, properties and energy applications

Jean-Charles Arnault

Université Paris-Saclay, CEA, CNRS, NIMBE, CEDEX, 91191 Gif sur Yvette

Among the nanocarbon family, nanodiamond (ND) behaves outstanding chemical, electronic, thermal and optical properties. This explains why such nanoparticles are actively investigated for nanomedecine, energy applications, quantum technologies or advanced lubricants and composites. Nanodiamond inherits semiconducting properties from bulk diamond. The surface chemistry of ND strongly governs their electronic properties leading to a large energy shift of their band structure (valence and conduction bands) tuning the electronic affinity from positive to negative for oxidized and hydrogenated ND, respectively [1]. In addition, through the controlled introduction of structural defects or chemical impurities into its crystal lattice, this material can absorb part of the visible radiation range despite its large band gap (5.5 eV) [2].

In this presentation, we will first discuss the different nanodiamonds and their respective synthesis routes. We will show how it is possible to control the ND surface chemistry using gas-phase treatments. The surface terminations of ND (oxidised, hydrogenated, graphitised) lead to very different colloidal properties in the aqueous phase [3, 4]. We will then illustrate the main properties of nanodiamonds. In a last part, we will review our current activities towards energy applications with a particular focus on our recent study reporting a hydrogen production by water photocatalytic dissociation for oxidized nanodiamonds [5].



Hydrogen production versus time for oxidized ND (red squares) (TEOA: 1 vol.%) compared to TiO_2 nanoparticles (green triangles) and TEOA alone (blue circles) [5].

References

[1] D. Miliaieva et al., Nanoscale Advances 2023, **5**, 4402.
[2] F. Buchner et al., Nanoscale 2022, **14**, 17188.
[3] L. Saoudi et al., Carbon, 2023, **202**, 438.
[4] F. Ducrozet et al., Nanomaterials, 2021, **11**, 2671.
[5] C. Marchal et al., Adv. Energy Sustainability Res., 2023, **2300260**, 1-8.

Laboratory measurements of the H2O-CO2 collision system: beyond-Voigt profiles

Émile Ducreux*†[1,2,3], Bruno Grouiez[1], Séverine Robert[2], Muriel Lepère[3], Bastien Vispoel[3], Robert Gamache[4], and Laurence Régalia[1]

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

[2]Planetary Atmospheres, Royal Belgian Institute for Space Aeronomy, 3 Avenue Circulaire, 1180 Brussels, Belgium – Belgique

[3]Research Unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur (UNamur), 61 rue de Bruxelles, Namur, 5000, Belgium – Belgique

[4]Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell – États-Unis

Résumé

Studying the distribution of water vapor in the CO2-rich atmospheres of Mars and Venus, our planetary neighbors, provides essential information for a better understanding of the solar system evolution. For many years, due to a lack of data and the low signal-to-noise ratio of space measurements, radiative transfer models have used the air collisional parameters for the H2O molecule as spectroscopic data. However, the constant improvement of ground- and space-based measurement instruments requires the use of more precise collisional parameters to better study the measured atmospheric spectra. Following on from previous measurements published in 2019 (1) and in the context of the preparation of the next European space mission to Venus, EnVision, new experimental spectra of H2O broadened by CO2 were measured at room temperature at the GSMA, in Reims, in the 2.7 μm spectral region. A high-resolution Fourier transform infrared spectrometer was used and coupled to a 2-meter White-type cell in stainless steel. The line parameters were then determined with a multispectrum fitting procedure using the Voigt profile. This led to characteristic W-shape residuals that have been reduced using beyond-Voigt profiles, as the Rautian, the quadratic Speed-Dependent Voigt and the quadratic Speed-Dependent Rautian profiles. The partial pressure of water vapor was corrected downwards to take account of the adsorption effect of H2O on the cell's walls, fixing the intensity values at those of HITRAN2020 database (2). In the experimental conditions, it appeared that considering the speed-dependence of collisional line parameters is necessary to obtain lower residuals and improved line-shape parameters. Finally, a comparison was made with the only existing data in the literature on broadening coefficients and their speed-dependence. The method applied in this study will be used to measure other spectral regions of atmospheric interest and to provide the planetary community with the most complete and accurate list possible of collisional line parameters for H2O broadened by CO2. An article has just been accepted for publication (3).

---

*Intervenant

†Auteur correspondant: emile.ducreux@univ-reims.fr

sciencesconf.org:emie2024:555490

(1) L. Régalia et al., Laboratory measurements and calculations of line shape parameters of the H2O–CO2 collision system, JQSRT 231 (2019)

(2) I.E. Gordon et al., The HITRAN2020 molecular spectroscopic database, JQSRT 277 (2022)
(3) É. Ducreux et al., Measurements of H2O broadened by CO2 line-shape parameters: beyond the Voigt profile, JQSRT Accepted (2024)

Submillimeter Wave Spectroscopy of Furoic Acid Isomers

Sathapana Chawananon*†[1] and Marie-Aline Martin-Drumel[2]

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

Résumé

Furans and their derivatives, notably methylfurans and furfural, are significant volatile organic compounds (VOCs) released from a variety of sources, such as biomass combustion (1), industrial activities (2), and natural phenomena like wildfires (3). These substances are major contributors to atmospheric pollution and the formation of Secondary Organic Aerosols (SOA) (4), adversely affecting air quality and influencing climate change through reactions with atmospheric oxidants.

Furoic acids (FAs), oxidation byproducts of these compounds, could potentially be a key participant factor in atmospheric chemistry, owing to its distinct chemical attributes and its potential to impact the mass and composition of SOA, as well as to contribute to acid rain formation (5). Recent research on 2-furoic acid has unveiled FA's structural variety and its capacity for conformational change, highlighting its ability to form stable dimers and to undergo proton tunnelling.

This study delves into the rotational spectra of FA isomers, focusing on the primary monomeric conformers within the submillimeter wave spectrum at ambient temperatures, ranging between 75 and 110 GHz. Specifically, for 2-FA, our investigation seeks to broaden the understanding of rotational parameters, including the quadratic centrifugal distortion constants of the ground states alongside parameters from their first excited states, which previous study (6) has not fully explored. Additionally, this work introduces the first rotational study of the ground and first excited states of predominant 3-FA conformers.

(1) X. Jiang, N. T. Tsona, L. Jia, S. Liu, H. Zhang, Y. Xu and L. Du, Atmos. Chem. Phys., 2019, 19, 13591–13609.
(2) A. Tapia, F. Villanueva, M. S. Salgado, B. Cabañas, E. Martínez and P. Martín, Atmos. Chem. Phys., 2011, 11, 3227–3241.
(3) M. J. Newland, Y. Ren, M. R. McGillen, L. Michelat, V. Daële and A. Mellouki, Atmos. Chem. Phys., 2022, 22, 1761–1772.
(4) A. Elwardany, E. Es-sebbar, F. Khaled and A. Farooq, Fuel, 2016, 166, 245–252.
(5) W. C. Keene and J. N. Galloway, Atmospheric Environment (1967), 1984, 18, 2491–2497.
(6) A. Insausti, J. Ma, Q. Yang, F. Xie and Y. Xu, ChemPhysChem, 2022, 23, e202200176.

---

*Intervenant
†Auteur correspondant: sathapana.chawananon@universite-paris-saclay.fr

Dynamical interplay between molecular chirality and electrons

Valerie Blanchet*[1]

[1]Centre dÉtudes Lasers Intenses et Applications – Université de Bordeaux, Commissariat à l'énergie atomique et aux énergies alternatives : DAM/CESTA, Centre National de la Recherche Scientifique : UMR5107, Commissariat à l'énergie atomique et aux énergies alternatives, Centre National de la Recherche Scientifique – France

Résumé

By scattering in a chiral molecular potential of pure handedness, photoelectrons exhibit a unique forward-backward antisymmetry in their momenta with respect to the axis of the ionizing light pulse owing a transient helicity. Resolving angularly this chiroptical dichroism in the momentum distributions allows to selectively filter out the electrons that are most sensitive to the electronic potential. This fascinating aspect of the light-matter interaction that survives the random distributions of molecular orientations, will be illustrated in various experimental results, such as multiphoton experiments involving pump-probe with local or non-local probes (1-2), and strong laser field experiments (3). Fenchone is a chiral terpene on which we will present femtosecond dynamics probed by valence or core-level C1s chiral ionization using a Velocity map photoelectron imaging detector (1). This technique is called TR-PECD for Time-Resolved Photoelectron Circular Dichroism and will be also illustrated on quantum electronic beating in enantiopure sample of methyl lactate. Electrons' chirosensitive scattering can be also manipulated at the attosecond scale with an ionization laser pulse strong enough to compete with the molecular potential (3). In this tunnel ionization regime, we will show how to identify the electron trajectories the most sensitive to the chiral potential. This technique is called CHILIED, for chiral Laser-Induced Electron Diffraction. Our findings will shed light on the intricate interactions between chirality and electron scattering at ultrafast timescales.

1. Physical Review X 13, 011044 (2023)

2. https://doi.org/10.48550/arXiv.2301.02002

3. Phys. Rev. X 14, 011015 (2024)

Keywords: chirality, femtosecond, X-ray FEL, PECD, strong field ionization, attosecond.

---

*Intervenant

Ultrafast non-adiabatic relaxation in polycyclic aromatic hydrocarbons: Dynamics in correlation bands

Victor Despré*†1

1Institut Lumière Matière [Villeurbanne] – Université Claude Bernard Lyon 1, Centre National de la Recherche Scientifique – France

Résumé

The interaction of molecules with extreme ultraviolet (XUV) radiation populates highly-excited cationic states, triggering complex ultrafast electron-nuclear dynamics. A fully quantum description of these dynamics in small polycyclic aromatic hydrocarbons (PAHs) relevant for astrochemistry will be presented and compared to time-resolved experimental results (1,2). It will be demonstrated that the non-adiabatic relaxation dynamics slows down with increasing system size and proximity of the initial excitation to the double-ionization threshold. Furthermore, it will be shown that the dynamics in this energy range are governed by so-called correlation bands, regions of high density of states created by strong electron correlation in the inner-valence. A simple electron-phonon scattering model may be used to explain and predict the relaxation timescale of entire classes of molecules (3,4).

These results will be contextualized within the framework of attosecond physics, particularly the emergence of an attosecond chemistry or attochemistry. Attochemistry involves controlling chemical reactions through the manipulation of pure electron dynamics occurring in the initial moments following system excitation. Recent discoveries, such as the identification of long-lived electronic coherences (5) and the ability to alter molecule stability through pure electron dynamics, as demonstrated for correlation bands (6), mark an exciting era for its study. In this context, correlation bands emerge as a promising playground for exploring the possibilities offered by attochemistry.

(1) A. Marciniak, *et al. Nature Commun.* 2015, **6**, 7909.

(2) A. Marciniak, *et al. Nature Commun.* 2019, **10**, 337.

(3) M. Hervé, *et al. Nature Phys.* 2021, **17**, 327.

(4) A. Boyer, *et al. Phys. Rev. X* 2021, **11**, 041012.

(5) D. Matselyukh, *et al. Nature Phys.* 2022, **18**, 1206.
(6) V. Despré and A. I. Kuleff, *Phys. Rev. A* 2022, **106**, L021501.

---

*Intervenant

†Auteur correspondant: victor.despre@univ-lyon1.fr

Étude de la structure vibrationnelle des molécules de la famille de la chlorophylle par photodétachement

Ali Muhieddine*†[1], Roxane Bercy[2], Benoît Soep[1], Satchin Soorkia*[1], Michel Broquier[1], Manuel Llansola-Portoles[3], and Niloufar Shafizadeh‡[1]

[1]Institut des sciences moléculaires d'Orsay – CNRS, CNRS : UMR8214 – France
[2]Institut de Biologie Intégrative de la Cellule – Centre National de la Recherche Scientifique - CNRS – France
[3]Institut de Biologie Intégrative de la Cellule – Commissariat à l'énergie atomique et aux énergies alternatives, Université Paris-Saclay, Centre National de la Recherche Scientifique, Commissariat à l'énergie atomique et aux énergies alternatives : DRF/I2BC, Centre National de la Recherche Scientifique : UMR9198 – France

Résumé

La nature, au cours de l'évolution a modelé un système très efficace pour utiliser l'énergie solaire : la photosynthèse qui transforme le dioxyde de carbone et l'eau en dioxygène et sucre en présence de la lumière. Les molécules de la famille des Chlorophylles et leurs dimères interviennent dans plusieurs étapes de la photosynthèse et en particulier au cours de l'étape initiale dite de séparation de charge qui a un rendement quantique très élevé. L'efficacité du mécanisme de séparation de charge peut être due à une résonance entre les modes vibrationnels des chlorophylles et les écarts énergétiques séparant ses paires neutres et ioniques or la structure vibrationnelle de ces molécules n'est pas connue avec précision. Le but de notre travail est d'étudier la structure vibrationnelle et vibronique de la Chlorophylle et de ses dérivés. Pour atteindre notre objectif nous réalisons la spectroscopie de photodétachement d'électrons à partir d'anions dipolaires refroidis. En effet si l'électron excédentaire de l'anion dipolaire est faiblement lié à la molécule, la structure moléculaire de l'espèce neutre et de l'anion dans cet état est très voisine. Les propriétés de l'anion sont caractérisées en mesurant l'énergie cinétique de l'électron éjecté après photoexcitation. Cette nouvelle spectroscopie permet d'accéder aux modes de vibration du cycle chlorophyllien en l'absence de solvant.

Au cours de cet exposé on présentera nos premiers résultats concernant la phéophytine-a, une Chlorophylle où l'atome de magnésium est remplacé par deux hydrogènes sur les azotes du macrocycle.

Nous avons mesuré les seuils de photodétachement d'une série de molécules modèle de la phéophytine, phéophorbide et Méthyl phéophorbide. Ces deux molécules sont identiques à une phéophytine où la chaine Phythyl C20H39 a été remplacée par une fonction H ou un Méthyl respectivement. Ces comparaisons nous ont permis de corréler la valeur des énergies de photodétachement avec les sites de déprotonation de la molécule. De plus, nous présenterons une comparaison des spectres d'action de la phéophytine et du phéophorbide autour de l'absorption du premier état excité de l'anion correspondant pour déterminer l'influence de la chaine phythyl sur la structure électronique de ces molécules.

---

*Intervenant

†Auteur correspondant: ali.muhieddine@universite-paris-saclay.fr

‡Auteur correspondant: niloufar.shafizadeh@universite-paris-saclay.fr

High-precision spectroscopic measurements and low-energy tests of fundamental physics using frequency metrology methods in the mid-IR

Benoit Darquié

There is an increasing demand for precise molecular spectroscopy, in particular in the mid-infrared fingerprint window, whether it be for modelling our atmosphere, interpreting astrophysical spectra or testing fundamental physics.

I will present our efforts towards building new-generation mid-infrared spectrometers specifically designed for precision vibrational spectroscopy of complex polyatomic molecules in the gas phase. This includes amongst other things producing gases of polyatomic species cooled to a few kelvins in cryogenic buffer-gas cells [1,2], developing frequency stabilised mid-IR lasers calibrated to some of the world's best frequency standards [3] and explore the opportunities offered by cutting-edge mid-IR photonics technologies [4]. The developments are at the forefront of cold molecule research and frequency metrology and have allowed us to measure absolute frequencies of a variety of species of atmospheric, astrophysical or fundamental interest with record up to 12-digit accuracies [3].

This opens possibilities for using polyatomic molecules to improve tests of fundamental physics and precision measurements in general. I will for instance present our ongoing work towards measuring the tiny energy difference between chiral enantiomers expected to result from electroweak interactions and to be a sensitive probe of dark matter [2,5].

References:

[1] Tokunaga *et al*, New J Phys **19**, 053006 (2017)

[2] Cournol *et al*, Quantum Electron **49**, 288 (2019)

[3] Argence *et al*, Nature Photon **9**, 456 (2015); Santagata *et al*, Optica **6**, 411 (2019); Tran *et al*, APL Photonics (2024)

[4] Lukusa Mudiayi *et al*, Phys Rev Lett **127**, 043201 (2021); Chomet *et al*, Appl Phys Lett **122**, 231102 (2023); Manceau *et al*, arXiv:2310.16460 (2023); Saemian *et al*, Nanophotonics (2024); Garcia Arellano *et al*, Nat Commun **15**, 1862 (2024)

[5] Darquié *et al*, PCCP **23**, 24140 (2021); Fiechter *et al*, J Phys Chem Lett **13**, 42, 10011 (2022)

Le spectre d’absorption infrarouge de H2 révèle des surprises

Hélène Fleurbaey[1], Samir Kassi[1], Aleksandra Koroleva[1], and Alain Campargue*†[2]

[1]Université de Grenoble Alpes – CNRS – France
[2]LIPhy – CNRS, Université Grenoble Alpes, CNRS : UMR5588, Université Grenoble Alpes – France

Résumé

La molécule de dihydrogène est la molécule la plus simple.
Molécule diatomique symétrique, elle ne donne pas lieu à des transitions dipolaires électriques (E1) et on dit parfois abusivement qu’elle n’a pas de spectre d’absorption rovibrationnel (de la même façon que O2 ou N2). Ceci n’est pas rigoureusement exact du fait de l’existence de transitions quadripolaires électriques (E2) qui sont très faibles mais dont la détection en laboratoire et dans les atmosphères planétaires est connue depuis plus de 80 ans (1). La caractérisation avec une exactitude ultime de ces transitions E2, notamment de leur fréquence est un sujet de recherche très actuel car il est lié à des problématiques de physique fondamentale (rayon du proton) et pourrait apporter des contraintes aux théories au-delà du modèle standard (2). Depuis quelques années, notre équipe participe à cet effort international de détermination des fréquences absolues des transitions E2 de la bande fondamentale (1-0) et de la première harmonique (2-0) avec une exactitude pouvant atteindre quelques dizaines de kHz (3). Un résumé des résultats obtenus par CRDS référencée à un peigne de fréquences sera présenté.

Outre les transitions E2, la molécule de H2 présente des bandes induites par collision (CIA) dues au dipôle électrique induit par interaction lors des collisions. Les bandes CIA très faibles et très larges ont un impact majeur dans le bilan radiatif des géantes gazeuses de notre système solaire. Alors que toutes les études antérieures ont dû utiliser des densités très élevées de plusieurs dizaines ou centaines d’amagat, nous avons pu déterminer la CIA dans la région (2-0) vers 1.2 μm par CRDS à une pression inférieure à 1 atm (4). Ces mesures obtenues avec une précision de 1.5 % ont mis en évidence une différence variant de 5 à 25 % par rapport aux valeurs calculées qui font référence en astronomie.
Très récemment, nous avons eu la surprise de détecter dans les spectres CRDS de H2 pur, des structures d’absorption très faibles, partiellement résolues, notamment au voisinage des raies quadripolaires. Ceci à température ambiante et à des pressions sub-atmosphériques. Ces structures ont été identifiées comme étant dues au dimère (H2)2 par comparaison à des spectres obtenus par McKellar dans H2 refroidi à... 20 K (5). Compte-tenu du fait que le dimère de H2 est un complexe de Van der Waals très peu lié (énergie de dissociation de l’ordre de 3 cm-1, seulement) la détection de (H2)2 à température ambiante était plus qu’improbable. Au-delà de la prouesse expérimentale, les spectres obtenus fournissent des données quantitatives dont l’interprétation théorique semble absente dans la littérature. Ceci alors que l’on aurait pu croire que (H2)2 constitue un cas d’école pour les calculs de chimie quantique....

---

[*] Intervenant

[†] Auteur correspondant: alain.campargue@univ-grenoble-alpes.fr

A VERNIER-FILTERED FREQUENCY COMB ABSORPTION EXPERIMENT: a new band of CrH?

Adrien Genoud[*][†][1], Jérôme Morville[‡][1], Patrick Crozet[§][1], and Amanda Ross[¶][1]

[1]Institut Lumière Matière [Villeurbanne] – Université Claude Bernard Lyon 1, Centre National de la Recherche Scientifique – France

Résumé

We present a cavity enhanced absorption experiment using a Vernier-filtered frequency comb to study the CrH spectrum in the region of the (1–0) P branches of the A $6\Sigma+$–X $6\Sigma+$ system. We use a mode-locked Ti:sapphire laser centered around 780 nm injecting a high finesse cavity (F=16 000) in a Vernier configuration where we deliberately introduce a controllable mismatch between the laser repetition rate and the cavity free spectral range. Therefore, the cavity output becomes a secondary frequency comb with an actively controlled comb spacing in the THz domain easily resolved by standard optical gratings. The grating separates the different Vernier orders into distinct beams. Vernier orders positions can be tuned in frequency through the use an Acousto Optic Modulator-Frequency Shifter in double pass configuration (Lu et al Photonics 9 222-2022) allowing for the measurement of an absorption spectrum typically covering 40 cm-1. We obtain Doppler-limited broadband spectra covering hundreds of cm-1 by incremental acquisition with an absorption baseline noise in the sub-1E-9 /cm level in tens of minutes. CrH was formed in a DC discharge sputter source, fitted with a pierced cathode made of iron/chromium alloy. A continuous flow of H2 in argon passed through the cathode into a vacuum chamber with high reflectance mirrors mounted on its side-arms. Some CrH lines were also recorded in cw laser excitation, offering a cleaner baseline and giving some reference calibration for the Vernier spectrum, as part of a search for weaker (satellite) transitions needed to confirm our assignments. Our preliminary result shows hitherto unassigned (and irregularly spaced) features around 775 nm, and are tentatively assigned as B $6\Pi 7/2$–X $6\Sigma+$ transitions.

---

[*] Intervenant

[†] Auteur correspondant: Adrien.genoud@univ-lyon1.fr

[‡] Auteur correspondant: jerome.morville@univ-lyon1.fr

[§] Auteur correspondant: patrick.crozet@univ-lyon1.fr

[¶] Auteur correspondant: amanda.ross@univ-lyon1.fr

Reactivity of small aggregates of protonated acetic acid with methylamine

émilie-Laure Zins*[1,2], Olivier Aroule[2], Nicolas Solem[3], Roland Thissen[3], Christian Alcaraz†[3], and Claire Romanzin[3]

[1]De la Molécule aux Nanos-objets : Réactivité, Interactions et Spectroscopies (MONARIS UMR 8233) – Sorbonne Universités, UPMC, CNRS – Sorbonne Université UPMC 4, place Jussieu CC49 - 75252 PARIS Cedex 05, France

[2]De la Molécule aux Nanos-objets : Réactivité, Interactions et Spectroscopies (MONARIS) – Institut de Chimie - CNRS Chimie, Sorbonne Universite, Centre National de la Recherche Scientifique – Sorbonne-Université Bâtiment F 4, place Jussieu - 75252 PARIS Cedex 05, France

[3]Institut de Chimie Physique (ICP) – Institut de Chimie - CNRS Chimie, Université Paris-Saclay, Centre National de la Recherche Scientifique – Bâtiments 349/350, Avenue Georges Clémenceau, 91405, Orsay, France

Résumé

Intermolecular interactions can strongly affect the local electron density, and therefore the reactivity of species. For example, the formation of a network of hydrogen bonds with water molecules leads to an electronic redistribution (and possibly proton transfers) and therefore to a modification of the electrophilicity and nucleophilicity of the reaction sites. Characterizing these changes in reactivity remains a major challenge for both theoretical chemistry tools and experiments. However, a better phenomenological description of these changes in reactivity seems essential for an accurate description of atmospheric, biochemical and astrochemical processes, among others. It is therefore essential to set a methodological approach based on both state of the art experiments and theoretical investigation in order to

- characterise simple and representative reactions between two partners A and B,

- determine the structures of the main microhydrated isomers of A (A(H2O)n

- study the reactivity and describe the reaction products of A(H2O)n complexes with the B partner

For this type of problem, mass spectrometry is a tool of choice for selecting the mass of the aggregates whose reactivity study, and therefore the number of hydration water molecules. It is also necessary to have a source suitable for generating aggregates, as well as a particularly sensitive detectors to identify and correlate reaction products that are present in very small quantities. From the point of view of computational chemistry tools, topological function approaches based on electron density (topological analyses of QTAIM electron density and ELF electron localisation function, catastrophe theory, BET bond evolution

---

[*] Intervenant

[†] Auteur correspondant:

theory) are particularly well suited to this type of study, since they enable to quantify the electronic redistribution along the reaction path. As a proof of concept, we demonstrated the relevance and feasibility of the coupled theoretical and experimental strategy during a study of the reactivity of micro-hydrated and non-hydrated aggregates of acetic acid and formic acid with methylamine, carried out with the CERISES set-up on the VUV delivering DESIRS beamline at the SOLEIL synchrotron. Quantum chemical calculations enabled us to propose a reaction mechanism for all the processes experimentally observed. Alongside this, we also demonstrated (in the case of neutral reagents) that the reaction leading to the formation of a peptide-like C-N bond was strongly favored from an energetic point of view in the presence of a few water molecules. We therefore carried out a second reactivity study using the CERISES set-up at SOLEIL. For this second study, the source was modified so as to ionize species produced in a supersonic expansion before the photoionisation.
Gaseous mixture of carboxylic acid and water was thus ionised. When Methylamine is added in the reaction cell, the formation of methylamine-containing products was systematically observed, with the concomitant loss of either a water or carboxylic acid molecule.

Mots-Clés: aggregates, reactivity, gas, phase, peptide, bond formation

Fundamental investigation of peptide fragmentation by collision mass spectrometry: structure/dissociation relationship

Lyna Bourehil[*1], Quentin Duez[2], Julien De Winter[2], Astrid Walrant[3], Denis Lesage[4],
Pascal Gerbaux[2], and Emmanuelle Sachon[3]

[1]Laboratoire des biomolécules – Sorbonne Universités, UPMC, CNRS – France
[2]Organic Synthesis and Mass Spectrometry laboratory - University of Mons – Belgique
[3]Laboratoire des biomolécules – Sorbonne Universités, UPMC, CNRS – France
[4]Institut Parisien de Chimie Moléculaire – Sorbonne Universités, UPMC, CNRS – France

Résumé

This work focuses on the fundamental study of peptide fragmentation in the gas phase, using collisional mass spectrometry to better understand the different pathways and improve the reliability of *de novo* peptide sequencing and protein identification. To achieve this goal, various peptide analogues of penetratin are analyzed to understand the effect of peptide sequence and gas-phase structure on the production of fragment ions.

Depending on the activation method used, peptide ions can produce different types of fragment ions. Collision-induced dissociation (CID) typically leads to the observation of b/y ions, while electron-based techniques (ExD) tend to produce c/z ions. (1) However, in the collisional fragmentation spectra of the peptides of interest, we observe an unusual c/z fragmentations type at specific locations in the sequence. This occurs mainly when the precursor ion is singly charged and cationized with lithium, sodium or potassium. Cationization with protons leads to lower intensity c/z fragments.

The aim is therefore to understand the fragmentation mechanisms leading to the production of c/z ions in CID from a given peptide sequence. We have recently developed the use of a new experimental gas-phase approach to measure these effects, based on mass spectrometry using activation by higher energy collision dissociation (HCD). (2) From these measurements, the thermodynamic parameters activation energy (Ea) and pre-exponential factor of Arrhenius (A) of the dissociation reaction can be obtained. These parameters will help determining the nature of the transition state (TS) (loose or tight) and the fragmentation mechanism involved in the production of fragment ions, in other words, a simple rupture mechanism or rearrangement. For example, values of A between 1014 and 1017 s-1 indicate a loose TS and therefore a simple bond rupture, whereas A values are lower for a rearrangement mechanism (between 106 and 1013 s-1). (3)

In the longer term, this project will enable us to decode, at the molecular, thermodynamic, and mechanistic levels, the production of c/z ions in fragmentation spectra, the most commonly used activation technique. It will certainly lead to improvements in *de novo* softwares

---

[*] Intervenant

needed to characterize new natural peptides.

References

- Y. Jami-Alahmadi, et T.D. Fridgen; J. Mass Spectrom., **429**, 136-141 (2018)
- L. Bourehil, C. Soep, S. Seng, S. Dutrannoy, S. Igoudjil, J. Forté, G. Gontard, D. Lesage, B. Bertrand, H. Dossmann; Inorg. Chem., **62**, 13304–13314 (2023)
- P. D. Schnier, W. D. Price, R. A. Jockusch, E. R. Williams; J. Am. Chem. Soc., **118**, 7178–7189 (1996)

Observing collisions using laser-aligned molecules

Jean-Michel Hartmann*[1]

[1]Laboratoire de Météorologie Dynamique (UMR 8539) – Institut National des Sciences de l'Univers, Ecole Polytechnique, Ecole des Ponts ParisTech, Sorbonne Universite, Centre National de la Recherche Scientifique, Département des Géosciences - ENS Paris, Centre National de la Recherche Scientifique : UMR8539 – France

Résumé

When a linearly-polarized non-resonant, intense and short laser pulse is sent into a gas of (linear) molecules, it tends to align le molecular axis **u** along the field polarization direction **p**. Then, due to the commensurability of the quantified rotational speeds, the molecules realign periodically, leading to alignment revivals, sharp features in the measurable quantity (t), where theta is the angle between **u** and **p**. At finite pressure, the amplitude of these revivals decay with time due to inter-molecular collisions and thus bring information on the associated decoherence process. Furthermore, additive information is brought by the permanent component of the alignment as well as by the alignment echo generated, at t=2tau, when the system is excited by two consecutive pulse at t=0 and t=tau. I will show that measurements of the pressure-induced decays of all these features bring detailed information for the development and test of collisional models. In particular, they enable to investigate the limits of validity of the widely used secular and Markovian approximations which are the counterparts, in the time domain, of the neglect of line-mixing and finite collision duration effects in frequency domain spectroscopy.

Mots-Clés: molecular alignment, collisions

---

*Intervenant

An innovative method to identify structural change through ion-molecule collision, making use of Time-Of-Flight measurements and SIMION simulations

Nicolas Solem*[1], Claire Romanzin[2], Christian Alcaraz[1], and Roland Thissen†[3]

[1]Institut de Chimie Physique – Institut de Chimie - CNRS Chimie, Université Paris-Saclay, Centre National de la Recherche Scientifique – France

[2]Institut de Chimie Physique (ICP) – Institut de Chimie - CNRS Chimie, Université Paris-Saclay, Centre National de la Recherche Scientifique – Bâtiments 349/350, Avenue Georges Clémenceau, 91405, Orsay, France

[3]Institut de Chimie Physique – Institut de Chimie du CNRS, Université Paris-Saclay, Centre National de la Recherche Scientifique – France

Résumé

HCO+ and HOC+ are two isomeric cations detected in Photon Dominated Regions(1), diffuse clouds(2), and Mars atmosphere(3,4). They correspond to the protonation of carbon monoxide on either the carbon or oxygen atom and are important intermediates in the formation of complex molecules, as HCO+ is the most abundant molecular ion in molecular clouds. The isomers have a difference of energy of 1.7 eV (HCO+ being more stable) and are separated by an isomerization barrier of 1.5 eV(5) (from HOC+).
We studied structural change of ions induced by collision with a neutral in a guided ion beam tandem mass spectrometer, combining Time-Of-Flight (TOF) measurements and SIMION simulation. The exothermic isomerization of HOC+ to HCO+ is used to explore the new methodology. Structural change occurs via a proton transport mechanism(6–9) through the interplay of a neutral molecule, acting as a catalyst. Four different potential catalysts, Ne, D2, CH4, and C18O, were studied at various collision energies. SIMION simulation of the ion path and collision in the instrument highlights a specific signature related to the catalytic isomerization in the TOF spectra. This signature is used to track conditions (nature of target, collision energy) where collision-induced isomerization takes place. If a clear trend in terms of occurrence of the process related to the neutral target proton affinity is observed, C18O, at low collision energy, exhibits the strongest signature of catalytic isomerization, and a quantitative estimate of the catalyzed isomerization cross-section and rate constant is derived(10).

This new methodology is sensitive to clear presence of catalyzed isomerization and can be used in instruments designed for quantitative Collision Induced Dissociation (CID) measurements (Triple Quadrupole), provided low collision energy is used and ion bunching is available.

---

*Intervenant

†Auteur correspondant: roland.thissen@universite-paris-saclay.fr

(1) Fuente, A. et al. (2003). *A&A*. DOI: 10.1051/0004-6361:20030712.

(2) Liszt, H. et al. (2004). *A&A*. DOI: 10.1051/0004-6361:20041649.

(3) Fox, J.L. (2015). *Icarus.* DOI: 10.1016/j.icarus.2015.01.010.

(4) Matta, M. et al. (2013). *J. Geophys. Res. Space Phys.* DOI: 10.1002/jgra.50104.

(5) Chalk, A.J. and Radom, L. (1997). *J. Am. Chem. Soc.* DOI: 10.1021/ja971055c.

(6) Wagner-Redeker, W. et al. (1985). *J. Chem. Phys.* DOI: 10.1063/1.449474.

(7) Freeman, C.G. et al. (1987). *Int. J. Mass Spectrom.* DOI: 10.1016/0168-1176(87)87034-9.

(8) Ferguson, E.E. (1989). *Chem. Phys. Lett.* DOI: 10.1016/0009-2614(89)87100-3.

(9) Bohme, D.K. (1992). *Int. J. Mass Spectrom.* DOI: 10.1016/0168-1176(92)85035-X.
(10) Solem, N. et al. (2024). *J. Mass Spectrom.* under review

Unexpected and delayed fragmentation dynamics of the organometallic ferrocene induced by ion-collision

Fernando Aguilar-Galindo[1], V. T. T. Nguyen[2], Raj Singh[2], Alicja Domaracka[2], Bernd Huber[2], Sergio Díaz-Tendero Victoria[1], Patrick Rousseau[2], and Sylvain Maclot*†[2]

[1]Universidad Autonoma de Madrid – Espagne

[2]Centre de recherche sur les Ions, les MAtériaux et la Photonique – Université de Caen Normandie, Institut Rayonnement Matière de Saclay (DRF), Ecole Nationale Supérieure d'Ingénieurs de Caen, Centre National de la Recherche Scientifique, Institut de Recherche sur les Matériaux Avancés – France

Résumé

Metal-ligand bonds are central in coordination chemistry involving a metallic cation bound to several molecular anions. Ferrocene Fe(C5H5)2 is the prototype of organometallic complexes, and more specifically of metallocene compounds. Thus, it exhibits the typical stable sandwich structure with the Fe atom between the two C5H5 rings. In the ferrocene molecule, the iron atom which has an 18-electron configuration, exists in the +2 oxidation state. Both cyclopentadienyl rings satisfy Huckel's rule for aromatic compounds. Bonds are formed between a Fe2+ ion and two C5H5 rings. These bonds are remarkably stable, so they rarely break under normal reaction conditions. Serving as a model system for iron containing organic molecules of biological relevance, ferrocene is also an important molecule for studying fundamental multi-electron processes in complex quantum systems. For instance, organometallic compounds containing ferrocene can enhance conversion efficiency in organic photovoltaic cells. In general, metallocene in general and ferrocene derivatives in particular play a prominent role in synthetic chemistry, nano-medicine and material science thanks to their ubiquitous applications.

Regarding astrochemistry, no ferrocene molecules or ions have been detected in space yet even though several organometallics are observed in the ISM, cosmic clouds and meteorites. Whereas the iron cation Fe+ (most abundant metal in space) and cyclopentadienyl rings C5H5 were detected and iron-aromatics compounds are suspected. Thus, one could easily imagine that signatures of the presence of ferrocene or larger related species will be evidenced in the future.

In the present study (1), we propose to investigate the dissociation dynamics of ferrocene cations induced by ion collisions, which relies on the transfer of charge and energy in the interaction. For this, we chose the combined experiment/theory approach using multicoincidence mass spectrometry and quantum chemistry calculations. We mainly focus on the fragmentation dynamics of doubly charged ferrocene and show that some fragmentation pathways involve a long-lived excited state leading to metastability of the dication and specific fragmentation dynamics.

---

*Intervenant

†Auteur correspondant: smaclot@gmail.com

Reference:
(1) F. Aguilar-Galindo, V.T.T. Nguyen, R. Singh, A. Domaracka, B.A. Huber, S. Díaz-Tendero, P. Rousseau and S. Maclot, Phys. Chem. Chem. Phys., 26, 7638, 2024

Acid-base chemistry when a solid surface meets liquid water

Simone Pezzotti*[1]

[1]PASTEUR, ENS, CNRS – CNRS : UMR8640 – France

Résumé

Chemistry at interfaces often exhibits mixed characteristics between solution chemistry and (surface) chemistry in gas phase but remains remarkably different from both of them. The reason is the unique way a surface and liquid water rearrange once in contact with each other. Understanding the connection between the molecular complexities of an interface and its chemistry could open interesting perspectives for reaction steering by playing with the composition of both surface and liquid. To this end, combining surface-specific vibrational spectroscopies with theoretical modelling is a promising approach.

In this talk, I will present two examples of acid base chemistry, one of the most ubiquitous reactions, and how it is tuned at aqueous interfaces by the molecular properties of the surface and liquid water in contact with it. In the first example, I will discuss the protonation state and reconstruction of a silica surface in contact with liquid water as a function of pH, combining molecular dynamics simulations and sum frequency generation spectroscopy1. In the second, I will show how the (de)protonation reaction of an amino acid is regulated by local hydrophobicity and strong electric fields at play at electrified metal/water interfaces2.

- Wei-Tao Liu, Xiaoqun Li, Flavio S. Brigiano et al. Unveiling the structural evolution of oxide surface in liquid water, 13 September 2023, PREPRINT (Version 1) available at Research Square (https://doi.org/10.21203/rs.3.rs-1948606/v1).
- S. Murke, W. Chen, S. Pezzotti, M. Havenith. Tuning acid-base chemistry at an electrified gold-water interface. JACS just accepted 2024.

---

*Intervenant

Pump-probe spectroscopy of a microhydrated sugar-peptide complex

Arsène Kossov*[1], Ander Camiruaga†[1], and Pierre Carcabal‡[1]

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

Résumé

Sugars are a family of biomolecules that plays numerous roles in biological processes of living organisms such as energy transfer, or structural roles. Among those roles stands molecular recognition, allowed by the flexible structures adopted by sugars that can reorient themselves and non-covalently bond to other molecules thanks to an extended hydrogen bonding network. Some sugars can then be selectively recognized by some proteins which plays a key role in the immune system and some diseases. It is then interesting and important to understand the structural properties of this key-lock association and the role of water that can strongly influence those structures. We studied in environment-free conditions the association of a functionalized mannose molecule with a functionalized glutamic acid that reproduces a peptide bond. With double resonance laser spectroscopy in the far-IR and mid-IR range, we compared the structure of this dimer with a micro-hydrated one to which one water molecule was added. The resulting spectra are selective in mass and conformer specific. By comparing those spectra to a theoretical study conducted at the B3LYP-D3/def2-TZVPP level of theory of the density functional theory, we obtained a correct match for the two most stable structures observed for the dimer and for the mono-hydrated dimer. The water molecule appears to be inserted between the mannose and the glutamic acid in two different ways leading to a complete reorganization of the hydrogen bonding network, with some very explicit differences in vibration signatures.

---

*Intervenant

†Auteur correspondant: ander.camiruaga@gmail.com

‡Auteur correspondant: pierre.carcabal@universite-paris-saclay.fr

Comprendre les effets de site en matrice : une nouvelle approche par spectroscopie multidimensionnelle infrarouge (2D-IR)

Armel Jouan*[1], Wutharath Chin[1], Jan Helbing[2], and Claudine Crépin-Gilbert†[1]

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

Résumé

La spectroscopie bi-dimensionnelle infrarouge (2D-IR) est un outil puissant pour étudier les propriétés structurales et dynamiques de systèmes moléculaires dans divers environnements. Cette technique de spectroscopie non linéaire nous permet d'aller au-delà de la spectroscopie d'absorption linéaire, et ainsi d'obtenir simultanément des informations sur la structure et la dynamique : modes vibrationnels, anharmonicité, couplage entre modes, transferts d'énergie, contributions homogènes et inhomogènes, et ce avec une résolution temporelle de l'ordre de la centaine de femtosecondes (1).

Nous avons obtenu, pour la première fois, des spectres 2D-IR en matrice cryogénique, avec l'étude du complexe métal-carbonyle W(CO)6 piégé dans l'azote solide. Le spectre linéaire (par FTIR) se présente sous la forme de quatre bandes fines (largeur spectrale < 1 cm-1) dans la région des vibrations d'élongation CO, contre une seule bande en solution (voir Fig. a). Ceci est dû à l'existence de plusieurs familles de site de piégeage. Pour démêler les différents mécanismes contribuant à la dynamique vibrationnelle en matrice, nous avons développé un dispositif 2D-IR capable d'atteindre la résolution spectrale nécessaire (< 0.5 cm-1) grâce en particulier à une caméra infrarouge multi-pixels (320x50) en détection du signal (2).

Les spectres 2D-IR obtenus (voir Fig. b) permettent directement de comprendre la structure du spectre FTIR. Cette structure (bandes 1, 2, 3, et 4) se retrouve sur la diagonale de la carte 2D-IR (Fig. b). On observe de plus des pics hors-diagonaux (*cross-peaks*) uniquement à l'intersection des bandes 1,3 et 4 : cela montre immédiatement que W(CO)6 occupe deux familles de sites dans le solide. Dans l'une (bandes 1, 3, et 4) la symétrie Oh est brisée, et le niveau T1u est alors éclaté en trois niveaux distincts par levée de dégénérescence (voir Fig. c). Dans la seconde (bande 2), la symétrie est conservée et le niveau T1u reste dégénéré. Ceci est une confirmation nette des conclusions de nos précédents travaux (3). De plus, nous avons observé de nouvelles caractéristiques intéressantes, comme un couplage anharmonique positif inattendu (pics rouges) et un transfert d'excitation cohérent entre les modes non dégénérés (1, 3, et 4).

---

*Intervenant

†Auteur correspondant: claudine.crepin-gilbert@universite-paris-saclay.fr

sciencesconf.org:emie2024:552929

Increasing specificity of Mass Spectrometry by Laser Induced Dissociation: Application to plasma protein oxidation

Marion Girod[1], Jean-Valery Guillaubez[1], Romain Ladouce[2], Mladen Mercep[2], Luke MacAleese[3], Jérôme Lemoine[1]

1. Institut des Sciences Analytiques, UMR 5280, Université Lyon 1 et CNRS, Villeurbanne.
2. Mediterranean Institute for Life Sciences (MedILS), Split, Croatia
3. Univ Lyon, CNRS, Université Claude Bernard Lyon 1 – Institut Lumière Matière, Lyon.

In a context of population aging, discovery and validation of novel oxidative stress biomarkers for neurodegenerative diseases is a key issue [1]. However, this quest remains a challenge for low concentrated biomarkers, mainly due to the complexity and concentration dynamic range of the biological fluids.

Photo-dissociation methods, also known as action spectroscopy in the field of physical-chemistry, may be used to enhance the sensitivity of mass spectrometry (MS)-based analytical approaches and here to improve the detection specificity towards the oxidized protein subpopulation. We use an experimental setup coupling MS and laser induced dissociation (LID) in the visible range (473 nm) to add a stringent optical specificity to the mass selectivity [2]. Since peptides do not naturally absorb in the visible range, this new methodological approach relies on the specific chemical derivatization of oxidized proteins with a chromophore. As a result, only the subset of derivatized peptides are specifically fragmented in LID after enzymatic digestion. Our method allows to localize individual oxidized sites by observing fragments of derivatized peptides, and therefore their quantification.

In this presentation, the characterization of two types of oxidation by visible LID in complex samples will be presented. First, in the presence of reactive oxygen species, cysteine residues (Cys) are oxidized in sulfenic acid (SOH). These SOH groups are specifically grafted to a chromophore, absorbing at 473 nm, functionalized with a cyclohexanedione. To compensate for the significant variability in total protein expression within samples and any experimental bias, a normalizing strategy using free thiol Cys peptides derivatized with a maleimide chromophore as internal references was used. Thanks to the differential tagging, oxidative ratios were then obtained for 69 Cys-containing peptides from 19 proteins, in a cohort of 49 human plasma samples from Alzheimer disease patients [3].

Protein carbonylation is also an important modification due to oxidative stress. In this case, the optical specificity is obtained after grafting the chromophore by the reaction of the protein carbonyl group with the reactive aminooxy group. Two model proteins, α-synuclein and β-lactoglobulin, were oxidized and carbonylation sites were detected, resulting in the identification of respectively 34 and 77 different carbonylated amino acids [4].

Laser induced dissociation mass spectrometry is a direct and sensitive method for studying low concentrated protein oxidation in complex biological extracts.

[1] I. Dalle-Donne, et al., *Mass Spectrometry Reviews*, **2005**, 24, 55-99.

[2] M. Girod, J. Biarc, Q. Enjalbert, A. Salvador, R. Antoine, Ph. Dugourd, J. Lemoine, *Analyst,* **2014**, 139, 5523-5530

[3] J.-V. Guillaubez*,* D. Pitrat, Y. Bretonnière, J. Lemoine and M. Girod*, Talanta,* **2022**, 250, 123745

[4] R. Ladouce, L. MacAleese, K. Wittine, M. Mercep, M. Girod*, Analytical and Bioanalytical Chemistry,* **2023**, 415, 6619–6632

Cinétique chimique en phase gazeuse : défis présents et futurs

Olivier Durif*[1]

[1]KTH Royal Institute of Technology [Stockholm] – SE-100 44, Stockholm, Sweden, Suède

Résumé

Cette présentation portera sur la caractérisation de coefficients cinétiques de radicaux peroxy (ROO•) d'intérêt en chimie atmosphérique, par spectrométrie de masse à transfert de proton(1).
Je discuterai également de certaines particularités observées dans ce domaine de recherche, telles que le ralentissement de la cinétique chimique de certains systèmes avec l'augmentation de la température. Ces résultats sont couramment rapportés dans la littérature scientifique et souvent rappelés par le terme *negative temperature dependence.* En outre, ils se disent compatibles avec la loi d'Arrhenius à condition de considérer un facteur d'activation négatif. Ces résultats seront mis en perspective avec ceux observés dans le domaine analogue de la cinétique chimique à très basse température, qui révèle aussi cette dépendance en température négative, traduisant une augmentation critique de la réactivité chimique à des températures extrêmement basses(2). Je proposerai une lecture critique de ces observations et suggérerai de nouvelles interprétations et des effets expérimentaux à prendre en compte pour ces cas aux très basses températures(3).

Enfin, j'aborderai dans une démarche prospectiviste les défis actuels et futurs dans ce domaine de recherche, tels que la question de la fiabilité des mesures, ainsi que du défi que représente l'analyse de systèmes de plus en plus complexes, nécessitant la prise en compte d'une multitude d'effets.

(1) O. Durif, F. Piel, A. Wisthaler, B. Nozière, *Strong uptake of gas-phase organic peroxy radical (ROO•) by solid surfaces driven by redox reactions,* JACS AU (under review).

(2) Balucani, C. Ceccarelli, F. Vazart, F. Dulieu, D. Skouteris, M. Rosi, F. Pirani, E. Bianchi, P. Caselli, C. Codella, *Can astronomical observations be used to constrain crucial chemical reactions? The methoxy case.* SOLIS XVIII. Monthly Notices of the Royal Astronomical Society 528, 6706–6719 (2024).
(3) O. Durif, *Commentary Regarding the CRESU-SIS Experiment: Concerns About the Uniform Supersonic Flow Reactor.* arXiv:2306.12349. (2023)

---

[*] Intervenant

Photophysical properties of the charged GFP chromophore and its derivated

Jordan Dezalay*[1], Jennifer Noble[1], Mark Stockett[2], James Bull[3], and Eleanor Ashworth[3]

[1]CNRS, Aix-Marseille University, PIIM laboratory, Saint Jérôme, Av. Escadrille Normandie Niemen, 13013 Marseille, France. – PIIM, Aix-Marseille Université – France
[2]Department of Physics [Stockholm] – Suède
[3]University of East Anglia [Norwich] – Royaume-Uni

Résumé

Green fluorescent protein (GFP) has revolutionised fluorescence imaging due to the ease with which it can be incorporated into biological systems and its interesting characteristics for health (1). The photo-physics of GFP is governed by a deprotonated p-hydroxybenzylidene ((a) **HBDI**) chromophore, 2,3-dimethylimidene. In order to modulate the fluorescence properties to meet specific imaging requirements, a number of derivatives have been synthesised. In particular, by substituting a tryptophan group for a tyrosine residue of HBDI, the emission properties can be modified to produce a (b) **Cyan** Fluorescent Protein (CFP). In aqueous solution, these fluorescent molecules can evolve in different charge states and in the form of numerous conformers. Fluorescent properties within proteins are strongly linked to the molecular environment that surrounds them (hydration, intermolecular bonds). It is therefore important to study the photo-physical properties of the excited states of such molecules in different charge states and different conformations. Cryogenic ion trap action spectroscopy experiments have been used to probe the properties of the electronic states of isolated charged molecules (2). In the study of HBDI and Cyan molecules we revealed the presence of several protomers in the protonated forms, confirmed by ion mobility experiments (3). The action spectroscopy of deprotonate ions was used as a prelude to studying the processes of thermal electron emission following photo-excitation in the DESIREE cryogenic storage ring at Stockholm University.

(1) N. C. Shaner, P. A. Steinbach and R. Y. Tsien, Nat. Methods, 2005, 2, 905–909.

(2) Boyarkin, O. V., Mercier, S. R., Kamariotis, A., & Rizzo, T. R. (2006). Electronic spectroscopy of cold, protonated tryptophan and tyrosine. Journal of the American Chemical Society, 128(9), 2816-2817.
(3) E.K.Ashworth, J.Dezalay, Christopher.R.M.Ryan, C.Leritano, W.S.Hopkins, I.Chambrier, A.N.Cammidge, M.H.Stockett, J.A.Noble, J.N.Bull, Protomers of the green and cyan fluorescent protein chromophores investigated using action spectroscopy *Phys. Chem. Phys. Chem. (2023)*

---

*Intervenant

Molecular-scale view of the interaction of water and ice with organic species of atmospheric interest

Sophie Sobanska*†[1], Stéphane Coussan*‡[2], Michelle T Custodio Castro[3], Rosana M. Romano[4], Joëlle Mascetti[1], and Eric Villenave[5]

[1]Institut des Sciences Moléculaires – CNRS : UMR5255, Université de Bordeaux (Bordeaux, France) – France
[2]Physique des interactions ioniques et moléculaires – CNRS, Aix-Marseille Université - AMU – France
[3]CEQUINOR (UNLP – CONICET, CCT La Plata, associated with CIC PBA) – Argentine
[4]CEQUINOR (UNLP – CONICET, CCT La Plata, associated with CIC PBA) – Argentine
[5]Environnements et Paléoenvironnements OCéaniques – Univ. Bordeaux, CNRS, EPOC, EPHE, UMR 5805 – France

Résumé

The cryogenic techniques coupled to spectroscopies (FTIR, UV-visible, ...) are powerful tools to study room temperature unstable species (reaction intermediates, unstable isomers, ...). Molecules are trapped either in rare-gas matrix or on ice surface in controlled conditions. The low temperature and trapping conditions allow to explore molecular structures and interactions i.e. hydration process from complexes to aggregates and then to ice. Moreover, samples may be kept for long time period (over days) allowing multiple irradiation (selective or broad band) and heating cycles.

In this presentation, we will propose two examples of studies related to aerosol of atmospheric interest: the first on the hydration process of 3 methyl-1,2,3-butanetricarboxylic acid (MBTCA), a relevant tracer compound for monoterpene SOA formation and aging processes. The second will focus on the investigation of interactions between gaseous methyl iodine (from marine, vegetation or terrestrial sources) and various water ice surfaces, emphasizing the influence of trapping sites on the bonding and photofragmentation of CH3I.

Acknowledgments
The authors wish to thank the ANR for financial support of the SOAPHY project (ANR-21-CE29-0031), the Région Nouvelle Aquitaine for it support of the LEVIAERO project (convention n◦AAPR2022-2021-17126210) and the GDR EMIE for supporting this collaborative project.

---

*Intervenant
†Auteur correspondant: sophie.sobanska@u-bordeaux.fr
‡Auteur correspondant: stephane.coussan@univ-amu.fr

Posters

Molecular level characterization of multiphase processes relevant to the atmosphere

Céline Toubin*†[1], Rawan Abouhaidar , and Denis Duflot

[1]PhLAM (PhLAM UMR CNRS 8523) – University of Lille – France

Résumé

The ozonolysis of unsaturated hydrocarbons holds significant importance for the atmosphere because it results in the generation of diverse oxygen-containing compounds like aldehydes, ketones, and carboxylic acids. The resulting Criegee intermediates (CIs) contribute to the creation of secondary organic aerosols (SOAs) through subsequent reactions with trace chemicals. Herein, we have investigated the multiphase ozonolysis reaction in a water droplet containing maleic acid (MA) using classical and quantum theoretical methods (QM/QM'). The relative occurrence of interfacial and bulk reactions is dependent on the bulk affinity of O3and the interfacial affinity of reacting MA, which is predominantly found in the bulk phase. Then, the kinetics of the initial step in different environments leading to the formation of the primary ozonide compound (POZ) have been evaluated. The results (1) reveal that the presence of water molecules enhances the initial reaction step compared to the gas phase, with a significantly larger rate coefficient in the bulk phase than at the interface. Furthermore, Ab Initio Molecular Dynamics simulations were employed to delve into the formation of the POZ and its subsequent breaking into CIs within a water cluster. The current approach provides insights into how the environment influences the complex kinetics and dynamics of these reactions.
Ref: (1) R. AbouHaidar, D. Duflot & C. Toubin (2023) Aerosol Science and Technology, 2023.DOI: 10.1080/02786826.2023.2286341

-

Acknowledgment:
The presented work benefits from the support the CaPPA project (Chemical and Physical Properties of the Atmosphere) funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under Contract No. ANR-10-LABX-005; the Région Hauts de France and the Ministère de l'Enseignement Supérieur et de la Recherche (CPER Climibio) and the European Fund for Regional Economic Development for their financial support. This work was performed using HPC resources from GENCI-TGCC (Grant No. 2022–A0110801859) and the Centre de Ressources Informatiques (CRI) of the Université de Lille.

---

*Intervenant

†Auteur correspondant: celine.toubin@univ-lille.fr

High resolution infrared spectroscopy of furfural conformers and dioxane isomers from Fourier transform and quantum cascade laser jet-cooled and long path cell measurements

Pierre Asselin*†[1], Arnaud Cuisset*[2], Sathapana Chawananon[3], Goubet Manuel[4], Robert Georges[5], and Olivier Pirali[3]

[1]Laboratoire MONARIS UMR 8233 CNRS – Sorbonne Université – France
[2]Laboratoire de Physico-Chimie de lÁtmosphère – Université du Littoral Côte d'Opale – France
[3]Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[4]Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique, Université de Lille : UMR8523, Centre National de la Recherche Scientifique : UMR8523 – France
[5]Institut de Physique de Rennes – Université de Rennes, Centre National de la Recherche Scientifique – France

Résumé

Furanes and dioxines are volatile organic compounds (VOC) considered as atmospheric pollutants. Among them, furfural (C5H4O2) produced by biomass combustion oxidizes easily in the atmosphere to form secondary organic aerosols (SOA), while 1,4-dioxane (C4H8O2) used as fuel additive and stabilizer for chlorinated solvents is extensively released in the environment (atmosphere, groundwater). There is a fundamental interest in monitoring these molecules: firstly in the CHARME simulation chamber as the LPCA group has studied the reactivity of furans with day time and night time major oxidants (OH, NO3), and in a next step *in situ* monitoring during the oxidation processes, but it requires knowledge of their rovibrational signatures through high-resolution experiments over a broad spectral range.
The energetic of both molecules gives some details about their conformation and structure in the perspective of spectroscopic measurements. *Trans* and *cis* conformations in the furfural coexist in gas phase and depend on the orientation of oxygen atoms. Their energy difference, estimated to 3.4 kJ/mol between the two conformations as well as a very high conformational barrier height, suggest that neither observable splitting due to quantum tunneling nor relaxation at low temperature is expected. The centrosymmetric 1,4-dioxane and its rare isomer 1,3 are both cyclic ethers existing only as the *chair* configuration.

We report here a high resolution study of furfural and dioxane isomers on a wide infrared (IR) range combining the Jet-AILES set-up, a continuous supersonic jet implemented on the IR AILES beamline at SOLEIL, and a long path cell, both coupled to a Fourier Transform

---

*Intervenant
†Auteur correspondant: pierre.asselin@sorbonne-universite.fr

Spectrometer (FTS), and the SPIRALES set-up available at MONARIS laboratory, a pulsed supersonic jet coupled to external cavity mid-IR quantum cascade lasers (QCL).

In the fingerprint region, several bands of of *trans*- and *cis*-furfural were recorded in both continuous and pulsed supersonic jet expansions and then analyzed to derive reliable excited-state (ES) molecular parameters from global rovibrational fits involving up to 20000 lines distributed over 8 and 3 vibrational states, including the ground state. In the far-IR range, measurements of fundamental and related hot bands of low frequency vibrations in a room temperature long path cell enabled to determine vibrational energy levels, anharmonic coefficients and excited-state molecular parameters up to 700 cm-1.
Last, preliminary rovibrational analyses of mid-IR jet-cooled and long path cell spectra of dioxane isomers will be presented, which highlight the respective advantages and the complementarity between supersonic jet set-ups coupled to broadband FT and narrow band QCL infrared spectroscopies to characterize large molecules relevant for atmosphere science.

Absorption in Al13 cluster using Real-Time TDDFT: transitions involving the continuum

Rajarshi Sinha-Roy*† , Mohit Chaudhary[1,2], Franck Rabilloud[3], Jean Lermé[3], and Hans-Christian Weissker[4,5]

[1]Aix Marseille Univ, CNRS, CINAM, Marseille, France – Aix Marseille Univ, CNRS, CINAM, Marseille, France – France

[2]European Theoretical Spectroscopy Facility, etsf.eu – European Theoretical Spectroscopy Facility, etsf.eu – France

[3]Universite Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, UMR5306, F-69100, Villeurbanne, France – Universite Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, UMR5306, F-69100, Villeurbanne, France – France

[4]Aix Marseille Univ, CNRS, CINAM, Marseille, France – Aix Marseille Univ, CNRS, CINAM, Marseille, France – France

[5]European Theoretical Spectroscopy Facility, etsf.eu – European Theoretical Spectroscopy Facility, etsf.eu – France

Résumé

Unlike noble-metal nanoparticles (NPs) the localized surface plasmon resonance (LSPR) in Aluminum NPs occurs in the ultra-violet (UV) making them suitable for plasmonic application in the UV. This has stemmed research interest (1) in Al NPs and clusters despite their high sensitivity to oxidation and the difficulties in optical measurements in the UV. From theoretical aspect optical properties of Al clusters is difficult to obtain as the LSPR is above the ionization energy implying transitions that involve contribution from states which are largely part of the continuum, in particular for the anion. To this end, quantum mechanical calculations of Al clusters from different groups differ radically as evidenced by optical absorption in and neutral (2, 3) charged (4, 5) Al13$.

In this work we present a systematic way to obtain absorption spectra for Al clusters within the framework of real-time time-dependent density-functional theory using the real-space code octopus (6). This is done by systematic incorporation of contributions from "discretized" continuum states (which are not required to be explicitly calculated within RT-TDDFT,) to the propagation of occupied Kohn-Sham orbitals. The results are compared with linear-response TDDFT calculations where excited states are explicitly calculated. This comparison showed the advantages of grid based RT-TDDFT calculations which give correct spectra for all charge states, +1, neutral, and -1, of the Al13 cluster.

References:
(1) M. W. Knight, et al., ACS Nano 8, 834 (2014).
(2) M. D. Deshpande et al., Phys. Rev. B 68, 035428 (2003).
(3) S. Debnath et al., RSC Adv., 5, 58128 (2015).
(4) D. Casanova, et al., J. Phys. Chem. C, 120, 12742 (2016).

---

*Intervenant

†Auteur correspondant: rajarshi.sinha-roy@univ.lyon1.fr

(5) P. Pandeya, et al., J. Phys. Chem. A, 125, 4847 (2021).
(6) N. Tancogne-Dejean et al., J. Chem. Phys. 152, 124119 (2020).

Spectroscopie rotationnelle des traceurs d'explosifs : étude du 2,3 dimethyl 2,3 dinitrobutane.

Manuel Goubet*†1, Alexandre Deguine1,2, Pascal Drean1, Elias Neeman1, Colwyn Bracquart1,2, Fabien Simon2, Mhamad Chrayteh2, Francis Hindle2, Gaël Mouret2, Julien Mory3, and Arnaud Cuisset*2

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

[2]Laboratoire de Physico-Chimie de lÁtmosphère – Université du Littoral Côte d'Opale (ULCO) – France

[3]Institut franco-allemand de recherches de Saint-Louis – ISL – France

Résumé

La détection et la caractérisation des explosifs, de leurs marqueurs ou de leurs produits de dégradation est un sujet d'importance cruciale pour la sécurité publique. Elles jouent sans aucun doute un rôle clé dans le contrôle des bagages et les enquêtes sur les lieux d'attentats à la bombe. Au moins deux défis doivent êt re relevés par la spectroscopie haute résolution : la limite de détection doit être inférieure à 1 ppb et le pouvoir discriminant doit permettre d'identifier sans ambiguïté les différentes espèces chimiques malgré des propriétés similaires (1). En effet, l a détection directe des explosifs est hors de portée de la plupart des techniques spectroscopiques en raison de leur pression de vapeur à température ambiante extrêmement faible (voir Figure 1). Alternativement, il est possible de détecter des marqueurs explosifs plus volatils, intentionnellement ajoutés aux explosifs (2) ou présents comme impuretés en raison du processus de fabrication. Nous présentons ici l'étude du 2,3 dimethyl 2,3 ditrobutane (DMDNB), un marqueur très largement utilisé dans les explosif s plastiques. Le spectre microondes (2 20 GHz), enregistré à l'aide de spectromètres à impulsions microondes couplés à un jet supersonique (FP FTMW), a été analysé avec le soutien de calculs de chimie quantique. La conformation la plus stable en phase gazeuse a été identifiée et son spectre a été simulé en prenant en compte les constantes de couplage quadripolaires décrivant la structure hyperfine due à la présence des deux atomes 14 N, permettant ainsi de créer une base de données (position intensité des signaux) pour sa détection. L'état d'avancement du développement d'un spectromètre millimétrique basé sur cavité résonante (150 215 GHz), dont l'objectif est de détecter les marqueurs d'explosifs à l'état de traces, est également présenté (3). (1) Zhang,Wei et al ., Recent Developments in Spectroscopic Techniques for the Detection of Explosives, Materials 11, 1364 (2018).
(2) convention Montreal, International controls to regulate plastic explosives adopted in Montreal, UN Chronicle n2, 32 (1991
(3) Ce travail est soutenu par l'ANR sous le projet "Millimeter wave Ex plosive Taggant vapors Investigations using Spectral taxonomy" (METIS) ANR 20 ASTR 0016 03. Le LPCA et le PhLAM sont membres du LabEx CaPPA (ANR 11 LABX 005 01) et du CPER ECRIN.

---

*Intervenant

†Auteur correspondant: manuel.goubet@univ-lille.fr

Study of the interaction between Fenhexamid and Ca2+: Influence of water molecule number on the energetics

Quentin Desdion*[1], Fabienne Bessac[2], and Sophie Hoyau[2]

[1]Modélisation, Agrégats, Dynamique (LCPQ) – Laboratoire de Chimie et Physique Quantiques – France
[2]Modélisation, Agrégats, Dynamique (LCPQ) – Laboratoire de Chimie et Physique Quantiques (LCPQ), IRSAMC, UMR 5626 CNRS – France

Résumé

A large number of pesticides are authorised in the European Union and are used in agriculture. A better understanding of pesticides requires the study of their behaviour and fate in the environment (soil, water and air). This is a major challenge in order to limit their harmful impact on the environment. The global project in which my thesis subject is included follows a step-by-step approach to explore the interactions between a pesticide and the various components of a soil that can be modelled at the atomic scale. Thus, I am studying the micro-hydration (1). of two pesticides, fenhexamid (N-(2,3-dichloro-4-hydroxyphenyl)-1-methylcyclohexanecarboxamid) and metamitron (4-amino-3-methyl-6-phenyl-1,2,4-triazin-5-one), which are respectively a fungicide and an herbicide. Some results and the method used will be presented. First, in molecular dynamics with a DFTB potential, we extensively explore the potential energy surfaces of the Ca2+-pesticide-(H2O)i systems for i = 1-20. Along these trajectories, we select n structures that we optimise in DFTB. Among these minima, the m energy-lowest ones are re-optimised in B3LYP/6-311+G(2d,2p) to minimize basis set superposition error. The effects of dispersion are taken into account using the empirical corrections of S. Grimme (D3). In addition, the micro-hydration of the cation and the pesticide are studied through different characteristic energies (2), such as the relative energies of the different minima, the interaction, complexation and deformation energies, giving a better understanding of the micro-hydration of a pesticide interacting with a calcium ion. The first hydration spheres of the pesticide and the cation are also determined to rationalize the energetical.
(1) Takis, Panteleimon G. and Papavasileiou, Konstantinos D. and Peristeras, Loukas D. and Melissas, Vasilios S. and Troganis, Anastassios N., Phys. Chem. Chem. Phys., 2013, 15(19), 7354-7362
(2) Campo-Cacharrón, A., Cabaleiro-Lago, E. M., & Rodríguez-Otero, J., Theoretical Chemistry Accounts, (2012), 131, 1-13.

---

*Intervenant

DFT studies of the interactions between rotundone and fining agents in winemaking

Fabienne Bessac*[1], Corinne Lacaze-Dufaure[2], Sophie Hoyau*[3], Olivier Geffroy[4], and Valérie Simon[2]

[1]Laboratoire de Chimie et Physique Quantiques – CNRS, Universté de Toulouse, Université Paul Sabatier - Toulouse III, INP EI-Purpan – France

[2]Ecole nationale supérieure des ingénieurs en arts chimiques et technologiques – CNRS, Institut National Polytechnique de Toulouse - INPT, Université de Toulouse Paul Sabatier – France

[3]Laboratoire de Chimie et Physique Quantiques – Université de Toulouse Paul Sabatier, CNRS – France

[4]Physiologie, Pathologie et Génétique Végétales – INP EI-Purpan, Unversité de Toulouse – France

Résumé

In winemaking, clarification and stabilization are procedures which aim at eliminating particles suspended within the wine prior to bottling(1). In the process of clarification, fining involves the addition of a substance (known as a fining agent) to the wine. This substance forms either adsorbent, enzymatic, or ionic bonds with the suspended particles, leading to the formation of larger molecules and particles that can precipitate out of the wine. More specifically, fining can remove substances such as coloring phenols and polymerized tannins, which softens or reduces the astringency and/or bitterness of red wines. Fining agents can be minerals (bentonite clay), natural compounds such as ovalbumin, gelatin or pea proteins, or polymers (polyvinylpyrrolidone PVP).

Rotundone is a potent aroma compound found in certain grape varieties such as Syrah, Duras, Gamay or Tardif(2),(3). Up to date, it is the only compound known as responsible for peppery notes identified in wine and it comes from the skins of grapes. Even in small amounts, rotundone can significantly enhance the overall sensory experience of a wine, adding depth and intrigue to its bouquet. Significant rotundone losses are observed during racking, filtration and fining of the wine, likely in relation to its hydrophobic nature and its likelihood to bind to other particles(4). Thus, the impact of several fining agents used for wine clarification on rotundone concentration in wine need to be explored.

---

*Intervenant

Structure of Flexible Chiral Molecules and Unconventional Solvents by Vibrational Circular Dichroism Spectroscopy

Emeline Boyer*[1], Jessica Bowles[2], Anne Zehnacker[3], Florent Calvo[4], Rodolphe Vuilleumier[5], Nguyen-Thi Van-Oanh[1], and Carine Clavaguéra[1]

[1]Institut de Chimie Physique , Université Paris-Saclay, CNRS, UMR8000, 91405 Orsay, France – Institut de Chimie du CNRS, Université Paris-Saclay, Centre National de la Recherche Scientifique – France

[2]Laboratoire de chimie théorique – Sorbonne Universite – France

[3]Institut des Sciences Moléculaires d'Orsay (ISMO) – CNRS : UMR8214, Université Paris XI - Paris Sud – Université Paris-Sud 91405 Orsay cedex, France

[4]Université Grenoble-Alpes, CNRS, LIPhy, 38000 Grenoble – UMR5588 – France

[5]PASTEUR – Ecole Normale Supérieure de Paris - ENS Paris – France

Résumé

Vibrational circular dichroism (VCD) unveils molecular conformational nuances by discerning absorption differences in right- and left-circularly polarized light within the infrared range. This subtle technique elucidates molecular interactions, especially those that are sensitive to hydrogen bonding, thereby offering particular insight into the structure of unconventional solvents. Interpreting VCD signals necessitates meticulous comparison with theoretical models. However, incorporating environmental effects posed challenges, now mitigated by advancements in computational modeling. Notably, simulating VCD spectra in highly structured liquids like Ionic Liquids (ILs) presented formidable hurdles due to pervasive long-range interactions. We have recently proposed a new methodology based on classical molecular dynamics simulations associated with the AMOEBA polarizable force field to calculate VCD spectra of flexible molecules (1). A first study of a chiral and flexible molecule, namely phenylcyclohexanediol in a solvent of dimethyl sulfoxide (DMSO) was made successfully, leading to the calculation of infrared and VCD spectra. This work has now been extended to ILs, particularly spirocyclic pyrrolidinium with BF4-. Modeling both the infrared and VCD spectra for these systems reveals useful insights into their properties and the complex interactions with their environment.

---

*Intervenant

sciencesconf.org:emie2024:555274

Structure and spectroscopy of molecules of astrochemical interest and their aggregates with water

Ana Niedojadlo*†[1,2], Alejandro Gutierrez-Quintanilla[3], Gustavo Pino[1], Jordan Dezalay[4], and Jennifer Noble[4]

[1]INFIQC (CONICET, UNC), Department of Physical chemistry, Faculty of Chemical Sciences, Laser Center for Molecular Sciences, National University of Córdoba. Pab. Argentina, Ala 1, (5000) Córdoba, Argentina. – Argentine

[2]CNRS, Aix-Marseille University, PIIM laboratory, Saint Jérôme, Av. Escadrille Normandie Niemen, 13013 Marseille, France. – PIIM Laboratory – France

[3]University of Pau and the Adour Region, Helioparc Technopole, 2 avenue P. Angot, 64053Pau, France. – LCABIE - IPREM-UMR UPPA – France

[4]CNRS, Aix-Marseille University, PIIM laboratory, Saint Jérôme, Av. Escadrille Normandie Niemen, 13013 Marseille, France. – PIIM, Aix-Marseille Université – France

Résumé

Introduction: The first detection of an aromatic molecule in space was made in 2001, when benzene was identified in a protoplanetary nebula.(1) More recently, in 2018, the benzonitrile molecule was the first nitrogenous aromatic cycle detected in the interstellar medium (ISM).(2) In early 2021, the detection of 1- and 2-cyanonaphthalene was reported.(3) These findings confirm that nitrogenous polycyclic aromatic hydrocarbons (PANHs) are a component of the interstellar aromatic inventory. Both in the ISM and in different astronomical environments, PANHs can form aggregates with small molecules such as water, which alters their spectroscopy and their photophysical and photochemical properties. Therefore, the laboratory study of the spectroscopy, photochemistry and photophysics of this type of PANH and their aggregates with H2O is of great interest in understanding and predicting the chemical composition of the ISM. In this context, we present a study of the spectroscopy of 1-cyanonaphthalene (1CNN) and its aggregates with 1 and 2 molecules of H2O in the gas phase under conditions of low pressure and temperature to simulate as closely as possible those of the ISM.

Results and conclusions: The generation of 1CNN and its aggregates with 1 and 2 H2O molecules was carried out by supersonic expansion in a vacuum chamber, reaching pressures and temperatures of the order of 10-6 mbar and 30 K, respectively. The REMPI spectrum (1+1') was recorded in the 225-325 nm range, with shifts to lower energies observed for the case of the aggregates with respect to the spectrum of the 1CNN monomer, and signs of evaporation of a water molecule in the case of 1CNN:2H2O. The ionization energy of the aggregates was determined.

---

*Intervenant

†Auteur correspondant: aniedojadlo@unc.edu.ar

The experimental results showed good agreement with electronic structure calculations at the CAM-B3LYP/aug-cc-pvdz level. The small decrease observed in the ionization energy with the degree of solvation indicates that the effect of the water molecule is similar in the neutral and ionic states of 1CNN.

The excited states of the radical cation form of the aggregates were studied theoretically to evaluate the possible effect of Ly-α radiation on the photostability and ISM survival of these species. For both aggregates, calculations indicate that D2 is the closest state lying below the Ly- α photon energy, and that evaporation from this excited state is unlikely to occur due to the adiabatic energies observed.

References:

(1) Cernicharo, J., et al., ApJ., 546.2, L123 (2001).

(2) McGuire, B. A., et al., Sci., 359.6372, 202-205 (2018).

(3) McGuire, B. A., et al., Sci., 371.6535, 1265-1269 (2021).
* correspondant : aniedojadlo@unc.edu.ar

Super-Lorentzian effects and intensity depletion due to collision by classical molecular dynamics simulations

Ha Tran*[1], Gang Li[2], Volker Ebert[2], and Joseph Hodges[3]

[1]Laboratoire de Météorologie Dynamique, IPSL, CNRS, Sorbonne Université – CNRS – France
[2]Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig – Allemagne
[3]Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA – États-Unis

Résumé

The integrated line shape of an absorption line is widely obtained from fit of laboratory-measured spectra assuming a line profile model. Such a laboratory-measured intensity is so far assumed to be independent of the pressure. This major assumption is now questioned: to which extent the retrieved integrated line shape is proportional to the absorber density and independent of the total pressure of the gas mixture? In this paper, the pressure dependence of the line intensities retrieved from fits of absorption spectra of HCl are investigated both experimentally and theoretically. The retrieved line intensities reveal large decreases with increasing pressure - up to 3% per atm for pure HCl. We also show that the absorptions in between successive P and R transitions are significantly larger than those predicted using the usual Lorentz profile. Requantized classical molecular dynamics simulations have been made in order to predict absorption spectra of HCl matching the experimental conditions. The pressure dependence of the intensities retrieved from the calculated spectra as well as the predicted super-Lorentzian behavior between lines are in good agreement with the measurements. Our analysis shows that these effects are essentially due to incomplete collisions, which govern the dipole auto-correlation function at very short times.

---

*Intervenant

Supercritical fluid-aided vaporization of neutral biomolecules for structural studies by UV spectroscopy

Jean-Xavier Bardaud*†[1], Marc-André Gaveau[1], Michel Mons[2], and Eric Gloaguen[1]

[1]Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, Orsay, France – CNRS – France
[2]Laboratoire Interactions Dynamiques et Lasers, Gif-Sur-Yvette, France – CEA – France

Résumé

Introducing neutral systems into the gas phase proves to be challenging, especially for thermolabile molecules where the existing techniques may not always be suitable. (1)

In this context, a new source based upon a CO2 supercritical fluid chromatography (SFC) instrument (2) coupled to a molecular jet (3) is developed. The source is pulsed, enabling the structural characterization of isolated systems through conformer-resolved laser spectroscopic experiments following a resonant two-photon ionization (R2PI) scheme.

Molecules of interest are dissolved in a controlled manner in supercritical CO2 and then transported towards the pulsed nozzle, allowing a supersonic expansion of the mixture under vacuum conditions.

Initial tests were conducted using a solution of toluene in ethanol to characterize the performance of the source in terms of ion signal stability, internal and translational temperatures, and aggregation level. By incorporating a moderately heated channel, we also successfully obtained a R2PI-UV spectrum of caffeine preliminarily dissolved in acetonitrile. Further enhancements need to be implemented in order to optimize the cooling of target molecules, thereby enabling even finer spectroscopic resolution.

---

*Intervenant

†Auteur correspondant: jean-xavier.bardaud@universite-paris-saclay.fr

Substitution effect on electronic-excited photochemistry of meta-Nitrophenolate compounds: study by cold ion photodissociation and photoelectron spectroscopy

Franco Leonardo Molina*[1,2], Ali Muhieddine[1], Michel Broquier[1], Satchin Soorkia[1], Niloufar Shafizadeh[1], Benoît Soep[1], Gustavo Pino†[2], and Gilles Gregoire*‡[1]

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

[2]Instituto de Investigaciones en Físico Química [Córdoba] – Argentine

Résumé

Nitroaromatic compounds are employed in phototherapy due to their ability to photorelease nitric oxide (NO), which has several favourable physiological effects in pathological treatment. In this context, the light is used as a trigger to release NO, providing control in the concentration and spatiotemporal resolution.*1* Model compounds are the NitroPhenolates (NP-), considered as donor-acceptor (O–NO2) chromophores with a charge-transfer (CT) excitation in the visible region (lowest p-p* transition) which eventually photorelease NO.*2* Gas-phase action spectroscopy of NP- shows that o-, p- and m- substitution affects the donor-acceptor coupling tunning the absorption band, i.e., locating the m-NP- absorption near the biological transparency window (600-850 nm).*2*
Therefore, we select a set of mNP- derivatives, including a third substituent, -CH3 or -NH2, in the o- or p- position of the phenolate group to evaluate how it affects the electronic donor-acceptor coupling and the NO yield, expecting that the steric effect improves the NO release. The comparative study uses photodissociation (PDS) and photoelectron (PES) spectroscopy under cryogenic conditions.

The Electron Affinity (EA) energy, determined by PES, is found in the visible region for all the compounds and decreased by including -CH3 and -NH2 groups. The photodissociation spectra have been recorded below and above the EA. The spectra were assigned to the lowest p-p* transition by comparison with electronic excited states calculations and Franck-Condon simulations. Furthermore, resonances were found near the EA for the substituted compounds while for the mNP- a UV band is observed above its EA. The presence of electronic excitations below and above the EA suggests a competition between valence and non-valence excited states that are involved in the photofragmentation process.*3*

References

---

*Intervenant

†Auteur correspondant: gpino@unc.edu.ar

‡Auteur correspondant: gilles.gregoire@universite-paris-saclay.fr

1- Sortino S. Light-controlled nitric oxide delivering molecular assemblies. Chem Soc Rev. 2010. (8):2903-13. doi: 10.1039/b908663n

2- Wanko M, Houmøller J, Støchkel K, Suhr Kirketerp MB, Petersen MÅ, Nielsen MB, Nielsen SB, Rubio A. Substitution effects on the absorption spectra of nitrophenolate isomers. Phys Chem Chem Phys. 2012 Oct 5;14(37):12905-11. doi: 10.1039/c2cp41636k

3- Do Hyung Kang, Kwang Hyun Cho, Jinwoo Kim, Han Jun Eun, Young Min Rhee, and Sang Kyu Kim. Electron-Binding Dynamics of the Dipole-Bound State: Correlation Effect on the Autodetachment Dynamics. Journal of the American Chemical Society 2023 145 (47), 25824-25833. doi: 10.1021/jacs.3c10099

L’hème en phase gazeuse : un atout pour comprendre le mécanisme de fixation de l’oxygène sur les hémoprotéines

Niloufar Shafizadeh*†1, Mohamad Aarabi[2], Ali Muhieddine*3, Satchin Soorkia*4, Michel Broquier*4, Gilles Gregoire*3, Franco Leonardo Molina*4,5, Reza Omidyan*2, Aurélien De La Lande[6], and Benois Soep[1]

[1]Institut des Sciences Moléculaires d’Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[2]Department of Chemistry, University of Isfahan – Iran
[3]Institut des Sciences Moléculaires d’Orsay – CNRS – France
[4]Institut des Sciences Moléculaires d’Orsay – CNRS, Université Paris Sud, Université Paris Saclay – France
[5]Instituto de Investigaciones en Físico Química [Córdoba] – Argentine
[6]Institut de Chimie Physique – Institut de Chimie - CNRS Chimie, Université Paris-Saclay, Centre National de la Recherche Scientifique – France

Résumé

La réaction de fixation du dioxygène sur une hémoprotéine est l’une des réactions de production d’énergie les plus courantes dans la nature. Néanmoins, son mécanisme de fixation et de relâchement sur l’atome de fer au centre de l’hème (le site actif des hémoproteines) n’est pas connu avec précision au niveau moléculaire. Sur cette affiche nous ferons l’état des lieux sur nos connaissances en phase gazeuse de l’interaction entre de petites molécules comme O2, CO, H2O, et l’atome de fer de l’hème. En effet la phase gazeuse permet d’analyser les propriétés de l’hème graduellement avec un ligand, puis deux ligands, sur les deux sites disponibles grâce à une mesure directe de l’enthalpie de dissociation, par la méthode van’t Hoff. Ces mesures d’énergie de liaison fer-ligand sont directement comparables aux résultats obtenus par les calculs de chimie quantique. Surtout la phase gazeuse permet d’étudier des situations qui n’existent pas dans la nature comme l’hème isolé. On obtient ainsi un paysage aussi complet que possible des interactions des ligands avec l’hème. Nous avons ainsi constitué un ensemble de données qui permet de comparer les énergies de liaison de fer ferreux et ferrique avec différents ligands. Cette comparaison nous a permis de montrer que les mécanismes d’interaction ligand - atome de fer sont équivalents quel que soit le degré d’oxydation de l’atome de fer, ferreux ou ferrique. La stabilisation de la liaison se fait par un jeu de donation / rétrodonation, du ligand vers les orbitales vacantes du métal et vice versa. L’intensité de cette stabilisation dépendent de la nature ligand et du degré d’oxydation. Ces résultats sont en accord avec les calculs théoriques de densité électronique effectués. Nous avons également caractérisé l’influence critique de la molécule d’eau sur la réaction de fixation de l’oxygène sur l’hémoproteine.

---

*Intervenant

†Auteur correspondant: niloufar.shafizadeh@universite-paris-saclay.fr

sciencesconf.org:emie2024:555822

CARACTÉRISATION D'UNE SOURCE LASER UV ACCORDABLE A 308 NM POUR LA SPECTROSCOPIE DE L'OZONE

Coline Mahob*[1,2], Hadj Elandaloussi[2], Kentin Poncelet[3], Ruizhe Gu[3], Adèle Hilico[3], Pascal Jeseck[2], Patrick Marie-Jeanne[2], Christian Rouillé[2], Thomas Zanon-Willette[2], and Christof Janssen[2]

[1]Laboratoire d'Etude du Rayonnement et de la Matière en Astrophysique et Atmosphères (LERMA) – Observatoire de Paris, université Paris Dauphine, PSL Resarch University, Centre national de la recherche scientifique - CNRS (France), Sorbonne Université UPMC Paris VI, CY Cergy Paris Université – France

[2]De la Molécule aux Nanos-objets : Réactivité, Interactions et Spectroscopies (MONARIS) – Sorbonne Université UPMC Paris VI, Centre national de la recherche scientifique - CNRS (France) – France

[3]Laboratoire Photonique, Numérique et Nanosciences (LP2N) – Institut d'Optique Graduate School (IOGS), Centre national de la recherche scientifique - CNRS (France), Université de Bordeaux (Bordeaux, France) – France

Résumé

Les mesures de l'ozone atmosphérique sont largement influencées par les données spectroscopiques couvrant diverses gammes spectrales, en particulier dans l'UV. Des mesures de laboratoire réalisées à 325 nm laissent suggérer que les sections efficaces actuellement recommandées pour le sondage atmosphérique pourraient être biaisées de quelques pourcents dans la région de la bande de Huggins (1). Étant donné que cette région de longueur d'onde est utilisée par différentes plates-formes de mesure de l'ozone, telles que les LIDAR stratosphériques à 308 nm, les spectrophotomètres Brewer et Dobson, et diverses missions satellitaires, nous proposons de revisiter la section efficace de l'ozone dans cette gamme spectrale par méthode laser. La spectroscopie laser permet d'obtenir une résolution spectrale et un contrôle de fréquence difficilement atteignable avec des méthodes spectroscopiques traditionnelles.
Nous envisageons une étude basée sur deux systèmes laser différents. La première source est configurée avec une plage étroite de 307.8 nm à 308.2 nm, adaptée aux applications du LIDAR stratosphérique. Quant à la seconde source, elle est conçue pour être largement accordable entre 308 nm et 318 nm, ce qui la rend adaptée pour les mesures spectroscopiques et permet une exploration étendue de la gamme spectrale.

La présentation actuelle ciblera le premier système. En utilisant des techniques de génération de somme de fréquences (SFG), le système laser est capable d'émettre de la lumière monochromatique dans une gamme de longueurs d'onde allant de 307.8 nm à 308.2 nm. Nous présenterons le montage du système et en caractériserons l'accordabilité, la résolution spectrale et la puissance. La source UV est réalisée par somme de fréquence d'un laser bleu à

---

*Intervenant

441.6 nm et une source laser accordable dans l'infrarouge autour de 1μm. La puissance de sortie de cette dernière est amplifiée grâce à un amplificateur à fibre dopée Ytterbium. Les deux signaux sont combinés avec une lame dichroïque, et la somme de fréquence est réalisée avec un cristal de BBO.

Notre objectif est de parvenir à une incertitude sur la section efficace d'absorption de l'ozone inférieure à 1 % ce qui permettra de réduire les incertitudes des sections efficaces des molécules d'ozone dans cette gamme de longueurs d'onde.

Ce travail a bénéficié du soutien de l'ANR (projet ALPHA-O3, sous numéro ANR-22-CE01-0007) et du programme national LEFE (Les Enveloppes Fluides et l'Environnement) de l'INSU-CNRS.

(1) Janssen et al., Atmos. Meas. Tech. 11, 1707-1723 (2018). Doi: 10.5194/amt-11-1707-2018

Theoretical description of cresols isomers/water complexes : stability and optical properties

Alejandro Gutierrez-Quintanilla* , Daniel Daniel Camacho Granados , and Karinne Miqueu[1]

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

Résumé

Aromatic compounds are released into the atmosphere as byproducts of biomass and coal combustion. Under atmospheric conditions, these compounds undergo chemical and photochemical transformations, ultimately leading to the formation of secondary organic aerosols (SOAs). While the importance of SOAs in the atmospheric thermal equilibrium is acknowledged, their exact contribution remains elusive. Exploring the mechanisms that drive SOA formation, with a particular emphasis on understanding precursor-solvent interactions, represents an active and dynamic area of research. Utilizing a simplistic theoretical model of microsolvation offers an initial approach to grasp the influence of solvation on the stability of these systems. In this work, we used metadynamics simulations (CREST package) to explore how microsolvation develops in the series of isomers: ortho, meta and para-cresol (methylphenol), some of the most important aromatic byproducts of biomass burning. Water complexes, from N=1 to 6 water molecules, were considered. The differences in stability within each isomer are discussed based on the specific interactions established with the "solvent" molecules. The impact of solvation on the optical properties is also discussed. Finally, the probability of finding these complexes in the troposphere conditions was also explored, through free solvation energies comparison.

---

*Intervenant

Structural studies of host-guest complexes between molecular cages and small drugs

Nicolas Nieuwjaer*[1], Giel Berden[2], Jos Oomens[3], Debora Scuderi[4,5], Fabien Chirot[6], Ayoub Badri[7], Charles Desfrançois[8,9], Frédéric Lecomte[9], and Bruno Manil[9]

[1]Laboratoire de Physique des Lasers – Institut Galilée, université Paris 13, CNRS : UMR7538 – France
[2]HFML – FELIX, Radboud University , Toernooiveld 7c, 6525 ED Nijmegen – Pays-Bas
[3]Radboud university [Nijmegen] – Pays-Bas
[4]Université Paris-Saclay – Université Paris-Saclay,Sorbonne Universités – France
[5]Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, 91405 Orsay Cedex, France – CNRS, Université Paris Sud, Université Paris Saclay – France
[6]Institut Lumière Matière [Villeurbanne] – Université Claude Bernard Lyon 1, Centre National de la Recherche Scientifique – France
[7]Laboratoire de Physique des Lasers, 93430 Villetaneuse – CNRS, Université Sorbonne Paris nord – France
[8]Laboratoire de Physique des Lasers – université Paris 13 : Université Sorbonne Paris Nord, CNRS : UMR7538 – France
[9]Laboratoire de Physique des Lasers – CNRS, Université Sorbonne Paris nord – France

Résumé

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of a varying number of a-1-4-linked glucopyranose units. The three main types of cyclodextrins include a-, b and g-CDs formed by six, seven and eight glucose units, respectively. CDs have a truncated cone tri-dimensional structure. Their central cavity is hydrophobic, allowing low-polarity molecules to be encapsulated partially or entirely by host-guest interaction, meanwhile the external part is hydrophilic because of the presence of hydroxyl groups making CDs soluble in water. This host-guest type relationship can modify the physical, chemical or biological characteristics of the guest molecule, and applications are found in practically all sectors of industry. The advent of soft ionization techniques has allowed for extensive examination of cyclodextrin complexes by mean of mass spectrometry, and structural information on b-CD complexes have recently been provided by IRMPD and IM spectroscopy (2) or also action-FRET (3). We have performed structural studies on host-guest complexes between b-cyclodextrins and small drugs (paracetamol and salicylic acid) for Surface Enhanced Raman Spectroscopy detection in drinking water. We have extended these studies to larger cages (g-CD) and to different molecular cages, more precisely methylated b-cyclodextrins: the degree of methylation modifies characteristics such as complex formation, toxicity and solubility for the included guest molecule.

The structures are obtained by combining Ion Mobility Spectrometry, IRMPD spectroscopy experiments and quantum calculations for simulating IR spectra on mass-selected ions. Comparison with studies in the condensed phase will give information on the possible conversion

---

*Intervenant

of inclusion complexes to nonspecific complexes (and vice versa) and on the importance of relative interactions for the formation of the complexes.

(1) I. Tijunelyte, N. Dupont, I. Milosevic, C. Barbey, E. Rinnert, N. Lidgi-Guigui, E. Guenin, M. Lamy de la Chapelle *Environ. Sci. Pollut. Res.,* **24**, 27077-27089 (2015).

(2) J.U. Lee, S.-S. Lee, S. Lee, H.B. Oh *Molecules* **25***,* 4048 *(*2020).
(3) Q. Duez, G. Knight, S. Daly, J. De Winter, E. Halin E, L. MacAleese, R. Antoine, P. Gerbaux, P. Dugourd *New J. Chem.* **41**, 41, 1806 (2017).

Laser desorption on water microdroplets for gas phase characterization

Ayoub Badri*[1], Manal Al Sahmarani[1], Charles Desfrançois[1], Frédéric Lecomte[1], Bruno Manil[2], and Nicolas Nieuwjaer†[3]

[1]Laboratoire de Physique des Lasers – CNRS, Université Sorbonne Paris nord – France
[2]Laboratoire de Physique des Lasers – CNRS, Université Sorbonne Paris nord – France
[3]Laboratoire de Physique des Lasers – CNRS, Université Sorbonne Paris nord – France

Résumé

The gas phase desorption of large biomolecules has been made possible by the advent in the last decades of soft sources, such as electrospray ionization or matrix assisted laser desorption sources. Even if these sources have the capability to preserve low interactions in the gas phase, the desorption process might generate structural changes of the biomolecules and relevance for biological understanding is not always assessed. In this context, we have started the development of a new laser induced liquid bead ion desorption (LILBID) source1,2 : liquid micro droplets (50 μm diameter), containing the biomolecules of interest, are laser ablated directly under vacuum. This innovative source will allow to benefit from the gas phase advantages (stoichiometry control, ions manipulation and trapping) while preserving the biomolecules native structure. The analysis is made by a time of flight mass spectrometer. We have obtained a water microdroplet under vacuum. We are now coupling our system with an infrared desorption laser to study the desorption phenomenon in detail and to potentially confirm the desorption possibility of hydrated species. It opens perspectives for a better preservation of native structures and towards radical chemistry studies inside the droplets.

---

*Intervenant

†Auteur correspondant: nicolas.nieuwjaer@univ-paris13.fr

Gas-phase chemistry of the photo-reduced (Mo6I13)2- and photo-oxidized (Mo6I14)1- cluster species

Luke Macaleese*[1], Aikaterini Tsirkou[2], Nina Tyminska[3], Richard O'hair[4], Karine Costuas[5], Fabien Grasset[3], Yann Molard[3], and Stéphane Cordier[3]

[1]Institut Lumière Matière (ILM) – CNRS : UMR5306, Université Claude Bernard - Lyon I (UCBL) – UMR5306 CNRS Université Claude Bernard Lyon 1, 5 rue de la Doua, 69100 Villeurbanne, FRANCE, France

[2]Institut Lumière Matière (iLM) – CNRS : UMR5306, Université Claude Bernard - Lyon I (UCBL) – France

[3]ISCR – Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000 Rennes, France, Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000, Rennes, France – France

[4]University of Melbourne – Australie

[5]ISCR – Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000 Rennes, France – 263 Av. Général Leclerc, 35700 Rennes, France

Résumé

Photocatalytic reduction of CO2 for the production of hydrocarbons could be one of the viable solutions to address climate change as well as energy shortage. Molybdenum (Mo6) nanoclusters were reported to be effective photo-catalysts for the reduction of CO2. These hexanuclear clusters are robust, highly stable and represent promising dye alternatives in the frame of sustainability. They can be reversibly oxidized in solution and halogen ligands exchanged by solvent molecules. However, the precise reaction mechanism of these photo-catalysts is not clear yet and, in order to improve their catalytic properties, it is important to gain information on their reactivity, especially under irradiation. Ion molecule reactions in ion traps coupled to light sources provide opportunities to gain fundamental insights into structure and reactivity.
A LTQ Velos ion trap (Thermo Scientific) was used to generate Mo6I142- via ESI from Cs2Mo6I14 dissolved in acetonitrile (1 μM). In order to generate the reduced Mo6I132- species,precursor ions Mo6I142- were mass selected and irradiated with a single, 1 mJ, 5 nanosecond laser pulse at 260 nm (Horizon, Continuum). The resulting Mo6I132- ions were isolated and allowed to relax and/or react with the background trapping gas. In order to probe the reactivity of the reduced Mo6I132- species,the trapping helium buffer gas was seeded with O2 or CO2 at 5000 ppm. Reaction times, varied by using the ion "activation time" with no collisional energy, were explored up to 10 s before MS acquisition.

Preliminary results revealed that UV-Vis irradiation of the (Mo6I14)2- dianion produced both the oxidized (Mo6I14)1- and reduced (Mo6I13)2- species, while collisional heating could

---

[*] Intervenant

only yield isoelectronic Mo6 clusters (loss of I- and n I2). This photospecificity might be at the origin of the photocatalytic activity of these clusters. The reduced species is particularly interesting as it can further act as a highly potent reducer, which represents the major chemical effect desired.

The stability of this cluster is examined by mass selection and trapping allowing relaxation and/or reaction with background gas. Traces of O2 (from the ESI source) are enough for trapped ions to react and yield (Mo6I13O2)2- without collisional activation. Following O2 addition, iodine can be lost as neutral I• or as iodide I-, in a mechanism similar to what was observed for (Mo6In)1- ions (n $<$ 13). However, another specific reactive path opens with the destabilization of the Mo6 cluster core and the generation of two singly charged complementary fragments: (Mo5I11)1- and (MoI2O2)1-.

The reactivity of the reduced species with O2 was more specifically examined using helium seeded with O2. As expected from the interaction between a reducer and an oxidant, (Mo6I13)2- reacts very rapidly ($<$ 100 ms) and quantitatively with O2 to generate (Mo6I13O2)2-. The monoanionic species produced after secondary I- loss react further with additional O2 additions and I• losses and progress towards the highly oxygenated Mo6O121-. The specific reactivity of (Mo6I13)2- was also examined with CO2. Longer reaction times will be explored in search for potential specific CO2 partial reduction products.
More generally, the effect of the halogen (I/Br) on the photo-production of the reduced species will be discussed. The influence of the irradiation wavelength on the production of oxidized vs. reduced species will be shown. Quantum simulations on the various species generated will provide mechanistic insights.

A la recherche de l'EDM de l'électron par l'étude du Césium en matrice cryogénique

Sebastian Lahs , Thomas Battard , Claudine Crepin*[1], and Daniel Comparat[2]

[1]Institut des Sciences Moléculaires d'Orsay (ISMO) – CNRS : UMR8214, Université Paris XI - Paris Sud – Université Paris-Sud 91405 Orsay cedex, France

[2]Laboratoire Aimé Cotton – Centre national de la recherche scientifique - CNRS (France), Université Paris Sud, Université Paris Saclay – France

Résumé

La recherche de moments dipolaires électriques permanents (EDM) de particules élémentaires offre des contraintes sur la physique au-delà du modèle standard, en particulier sur les brisures de symétrie CPT. Le projet EDMMA (porté par le LAC, collaboration LAC/ CIMAP/ LPL/ISMO) vise à obtenir une meilleure valeur maximale de cet EDM, à comparer aux prédictions des modèles BSM (au-delà du modèle standard). L'idée est de mesurer l'EDM de l'électron (aligné avec le spin) dans des atomes lourds (Cs) par des mesures de précession de spin après alignement des spins par pompage optique sur un ensemble d'atomes en champs électrique et magnétique. Les atomes sont piégés en matrice cryogénique pour bénéficier d'un très grand nombre d'atomes accessibles à la mesure et de temps de mesure extrêmement longs, menant théoriquement à une limite 1000 fois inférieure à l'état de l'art.

La première étape consiste en une caractérisation la plus poussée possible des échantillons cryogéniques. Les premières expériences, menées au LAC, portent sur le césium en matrice d'argon. Les spectres électroniques sont composés de plusieurs bandes larges, reflétant les différentes interactions de Cs avec le réseau cristallin d'Ar et en particulier les différents sites de piégeage. Les études en température des spectres d'absorption et une modélisation théorique du système Cs/Ar a mis en évidence deux sites principaux de symétries différentes (1). La fluorescence de Cs par excitation dans les différentes structures d'absorption montre plusieurs bandes dont l'analyse est en cours.

(1) T. Battard, S. Lahs, C. Crépin and D. Comparat, Phys. Rev. A, **108**, 042820 (2023)

---

*Intervenant

Séparation statistique de précurseurs activés simultanément

Félix Servant*[1,2], Laurent Nahon†[1], and Alexandre Giuliani‡[1,2]

[1]Synchrotron SOLEIL – CNRS : UMRUR1, CNRS – France
[2]INRAE – INRAE – France

Résumé

Ce poster présente des résultats sur des spectres de masse en tandem modèles, dans lesquels plusieurs précurseurs d'ions polypeptidiques ont été sélectionnés et activés, produisant ensemble des mélanges de précurseurs et de fragments. Notre analyse statistique des séries de spectres MS/MS est basée sur des mesures de corrélation ou des quantités de la théorie de l'information. Chaque coefficient mesure la relation entre deux variables (ions) tout en contrôlant un effet externe (nombre total d'ions). Le traitement peut être appliqué aux spectres de masse complets ou aux données réduites après la sélection des pics. La relation entre chaque paire d'ions est ensuite calculée, ce qui donne une carte bidimensionnelle de coefficients dans laquelle la relation entre chaque ion est fournie. Ces cartes permettent de déchiffrer la relation entre les précurseurs et les ions produits.

L'analyse est poussée plus loin et nous appliquons un algorithme de plongement pour réduire et visualiser les données à haute dimension. Ensuite, un algorithme de clusterisation est utilisé pour créer des spectres de masse individuels. Ces spectres de masse déconvolués sont comparés aux spectres expérimentaux obtenus par MS/MS de chaque précurseur. Nous observons un excellent accord entre les spectres expérimentaux et calculés.

Notre méthode numérique permet de décrypter des spectres de masse en tandem complexes et d'obtenir des spectres de masse en tandem purs à partir de mélanges d'ions précurseurs.

---

*Intervenant

†Auteur correspondant: laurent.nahon@synchrotron-soleil.fr

‡Auteur correspondant: alexandre.giuliani@synchrotron-soleil.fr

sciencesconf.org:emie2024:557019

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

Marc Briant*[1], Olivier Sublemontier[2], and Cesar Alvarez-Ilamas[3]

[1]LEDNA – Université Paris-Saclay, CEA, CNRS, NIMBE, 91191, Gif-sur-Yvette – France
[2]LEDNA – Université Paris-Saclay, CEA, CNRS, NIMBE, 91191, Gif-sur-Yvette – France
[3]LEDNA – Université Paris-Saclay, CEA, CNRS, NIMBE, 91191, Gif-sur-Yvette – France

Résumé

Air quality monitoring is a major challenge for this decade. One of the most important and difficult issues concerns the monitoring of fine particles (1 μm <), and in particular ultrafine particles (100 nm <). In mid-2018, ANSES published a report recommending strengthening the monitoring of ultrafine particles, classified as priority pollutants in the air (1). Furthermore, access to the number concentration of fine and ultrafine particles of a given elemental composition is crucial for the following reasons:
- Ultrafine particles typically represent less than 1 % of the mass of aerosols, but more than 80 % of the total number of particles in the atmosphere.

- Unlike micrometric particles, ultrafine particles remain suspended in the air for a very long time.

- The health risks associated with inhalation of ultrafine particles are high. They are linked not only to their chemical composition, but also to their very small size, which enables them to penetrate deep into the respiratory system and can pass into the bloodstream.

The aim of the project proposed here is to obtain the number and mass concentrations, in real time and in situ, of particles of a given elemental composition, without limiting the type of particle. The size range considered is from a few tens of nm to 1000 nm, covering as far as possible the field of fine and ultrafine particles (2, 3).

To achieve these objectives, a new process based on Laser-Induced Breakdown Spectroscopy (LIBS) applied to aerosols is being developed. It differs from previous works (4) in that the interaction takes place under vacuum (and not at atmospheric pressure) between a focused pulsed laser with a high repetition rate and a jet of particles produced by an Aerodynamic Lens System (ALS) (5). Interaction with the laser is therefore solely with the particles, without interaction with the gas, and is quasi-continuous. The ALS enables a very fine, dense particle jet to be produced under vacuum, while avoiding contamination of the optical elements by particle deposition. This deposition is a major limitation of on-line aerosol analysis using optical techniques.

---

*Intervenant

The advantages of the presented technique over conventional ambient pressure techniques are:

- No background noise from the surrounding plasma gas.

- Highly enhanced sensitivity thanks to the concentration effect of ALS.

- Detection of individual particles, enabling counting, linked to the number of particles in the air.

- More efficient detection of elements emitting in the far UV range, even down to VUV.

References

(1) Rapport ANSES : Polluants " émergents " dans l'air ambiant : Identification, catégorisation et hiérarchisation de polluants actuellement non réglementés pour la surveillance de la qualité de l'air (2018). https://www.anses.fr/fr/system/files/AIR2015SA0216Ra.pdf

(2) Picard J. *et al.*, MRS Advances, **2**, p. 1487 (2017). https://doi.org/10.1557/adv.2016.633

(3) EP2889602, O. Sublemontier *et al.*, Dispositif de caractérisation de particules dans un jet de particules sous vide (2013). https://patentscope.wipo.int/search/fr/detail.jsf?docId=EP137965452

(4) Amodeo T. et al., Spectrochim. Acta B, **63**, p. 1183 (2008), http://dx.doi.org/10.1016/j.sab.2008.09.005

(5) Liu P., *et al.*, Aerosol Science and Technology, **22**, p. 314 (1995). http://dx.doi.org/10.1080/02786829408959749

* correspondant : marc.briant@cea.fr

Study of the electronic structure of iron metal complexes in aqueous solution by X-ray spectroscopies

Nour El Houda Azzouzza[1], Loic Journel*[2], Stéphane Carniato[3], Remi Dupuy[1], Jérôme Palaudoux[4], Marine Fournier[1], Gildas Goldsztejn[5], James Ablett[6], Jean-Pascal Rueff[7], and Denis Ceolin[8]

[1]Laboratoire de Chimie Physique - Matière et Rayonnement – Sorbonne Université UPMC Paris VI – France
[2]Laboratoire de Chimie Physique - Matière et Rayonnement – Sorbonne Université UPMC Paris VI – France
[3]Laboratoire de Chimie Physique - Matière et Rayonnement – Sorbonne Universite, Centre National de la Recherche Scientifique, Centre National de la Recherche Scientifique : UMR7614 – France
[4]Laboratoire de Chimie Physique - Matière et Rayonnement (LCPMR) – Sorbonne Universite, Centre National de la Recherche Scientifique : UMR7614 – 11 Rue Pierre et Marie Curie 75231 Paris Cedex 05, France
[5]Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[6]Synchrotron SOLEIL (SSOLEIL) – CNRS : UMRUR1 – L'Orme des Merisiers Saint-Aubin - BP 48 91192 GIF-sur-YVETTE CEDEX, France
[7]Synchrotron SOLEIL (SOLEIL) – Centre National de la Recherche Scientifique : UR1 – LÓrme des Merisiers Saint-Aubin - BP 48 91192 GIF-sur-YVETTE CEDEX, France
[8]Synchrotron SOLEIL – GALAXIES beamline, SOLEIL Synchrotron – France

Résumé

Transition metal complexes are versatile and find applications in fields such as chemistry and biology as photoactive materials, catalysts, and redox centers. Understanding the electronic structure of metal complexes in aqueous solutions is critical for gaining insights into their roles in various processes of biological relevance, or for chemical reactivity (1).
X-ray photoemission spectroscopy (XPS) and X-ray emission spectroscopy (XES) are powerful techniques for their study in solution. XPS provides valuable information about metal-ligand interactions and is highly sensitive to different types of ligands and coordination environments (2). On the other hand, XES directly probes the 3d orbitals involved in metal-ligand bonding and are highly sensitive to the distance between the metal center and ligands (3). Despite the significance of studying metal complexes in solution, experimental XPS and XES data (4, 5) for different oxidation states of the same metal center in solution are limited at the metal K edge.

---

*Intervenant

In this study, we present the spectra of potassium ferrous (FeII(CN)6)4- and ferric (FeIII(CN)6)3- hexacyanide complexes in aqueous solution. These two complexes share the same octahedral geometry but differ in their charge states. The experiments were conducted at the GALAXIES beamline of SOLEIL using a liquid micro-jet setup adapted to the high-energy photoemission spectrometer (HAXPES) and to the X-ray emission spectrometer.

We acquired resonant and non-resonant XES spectra and generated 2D maps for both compounds by monitoring the Kβ main lines at different incident photon energies across the iron Fe K edge. Non-resonant XES spectra were obtained above the iron K edge for the Kβ main lines, as well as the valence to core(VtC)-XES lines. Both compounds exhibit several contributions in their VtC spectra, including an elastic peak, and peaks which correspond to different orbital transitions involving N 2s, C 2s, N sp hybrid, and C sp hybrid orbitals.

Furthermore, XPS measurements were performed at the iron 1s, 2p, and 3p thresholds, as well as at the carbon and nitrogen 1s thresholds. Our results revealed that changes in oxidation states led to modifications in the photoemission spectra. Specifically, the C 1s and N 1s XPS spectra exhibited satellite structures for Fe(II), which were absent in Fe(III). Moreover, the Fe(III) 2p3/2 XPS spectrum exhibited a high binding energy shoulder that was not present in Fe(II).

These two type of measurements reveal significant differences between the two complexes due to the charge state of the metallic center. This emphasizes the importance of studying metal complexes in solution to gain a comprehensive understanding of their behavior and properties.

1. R. Golnak et al., Sci. Rep., 2016, 6, 24659.

2. A. Cano et al., J. Inorg. Chem., 2019, 1724.

3. P. Chandrasekaran et al., Inorg. Chem., 2013, 52, 11, 6286-6298.

4. M. Ross et al., J. Phys. Chem., 2018, 122, 19, 5075–5086.
5. T. Yamashita et al., Appli. Surface Sci., 2008, 254, 8, 2441-2449.

Liste des participants

Civilité	**Nom**	**Prénom**	**Courriel**
Mme	Al Sahmarani	Manal	manal98sahmrani@gmail.com
Mme	Alauzet	Camille	calauzet@irsamc.ups-tlse.fr
M	ARNAULT	Jean-Charles	jean-charles.arnault@cea.fr
M	Asselin	Pierre	pierre.asselin@sorbonne-universite.fr
M	Badri	Ayoub	ayoub.badri@univ-paris13.fr
M	bardaud	jean-xavier	jean-xavier.bardaud@universite-paris-saclay.fr
Mme	BESSAC	FABIENNE	fabienne.bessac@irsamc.ups-tlse.fr
Mme	blanchet	valérie	valerie.blanchet@u-bordeaux.fr
M	BOUDON	Vincent	Vincent.Boudon@u-bourgogne.fr
Mme	Bourehil	lyna	lyna.bourehil@sorbonne-universite.fr
Mme	Boyer	Emeline	emeline.boyer@universite-paris-saclay.fr
Mme	Brenner	Valérie	valerie.brenner@cea.fr
M	Briant	Marc	marc.briant@cea.fr
M	Broquier	Michel	michel.broquier@universite-paris-saclay.fr
M	Calvo	Florent	florent.calvo@cnrs.fr
M	Campargue	Alain	alain.campargue@univ-grenoble-alpes.fr
M	Carcabal	Pierre	pierre.carcabal@universite-paris-saclay.fr
M	Chawananon	Sathapana	sathapana.chawananon@universite-paris-saclay.fr
Mme	CLAVAGUERA	Carine	carine.clavaguera@universite-paris-saclay.fr
M	COUSSAN	stéphane	stephane.coussan@univ-amu.fr
Mme	Crépin-Gilbert	Claudine	claudine.crepin-gilbert@universite-paris-saclay.fr
M	cuisset	arnaud	arnaud.cuisset@univ-littoral.fr
M	Darquié	Benoît	benoit.darquie@univ-paris13.fr
M	Desdion	Quentin	qdesdion@irsamc.ups-tlse.fr
M	Desfrançois	Charles	charles.desfrancois@univ-paris13.fr
M	Despré	Victor	victor.despre@univ-lyon1.fr
M	Dezalay	Jordan	jordan.dezalay@univ-amu.fr
Mme	Dossmann	Héloïse	heloise.dossmann@sorbonne-universite.fr
M	du Chalard	michel	michel.duchalard@ganil.fr
M	DUCREUX	Emile	emile.ducreux@univ-reims.fr
M	GENOUD	Adrien	adrien.genoud@univ-lyon1.fr
Mme	GIROD	Marion	marion.girod@univ-lyon1.fr
M	GLOAGUEN	Eric	eric.gloaguen@cnrs.fr
M	Goldsztejn	Gildas	gildas.goldsztejn@universite-paris-saclay.fr
M	Goubet	Manuel	manuel.goubet@univ-lille.fr
M	Grégoire	Gilles	gilles.gregoire@universite-paris-saclay.fr
M	GUTIERREZ QUINTANILLA	Alejandro	agquintanill@univ-pau.fr
M	Hartmann	Jean-Michel	jean-michel.hartmann@lmd.ipsl.fr

Mme	HOYAU	Sophie	sophie.hoyau@irsamc.ups-tlse.fr
M	Jouan	Armel	armel.jouan@universite-paris-saclay.fr
M	Journel	Loic	loic.journel@sorbonne-universite.fr
M	Kossov	Arsène	arsene.kossov@gmail.com
Mme	Leboucher	Héloïse	heloise.leboucher@irsamc.ups-tlse.fr
M	MacAleese	Luke	luke.mac-aleese@univ-lyon1.fr
M	Maclot	Sylvain	maclot@ganil.fr
Mme	MAHOB	Coline	coline.mahob@sorbonne-universite.fr
M	MARCINIAK	Alexandre	alexandre.marciniak@irsamc.ups-tlse.fr
Mme	Mascetti	Joëlle	joelle.mascetti@u-bordeaux.fr
M	MICHAUT	Xavier	xavier.michaut@sorbonne-universite.fr
M	Molina	Franco Leonardo	franco.molina@universite-paris-saclay.fr
M	MUHIEDDINE	Ali	ali.muhieddine@universite-paris-saclay.fr
M	Neeman	Elias	elias.neeman@univ-lille.fr
M	Nguyen trung	Thibault	thibault.nguyen@ijclab.in2p3.fr
Mme	Niedojadlo	Ana	aniedojadlo@unc.edu.ar
M	NIEUWJAER	Nicolas	nicolas.nieuwjaer@univ-paris13.fr
M	Olivier	Durif	durif@kth.se
M	Pezzotti	Simone	simone.pezzotti@ens.psl.eu
M	Pirali	Olivier	olivier.pirali@cnrs.fr
M	Rousseau	Patrick	prousseau@ganil.fr
M	SALPIN	Jean-Yves	jeanyves.salpin@univ-evry.fr
M	Servant	Félix	felix.servant@synchrotron-soleil.fr
Mme	Shafizadeh	niloufar	niloufar.shafizadeh@universite-paris-saclay.fr
Mme	SOBANSKA	Sophie	sophie.sobanska@u-bordeaux.fr
M	SOEP	Clément	clement.soep@sorbonne-universite.fr
M	Solem	Nicolas	nicolas.solem@universite-paris-saclay.fr
M	Soorkia	Satchin	satchin.soorkia@universite-paris-saclay.fr
M	Sublemontier	Olivier	olivier.sublemontier@cea.fr
Mme	Toureille	Morgane	morgane.toureille@univ-grenoble-alpes.fr
Mme	Tran	Ha	htran@lmd.ipsl.fr
M	Zamith	Sébastien	sebastien.zamith@irsamc.ups-tlse.fr
Mme	Zins	Emilie-Laure	emilie-laure.zins@sorbonne-universite.fr

Partenaires

BIARRITZ

MÉDIATHÈQUE DE BIARRITZ
BIARRITZEKO MEDIATEKA

IPSL

nano X
NANOSCALE SCIENCE AND ENGINEERING

UNIVERSITÉ
DE PAU ET DES
PAYS DE L'ADOUR

université
PARIS-SACLAY

SCF
dcp
SFP

Modsim