ATELIER THÉMATIQUE
GRANDS INSTRUMENTS POUR LA PHYSICO-CHIMIE MOLÉCULAIRE

11-14 OCTOBRE 2021

VILLAGE VACANCES « LES TOURELLES »

ASNELLES

NOUS LES REMERCIONS POUR LEUR SOUTIEN.

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GDR EMIE - GRANDS INSTRUMENTS POUR LA PHYSICO-CHIMIE MOLÉCULAIRE

Asnelles sur mer (Calvados), France, October 11-14, 2021

Monday 11th October 2021	
	DAY 1
15:00-15:45	Registration
	Session 1 – Ions across the axis, *Chair: Patrick Rousseau (UNICAEN)*
15:45-16:20	*Ion-collision induced dynamics of complex molecular systems in the gas phase* **Alicja Domaracka,** Normandie Université, CIMAP, Caen, France
16:20-16:55	*Swift heavy ions and complex organic molecules in the solid phase for astrophysics* **Philippe Boduch,** Normandie Université, CIMAP, Caen, France
16:55-17:30	*Slow relaxation processes of cationic PAHs stored in electrostatic storage rings, DESIREE and Mini-Ring* **Jérôme Bernard,** Université Claude Bernard, ILM, Lyon, France
17:30-18:00	***Coffee break***
	Session 2 – Instrumental developments, *Chair: Aleksandar Milosavljevic (SOLEIL)*
18:00-18:20	*DESIREE: The Cryogenic Electrostatic Storage Ring* **Suvasthika Indrajith,** Stockholm University, Stockholm, Sweden
18:20-18:40	*Development of an electrostatic ion beam trap and its applications* **Raj Singh,** CIMAP, GANIL, Caen, France
18:40-19:00	*New Spectroscopic Methods for THz Synchrotron Beamlines* **Thomas S Hearne,** Université Paris-Saclay, ISMO, Orsay, France
19:00-19:20	*Performance and first results of a versatile home-built tandem mass spectrometer dedicated for experiments at advanced light sources* **Juliette Leroux,** Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany
	Dinner

Tuesday 12th October 2021	
	DAY 2
08:30-08:50	Registration
08:50-09:00	Opening and Introduction **Pierre Carcabal,** ISMO
	Grands instruments and theory, *Chair: Pierre Carcabal (ISMO)*
09:00-09:45	*Les TGIR à l'Institut de Physique du CNRS* **Sylvain Ravy,** CNRS, INP, France
09:45-10:20	*Equivocal identification of gas phase medium sized molecular species in mixture by high accuracy single photon ionization and ab initio computations* **Majdi Hochlaf,** Université Gustave Eiffel, COSYS/LISIS, Marne-la-Vallée, France
10:20-10:50	***Coffee break***
	Session 3 – Excited states, *Chair: Laurent Nahon (SOLEIL)*
10:50-11:25	*X-ray induced ultrafast dynamics in excited molecules* **Oksana Travnikova,** Sorbonne Université, LCPMR, Paris, France
11:25-11:45	*State-selected ion-molecule reactions with VUV synchrotron radiation of interest for depollution plasma development* **Roland Thissen,** Université Paris-Saclay, ICP, Orsay, France
11:45-12:05	*Photoelectron spectroscopy and circular dichroism of chiral oxirane radicals* **Gustavo Garcia,** Synchrotron SOLEIL, Saint Aubin, France
12:05-12:25	*Cage-opening dynamics of adamantane* **Sylvain Maclot,** University of Gothenburg, Gothenburg, Sweden
12:30-15:30	***Lunch break***

	Session 4 – Astrophysics and atmosphere, *Chair: Olivier Pirali (ISMO)*
15:30-16:05	*Enabling interstellar detections using synchrotron-based far-infrared spectroscopy* **Marie-Aline Martin-Drumel,** Université Paris-Saclay, ISMO, Orsay, France
16:05-16:40	*Vacuum-UV and soft X-ray induced photodesorption from molecular ices* **Mathieu Bertin,** Sorbonne Université, LERMA, Paris, France
16:40-17:15	*High-resolution far-infrared spectroscopy of spherical-top molecules using synchrotron radiation* **Vincent Boudon,** Université de Bourgogne, ICB, Dijon, France
17:15-17:35	*Competing energy dissipation pathways at the gas-grain interface: a study of astrophysically-relevant ices* **Jennifer Noble,** Aix-Marseille Université, PIIM, Marseille, France
17:35-18:00	***Coffee break***
	Conférence grand public, *Chair: Alicja Domaracka (CIMAP)*
18:00-19:00	*De Curie au GANIL* **David Boilley,** Normandie Université, GANIL, Caen, France
	Free time and Dinner

Wednesday 13th October 2021	
DAY 3	
	Session 5 – Free electron lasers, *Chair: Marc Simon (LCPMR)*
09:00-09:35	*Femtosecond molecular dynamics at free-electron laser sources* **Maria Novella Piancastelli,** Uppsala Universitet, Sweden and Sorbonne Université, LCPMR, Paris, France
09:35-10:10	*Free Electron Laser and IRMPD Spectroscopy: a perfect synergy to unravel the structure and reactivity of biomolecules in the gas phase* **Debora Scuderi,** Université Paris Saclay, ICP, Orsay, France
10:10-10:30	*Application of near edge X-ray absorption mass spectrometry for the study of bio-relevant molecules in the gas phase* **Lucas Schwob,** Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany
10:30-11:00	***Coffee break***
	Session 6 – Biomolecules, *Chair: Debora Scuderi (ICP)*
11:00-11:35	*Activation and spectroscopy of mass and charge selected ions stored in a linear ion trap* **Alexandre Giuliani,** INRA and Synchrotron SOLEIL, Saint Aubin, France
11:35-11:55	*Photo and Auger electron spectroscopies of phthalocyanines in the gas phase* **Gildas Goldsztejn,** Université Paris-Saclay, ISMO, Orsay, France
11:55-12:15	*Ion-collision dynamics of complex molecular systems in the gas phase* **Min Liu,** ENSICAEN, UNICAEN, CEA, CNRS, CIMAP, Caen, France
12:15-12:35	*Photoelectron circular dichroism as a probe for conformational isomerism in 1-indanol* **Jennifer Dupont,** Université Paris-Saclay, ISMO, Orsay, France
12:35-15:00	***Lunch break***
15:00-17:30	***Free time and Outdoor activities***
	Round table: "Grand Instruments pour la physico-chimie moléculaire", *Chair: Roland Thissen (ICP)*
17:30-19:30	*1. Future Plans and Major Evolutions:* *a. CLIO (D. Scuderi)* *b. SOLEIL (L. Nahon)* *c. GANIL (to be announced)* *2. Organizations and Representation of Users:* *a. GDR X-FEL (M. Simon)* *b. GDR EMIE (P. Carcabal)* *c. Users Organizations: Orgues, AFURS, ESUO* *3. Users Access* *4. Young Researchers and Trainees*
	Dinner

Thursday 14th October 2021	
	DAY 4
	Session 7 – Aggregates and environmental effects - 1, *Chair: Simon Aude (LCPQ - IRSAMC)*
09:00-09:35	*Surface chemistry of gold nanoparticles produced by laser ablation and perspectives as photosensitizers* **Anna Lévy,** Sorbonne Université, INSP, Paris, France
09:35-10:10	*Photoelectron angular distributions of chiral aerosol particles: Condensation effects on chiral asymmetries* **Sebastian Hartweg,** Synchrotron SOLEIL, Saint Aubin, France
10:10-10:30	*Investigation of ligand electronic effects on iron cyclopentadienyl complexes using photoelectron spectroscopy* **Lyna Bourehil,** Synchrotron SOLEIL, Saint Aubin, France
10:30-11:00	***Coffee break***
	Session 8 – Aggregates and environmental effects - 2, *Chair: Pierre Carcabal (ISMO)*
11:00-11:35	*Overview of neutron spectroscopic techniques and insight into the microscopic properties of water confined in nanopores* **Marie Plazanet,** Laboratoire Interdisciplinaire de Physique, Grenoble, France
11:35-12:10	*Jet-cooled far-infrared spectroscopy of molecules on the AILES beamline of SOLEIL* **Robert Georges,** Université Rennes 1, IPR, Rennes, France
12:10-12:30	*On the structure and electronic spectra of excited neutral argon rare gas clusters using Hole Particle Pseudopotential method* **Mukul Dhiman,** ENSICAEN, UNICAEN, CEA, CNRS, CIMAP, Caen, France
12:30-12:50	*Toward a better description of proteins electronic structure in a solvated state using electron spectroscopy* **Lucie Huart,** NIMBE, IRAMIS, CEA and Synchrotron SOLEIL, Saint Aubin, France
13:00-15:00	***Lunch***
	Departure

COLOR LEGEND

Yellow – Selected oral contributions: 20 min (5 min for questions and discussion)

Green – Invited lectures: 35 min (5-10 min for questions and discussion)

Blue – Plenary lecture: 45 min (35-40 min + 5-10 min); Conférence grand public: 60 min; Round table: 120 min

INSTITUTIONS' ACRONYMS (in the order of appearance)

UNICAEN - Université de Caen Normandie (Caen)
CIMAP - Centre de recherche sur les Ions, les Matériaux et la Photonique (Caen)
ILM – Institut Lumière Matière (Lyon)
GANIL – Grand Accélérateur National d'Ions Lourds (Caen)
ISMO – Institut des Sciences Moléculaires d'Orsay (Orsay)
TGIR – Les très grandes infrastructures de recherche (France)
CNRS – Centre National de la Recherche Scientifique (France)
INP – Institut de Physique (France)
COSYS – Composantes et Systèmes (Univ. Gustave Eiffel, Champs-sur-Marne)
LISIS – Instrumentation, Simulation et Informatique Scientifique (Univ. Gustave Eiffel, Champs-sur-Marne)
SOLEIL – Source Optimisée de Lumière d'Energie Intermédiaire du LURE (France)
(LURE - Laboratoire d'Utilisation du Rayonnement Électromagnétique)
LCPMR – Le Laboratoire de Chimie Physique-Matière et Rayonnement (Paris)
ICP - Institut de Chimie Physique (Orsay)
LERMA – Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères (Paris)
ICB – Laboratoire Interdisciplinaire Carnot de Bourgogne (Dijon)
PIIM – Physique des Interactions Ioniques et Moléculaires (Marseille)
INRA – Institut National de la Recherche Agronomique (France)
IPR – Institut de physique de Rennes (Rennes)
ENSICAEN – National Graduate School of Engineering and Research Center (Caen)
CEA – Commissariat à l'énergie atomique et aux énergies alternatives (France)
NIMBE – Nanosciences et Innovation pour les Matériaux, la Biomédecine et l'Énergie (Saclay)
IRAMIS – L'Institut Rayonnement-Matière de Saclay (Saclay)

GDR – Groupement de recherche (CNRS)
EMIE – Edifices Moléculaires Isolés et Environnés (GDR CNRS)
X-FEL – X-ray Free Electron Laser

ION-COLLISION INDUCED DYNAMICS OF COMPLEX MOLECULAR SYSTEMS IN THE GAS PHASE

A. Domaracka[1]

Normandie Université, ENSICAEN, UNICAEN, CEA, CNRS, CIMAP, 14000 Caen, France

Ion interaction with complex molecular systems rises a variety of phenomena of importance for our understanding in different fields, e.g. tailoring material properties, radiation damage at the molecular level of biological tissues, the formation and ageing of aerosols in the atmospheres of planets/moons, as well as the origin and evolution of molecules in space.

The collision of ions with matter leads to energy deposition via interaction with electrons and nuclei. These mechanisms are referred as electronic and nuclear stopping processes, respectively. The importance of this processes and the ratio depend on the projectile mass and velocity. The nuclear stopping, due to its localized character, can open specific fragmentation channel (non-statistical fragmentation). Such non-statistical process - knockout - has been observed in collisions with fullerenes and polycyclic aromatic hydrocarbon (PAH) molecules and produce reactive molecular species on the fs time scale. These react with other molecules of the cluster and intra-cluster growth processes drive the formation of a wide range of new large molecular species [e.g. 1, 2].

In this talk, I will give an overview of results on ion-induced fragmentation and ion-induced molecular growth processes of carbon containing clusters colliding with slow ions in the context of *bottom-up approach* to investigate formation of molecules in astrophysical environments. For example, formation mechanisms of large carbonaceous nanoparticles via ion single collision with fullerene/PAH clusters as well as a peptide bond formation in He^{2+} collision with β-alanine amino acid clusters (see Fig. 1) [3] will be discussed.

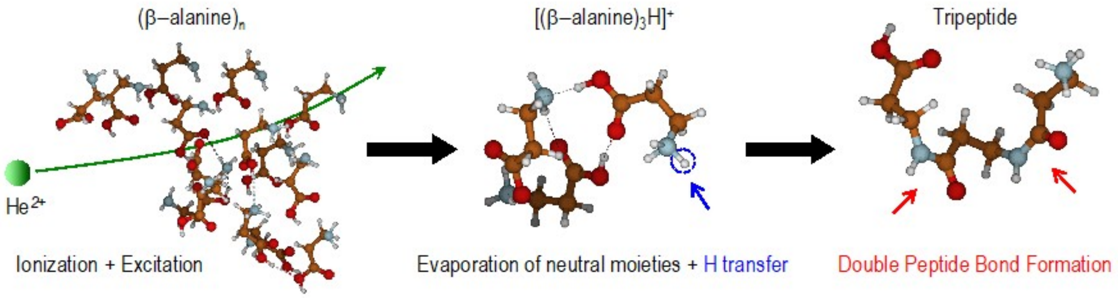

Figure 1: *Polypeptide formation in clusters of β-alanine amino acids induced by low-energy* He^{2+} *ions.*

Réferences

[1] R. Delaunay *et al. J. Phys. Chem. Lett.* **6,** 1536 (2015).
[2] R. Delaunay *et al. Carbon* **129**, 766 (2018).
[3] P. Rousseau *et al. Nat. Commun.* **11**, 3818 (2020).

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SWIFT HEAVY IONS AND COMPLEX ORGANIC MOLECULES IN THE SOLID PHASE FOR ASTROPHYSICS

P. Boduch[1]

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Ices are ubiquitous in space. These ices are mainly composed of simples molecules like H_2O, CO, CO_2… They are permanently irradiated by cosmic rays or stellar wind. The ice radiolysis leads to, among others, the production of more complex organic molecules. As an example, the simplest amino acid, the glycine has recently been detected on the 67P/Tchourioumov-Guérassimenko (Tchouri) comet. Since complex organic molecules (COMs) are produced, we have investigated the COM radiolysis to quantify their radio-resistance and their associated lifetime in space. We mainly focused our studies on nucleobases which have been detected on meteorites on earth. The solid film of nucleobases were irradiated with high energy ion beam in a wide energy domain (KeV to hundreds of MeV) in order to simulate the role of cosmic rays. The induced modifications were followed by infrared spectroscopy. We also studied the role of the sample temperature on the destruction process under irradiation and the role of water matrix when COMs are embedded inside.

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SLOW RELAXATION PROCESSES OF CATIONIC PAHS STORED IN ELECTROSTATIC STORAGE RINGS, DESIREE AND MINI-RING

J. Bernard(a)[1], M. Ji(b), N. Kono(b), M. H. Stockett(b), H. T. Schmidt(b), H. Zettergren(b), A. Al-Mogeeth(a), S. Martin(a), and C. Joblin(c)

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The advent of the polycyclic aromatic hydrocarbons (PAHs) hypothesis in the 1980s, which remains the most accepted interpretation of mid-IR and visible diffused interstellar bands (DIBS), has trigged a considerable amount of research on this family of molecules in the gas phase. Measurements of dissociation and radiative cooling rates, which vary in several orders of magnitude as a function of the internal energy, in high-isolation conditions, are of crucial importance for estimating the stability and lifetime of PAHs in the ISM. Electrostatic storage devices, especially the two storage rings used in the present work, namely DESIREE (Stockholm, Sweden) and Mini-Ring (Lyon, France), are suitable for such measurements in conditions that are relevant for the ISM. In particular, in the 2010s the Mini-Ring has been used to quantify the process of recurrent fluorescence in small PAH cations (naphthalene, anthracene, phenanthrene, pyrene).[1,2]

In this talk, we will focus on recent measurements on the cooling dynamics of anthracene and tetracene cations performed at DESIREE, where the cryogenic environment allows for much longer storage times than in the Mini-Ring (room-temperature) and therefore, to direct measurements of the dissociation and vibrational emission cooling rates.

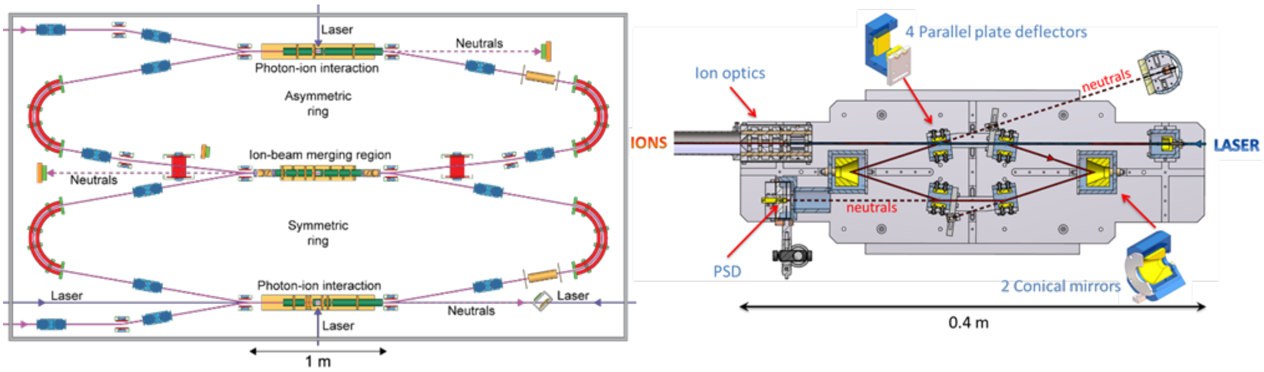

Figure 1: Scheme of DESIREE (left) and Mini-Ring (right).

Réferences

[1] S. Martin, et al. Phys. Rev. Lett. 110 (2013) 063003. https://doi.org/10.1103/PhysRevLett.110.063003.
[2] M. Ji, et al. J. Chem. Phys. 146 (2017) 044301. https://doi.org/10.1063/1.4973651.

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DESIREE: THE CRYOGENIC DOUBLE ELECTROSTATIC STORAGE RING

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A. Schmidt-May(a), R. Paul(a), B. Zhu(a), N. Kono(a), P. K. Najeeb(a), E. K. Anderson(a), M. Gatchell(a), M.C. Ji(a),
R. D. Thomas(a), S. Rosen(a), P. Reinhed(a), P. Löfgren(a), M. Blom(a), M. Björkhage(a), J. D. Alexander(a),
D. Hanstorp(b), A. Källberg(a), A. Simonsson(a), M. Larsson(a), W. D. Geppert(a), M. H. Stockett(a), H. Zettergren(a),
H. Cederquist(a) and H.T. Schmidt(a)

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The development of electrostatic ion-beam storage rings has opened up a new era for studies of atomic and molecular processes in new time domains. The DESIREE (Double ElectroStatic Ion Ring ExpEriment) is a storage ring facility at Stockholm University, Sweden [1]. A schematic view of the storage rings is shown in Figure 1. DESIREE has several unique features, the most distinct one being the double ring structure with two storage rings referred to as the symmetric ring and the asymmetric ring with a common merging section for studies of reactions between oppositely charged ions at sub-eV collision energies. The storage rings are largely based on the design of the ELISA storage ring in Aarhus, Denmark [2], where the ion-optical elements are completely electrostatic. One advantage of electrostatic optical elements as compared to their magnetic counterparts is that electrostatic elements are mass independent. Hence, for a given ion beam energy and ion charge, the voltages on the elements can remain fixed as the ion mass is changed.

DESIREE is cryogenically cooled to 13 K and has an extremely low residual gas background pressure (~10^{-14} mbar) which enables keV-beams of atomic, molecular, or cluster ions to be stored for hours. The excellent experimental conditions are also ideal for lifetime measurements and action spectroscopy on isolated atomic or molecular ions in single ring experiments. Merged-beams experiments are now possible at sub-eV collision energies where charge transfers between negatively and positively charged ions are monitored by detecting the two neutral products formed in the reactions. This allows for the first measurements of the final state distributions for atomic and molecular systems under astrophysical conditions [4, 5, 6].

Moreover, studies of the spontaneous decay of long-lived metastable excited states of atomic anions are performed by using lasers to state-selectively probe the populations in specific excited (metastable) states as functions of time [7]. In addition, the cooling dynamics of e.g., hot PAH, molecular and metal clusters ions have been studied in new time domains [8, 9, 10]. Here, laser probing is used to provide more detailed information on – for instance – the rotational temperature of the stored ions or the time evolution of the internal energy distribution in the case of studies on radiative cooling dynamics.

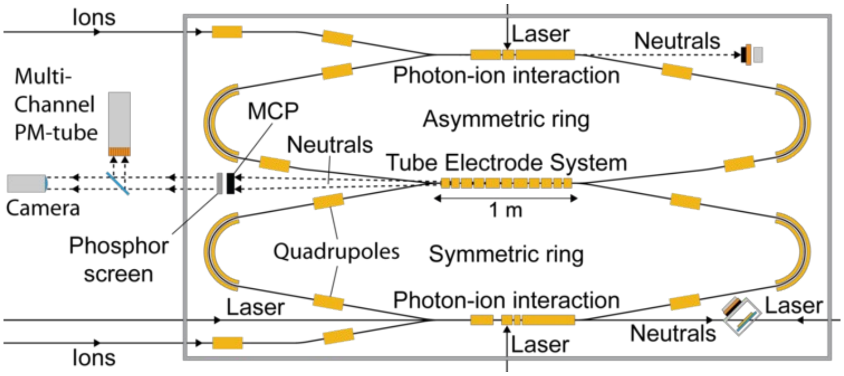

Figure 1: Schematic of the DESIREE ion-beam storage ring.

References
[1] R. D. Thomas *et al.*, Rev. Sci. Instrum., 82(6):065112, **2011**
[2] H. T. Schmidt *et al.*, Rev. Sci. Instrum., 84, 055115, **2013**
[3] S.P. Møller, Nucl. Instrum. Meth., 394(3): 281 – 286, **1997**
[4] P. S. Barklem *et al.*, ApJ 908, 245, **2021**
[5] G. Eklund *et al.*, Phys. Rev. A. 103, 032814, **2021**
[6] G. Eklund *et al.*, Phys. Rev. A 102, 012823, **2020**
[7] E. Bäckström *et al*., Phys. Rev. Lett. 114, 143003**, 2015**
[8] M. H. Stockett *et al.*, J. Chem. Phys. 153, 154303, **2020**
[9] E. K. Anderson *et al.*, Phys. Rev. Lett. 124, 173001, **2020**
[10] H. T. Schmidt *et al.*, Phys. Rev. Lett. 119, 073001, **2017**.

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DEVELOPMENT OF A ELECTROSTATIC ION BEAM TRAP AND ITS APPLICATIONS

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An electrostatic ion beam trap (EIBT) with extraction has been designed and simulated to study the formation, reactivity, and fragmentation of clusters arising from ion-cluster collisions [1]. Such studies are very important to understand the molecular formation in the space [2]. The schematic of the setup is shown in Figure1. This setup has three main parts: extraction region, an Einzel lens, and the electrostatic ion beam trap. Ions are formed in interaction zone by ion collisions with molecular clusters, then the collision products are extracted by a weak electrostatic field, and focused by an Einzel lens to the entrance mirror of the EIBT. In order to get extracted ions from the interaction zone to the center of trap, we lower down the voltages of the few electrodes of the entrance mirror, once the ions are in the field free region of the EIBT, the voltages of the electrodes raised to the standard trapping voltages. This allows the trapping of ions in the EIBT. The voltages on the extraction region, Einzel lens, and the EIBT have been optimized to obtain best trapping efficiency using Simion software. The EIBT works as high resolution mass spectrometer. Other spectroscopies can also be done in the field free region.

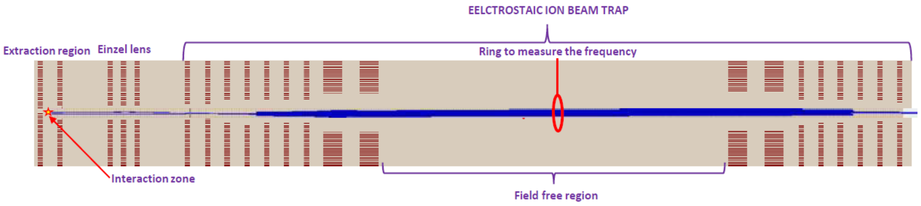

Figure 1. Schematic of the EIBT with extraction region and the Einzel lens. Trajectories of trapped ions are shown as blue lines.

A combination of two EIBTs can trap both positive and negative ions in the same filed free regions to study the merge beam cold collisions, which sheds light on the formation of molecules in the early universe. We recently designed, simulated, and fabricated such a setup, which is called hybrid electrostatic ion beam trap (HEBIT). Simulation supports as low as ≈4 meV resolution of the collision energy. Neutral products and laser induced cations can be readily imaged behind the HEIBT mirrors [3].

This project is partly co-financed by the Normandy Region and the European Union in the frame of operational program FEDER/FSE 2014-2020 (RIN MAGIC) and by the French ANR agency (ANR-18-CE30-0021).

Réferences

1. D. Zajfman et al, Phy. Rev. A 55 (1997) R1577.
2. P. Rousseau et al, Nat. Comm. 11 (2020) 3818.
3. A. Shahi et al, Rev. Sci. Instrum. 90 (2019) 113308.

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NEW SPECTROSCOPIC METHODS FOR THZ SYNCHROTRON BEAMLINES

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Synchrotron beamlines are extremely useful light sources for sensitive, broadband spectroscopy in the far-IR or terahertz (1-10 THz) region which lacks bright, broadband laboratory sources. Far-IR synchrotron beamlines across the world are equipped with Fourier-transform infrared (FTIR) spectrometers. These instruments provide broadband spectra thanks to the powerful multiplex advantage of interferometry. However, they are also inherently limited in their maximum resolution, to around 20 MHz for the best available instruments. This resolution is in excess of an order of magnitude larger than typical THz molecular gas-phase linewidths, and prevents the observation of many fine and hyperfine effects. The observation of such effects is vital for understating the physical properties of a chemical species through spectroscopy.

The goal of the HEROES (heterodyne receivers optimized for synchrotron sources) project is to unlock far-IR synchrotron sources for higher resolution spectroscopy, while simultaneously improving sensitivity and maintaining the broadband advantage of FTIR spectroscopy. Two new spectrometers are under development to achieve this goal. The first is an instrument based on the heterodyne mixing of the output of a QCL-pumped molecular laser with the far-IR continuum of the regular synchrotron radiation.[1] This instrument is able to produce spectra with a resolution of 80 kHz and an instantaneous bandwidth of 5 GHz, from 1 to 3.5 THz. The second instrument is a dual-comb spectrometer combining the THz frequency comb produced by the coherent synchrotron radiation mode of the synchrotron[2] with a comb produced from the incidence of a femtosecond laser onto a photoconductive mixer.

Réferences

1. Lampin, J.-F. *et al.* Broadband terahertz heterodyne spectrometer exploiting synchrotron radiation at mega-hertz resolution. *Opt. Lett.* **44**, 4985–4988 (2019).
2. Tammaro, S. *et al.* High density terahertz frequency comb produced by coherent synchrotron radiation. *Nat. Commun.* **6**, 7733 (2015).

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PERFORMANCE AND FIRST RESULTS OF A VERSATILE HOME-BUILT TANDEM MASS SPECTROMETER DEDICATED FOR EXPERIMENTS AT ADVANCED LIGHT SOURCES.

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The first experiments combining tandem mass spectrometers with synchrotron beamlines have been carried out 10 years ago in order to probe the electronic structure and radio-induced damage of electrosprayed biomolecules. Since then, vacuum-ultraviolet (VUV) and soft X-ray light have received growing interest from the mass spectrometric community thanks to their high potential for exploring physicochemical processes and properties of systems such as peptides, oligonucleotides, PAHs or metal-organic compounds. However, these experiments still remain very challenging to perform due to the relative low target density and the low absorption cross section of these molecules in the concerned energy ranges. Additionally, there is currently a lack of dedicated end-stations at synchrotron facilities worldwide.

A new tandem mass spectrometer has been recently built in our group in order to face these challenges and answer the growing demand for performing such experiments. The instrument has been specially conceived to easily interface with any advanced light sources' beamlines, including synchrotrons and free-electron lasers, as well as tabletop lasers. Briefly, the instrument consists of a high throughput electrospray ionization source, a quadrupole mass filter, an ion Paul trap and a reflectron time-of-flight. The performance of the instrument will be detailed, including comparison with SIMION simulations. The first results obtained on custom-made peptides at the nitrogen K-edge, recently measured at the P04 soft X-ray beamline of the PETRA III synchrotron (DESY, Hamburg, Germany), will be presented.

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LES TGIR À L’INSTITUT DE PHYSIQUE DU CNRS

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EQUIVOCAL IDENTIFICATION OF GAS PHASE MEDIUM SIZED MOLECULAR SPECIES IN MIXTURE BY HIGH ACCURACY SINGLE PHOTON IONIZATION AND AB INITIO COMPUTATIONS

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The investigation of the structure, the spectroscopy and the dynamics of the cationic species of medium sized molecular systems is important to understand the physical chemistry of biological, atmospheric and astrophysical media. Such compounds correspond at least to DNA bases, amino acids, their analogues, combustion products and atmospheric species. Such compounds may possess numerous tautomers, rotamers and isomers that lie close in energy. The experimental characterization of a unique form is challenging. For this purpose, we apply single photon VUV synchrotron based experiments combined with state-of-the-art ab initio computations.

Experimentally, we use the VUV light emitted by the DESIRS beamline of synchrotron SOLEIL coupled to the double imaging photoelectron photoion coincidence (i2PEPICO) spectrometer DELICIOUS3. [1] The coincidence scheme allows the photoelectron images to be filtered as a function of mass and ion kinetic energy in a multiplex manner. Treatment of such photoelectron images as a function of the photon energy leads to the threshold / slow photo electron spectra of the selected masses [3,4]. Theoretically, the structures and the energetics of neutral and cationic molecular systems are determined using post Hartree-Fock-density functional theory composite schemes. We also treat these species in their electronic excited states using configuration interaction methods. [2] Afterwards, we use the theoretical results to disentangle the complex features observed experimentally.

Our combined theoretical and experimental approach can be applied to several medium sized molecular entities presenting a dense pattern of electronic and/or isomeric and/or tautomeric forms in their spectra. In sum, we established an equivocal way to characterize the neutral molecules prior to photoionization. Also, we derive a set of thermodynamical data of specific gas phase tautomers/isomers/rotamers produced in a molecular beam (e.g. adiabatic ionization energies, bond energies). Several examples will be presented. [3],[4],[5],[6],[7]

This work is a long term collaborative project involving colleagues from Synchrotron SOLEIL, CNRS, CEA, U. Paris Saclay, Sorbonne U., U. PE Créteil, U. Gustave Eiffel, U. Loraine, King Saud U., City U. Hong Kong, Chinese Academy of Sciences, and U. Tunis.

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PHOTO-INDUCED ULTRAFAST NUCLEAR DYNAMICS IN CORE-EXCITED MOLECULES

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Absorption of an X-ray photon by a molecule may lead to the excitation of a localized core electron to a specific unoccupied valence orbital. The created core-hole states are highly unstable and decay on a very short timescale emitting a photon (radiative decay) or a so-called *Auger* electron (non-radiative or *Auger* decay). Core excitation of molecules by soft x-rays creates core holes with lifetimes of a few femtoseconds (typically, 3-8 fs), which is a sufficient duration for light nuclei/atoms to move from their equilibrium geometry. This results in a competition between two dynamical processes: electronic relaxation of the excited system and its nuclear dynamics. Ultrafast dissociation (UFD) is an extreme example of such a competition, where electronic decay occurs after dissociation. UFD was reported for the first time for CS_2 and SF_6 molecules in 1978 [1] and HBr in 1986 [2]. Observing traces of ultrafast nuclear dynamics requires time-resolved experiments. Alternatively, high-resolution electron spectroscopy can be used to imprint signatures of nuclear dynamics, such as UFD, into resonant X-ray emission (RIXS) or Auger decay spectra.

In larger molecules, dissociation pathways are observed to deviate from the two-body dissociation coordinate due to the internal motion of light linkages, which alters dissociation rates and may yield heavy fragments on very short time scales. For example, the rotation of the $(CH_2)_2$-moiety may enable dissociation of the C—Br or C—Cl bond in the Br *3d* or Cl *2p* core-excited state of 1-bromo-2-chloroethane, whose lifetime counts only about 7 fs. [3]

More complete information on molecular dynamics is obtained by performing electron-ion coincidence measurements, where correlation of emitted electrons with ionic fragments allows disentangling dissociation mechanisms and even tracking evolution of the valence orbitals during dissociation [4].

Hard X-ray photons (>1 keV) may reach deeper-lying core electrons. The lifetime (τ) of deep-core-hole states is very short – of the order of 1 fs or below. The decay of a deep core hole is complex, and occurs via a series of subsequent relaxation steps. In general, intermediate states with one or multiple holes in the shallower core electronic shells are generated in the course of such cascades. The longer lifetime and steep potential energy surfaces of these intermediates may enable ultrafast nuclear dynamics and even bond breakages if the reduced mass of dissociated fragments is sufficiently low. This phenomenon was called multistep ultrafast dissociation (MUST UFD) to distinguish it from the single-step UFD induced by soft X-rays. [5-7]

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STATE-SELECTED ION-MOLECULE REACTIONS WITH VUV SYNCHROTRON RADIATION OF INTEREST FOR DEPOLUTION PLASMA DEVELOPMENT

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The measurements were performed in the the frame of a collaborative project aiming at a better description and optimization of industrial plasmas used for depollution of factory exhausts. To this end, the chemistry of ionic form of the major atmospheric species with main industrial pollutants has to be described in great detail.

In this contribution, we will present recent results on state-selected ion-molecule reactions obtained with the CERISES set-up: a quad/oct/oct/quad guided ion-beam experiment [1]. In these experiments, the photoionization of a neutral precursor by VUV synchrotron radiation and the TPEPICO technique are used to prepare state-selected cations before reaction, and absolute reaction cross sections are measured as a function of the cation excitation and collision energy.

Here, molecular oxygen, O_2 has been used to produce molecular ions by photoionization. By means of coincidence methods, they were prepared in selected, long-lived vibrational and electronic states (X, v=0-15 and a, v=0-4).

The reactivity with the propene, formaldehyde, acetone, ethanol molecule has been studied by varying the excitation energy and the collision energy, and recording the absolute cross sections of all ionic products, as well as branching ratios.

Contrasted results have been obtained, and though they can be described in terms of charge transfer and dissociative charge transfer, specific sensitivity to the ionic state as well as to the collision energy have been observed, and will be discussed.

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Photoelectron spectroscopy and circular dichroism of chiral oxirane radicals

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Oxirane derivatives are commonly used as model systems for chiral studies due to their small size and the rigidity of their three-member ring.[1] In addition, they often appear as key intermediates in chemical synthesis and reactions and have even been detected in the interstellar medium, albeit with no enantiomeric excess.[2] In this work, chiral oxirane radicals have been studied by photoelectron spectroscopy (PES) and circular dichroism (PECD) coupled to mass spectrometry, using circularly polarized light produced at the VUV DESIRS beamline, synchrotron SOLEIL (France), and double imaging electron/ion coincidence techniques. The radicals were produced in a fast flow reactor by H-abstraction using F atoms ($c\text{-}RH + F \rightarrow R^{\bullet} + HF$, $R=\{C_3H_5O, C_3H_2F_3O\}$). Several abstraction sites are possible and the exothermicity of the reaction leads to several cyclic and linear isomers. Nevertheless, a large dichroism is measured for the first time on reactive intermediates. I will show how this complex isomeric distribution can be determined in combination with theoretical methods and the important role that PES and PECD coupled to mass spectrometry can play in analytical chemistry.

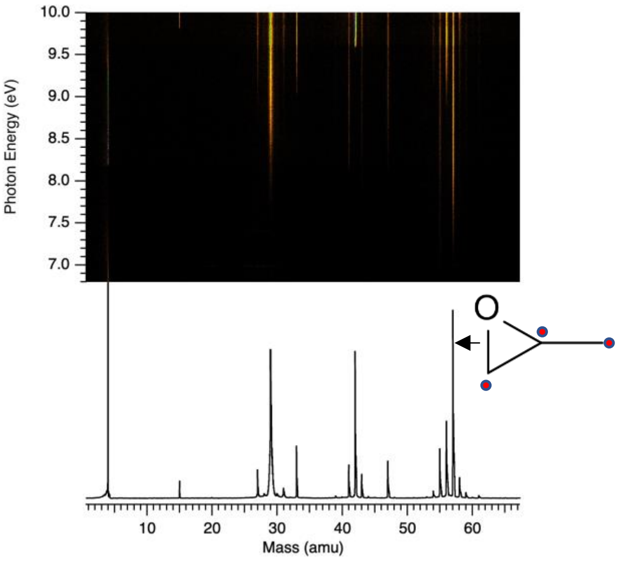

***Figure**: Time-of-flight mass spectra (TOFMS) as a function of photon energy (top) and integrated TOFMS (bottom) showing the complex chemistry occurring within the flow reactor after H abstraction from the methyloxirane precursor, including production of the C_3H_5O radicals at m/z 57. The red dots show the three possible abstraction sites.*

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CAGE-OPENING DYNAMICS OF ADAMANTANE

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Diamondoids are a class of carbon nanomaterials based on carbon cages with well-defined structures formed by C(sp3)-C(sp3)-hybridised bonds and fully terminated by hydrogen atoms. All diamondoids are variants of the adamantane molecule, the most stable among all the isomers with formula $C_{10}H_{16}$. A recent series of photoionisation experiments have been performed in various large-scale facilities to reveal the fragmentation dynamics of adamantane cations.

The initial experiment was done at Lund University using femtosecond XUV pulses produced via high-order harmonic generation and ion/electron spectroscopy [1]. As a main result we were able to show that the doubly charged adamantane molecule is metastable and will spontaneously dissociate. But, preceding dissociation, the cage structure will open and hydrogen migration(s) will occur (see Fig. 1). In addition, we were able to assess the energetic picture of the dication processes thanks to the measured ion and electron kinematics combined with theoretical calculations, allowing us to discuss the internal energy distribution of the system.

To delve deeper into adamantane's properties we recently performed a set of complementary studies such as time-resolved photoionisation experiments using pump-probe techniques (XUV-IR at the Lund Attosecond Science Center and XUV-XUV at the Free-electron laser FLASH2), core-ionisation measurements at the synchrotron SOLEIL (FR) and time-dependent photoabsorption spectroscopy at the cryogenic ring DESIREE (SE) from which preliminary results will be presented.

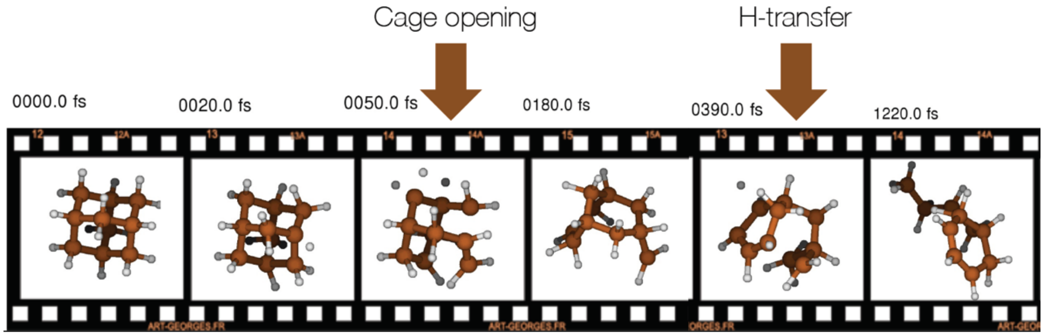

Figure 1: Molecular dynamics simulations showing the opening of the carbon cage.

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ENABLING INTERSTELLAR DETECTIONS USING SYNCHROTRON-BASED FAR-INFRARED SPECTROSCOPY

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New molecular identifications of molecules in the interstellar medium are intrinsically linked to their prior study in the laboratory, especially at the lowest frequencies of the electromagnetic spectrum where the recorded spectra act as identity cards. Current interstellar radio observations extend from the microwave domain well into the far-infrared (or terahertz) region. With its exceptional brightness and broadband coverage, synchrotron radiation has proven a well suited tool to investigate the latter spectral range which remains a challenging region, often referred to as the "terahertz gap" as a reflection of the lack of bright and broadband (or tunable) laboratory sources available for laboratory spectroscopy.

We are exploiting high resolution Fourier-transform far-infrared spectroscopy using synchrotron radiation to investigate the pure rotational and ro-vibrational spectra of astrophysically-relevant molecules on the AILES beamline of the SOLEIL synchrotron facility. The beamline is equipped with a Bruker IFS125 spectrometer allowing a highest resolution of 0.001 $\mathrm{cm^{-1}}$. Several set-ups have been developed in the last 15 years to study both stable and reactive species (transient molecules, radicals, ions), produced for instance by plasma sources. In this talk I will present an overview of our experimental capabilities illustrated by recent works that have enabled the first interstellar detections of NHD and ND_2, and the detection of new vibrational satellites of ethyl cyanide (propionitrile, CH_2CH_2CN) and aminoacetonitrile (NH_2CH_2CN).

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VACUUM-UV AND SOFT X-RAY INDUCED PHOTODESORPTION FROM MOLECULAR ICES

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Desorption induced by photon-impact on molecular solids, so-called photodesorption, is a process playing a central role in many fields of physics and chemistry. In astrochemistry, for instance, the desorption induced by UV or X-ray photons is one of the non-thermal processes that drive the balance between observed gas phase molecules and frozen molecular mantles coating the interstellar dust grains [1]. It is a key mechanism which could explain the otherwise puzzling observation of small organics molecules in the gas of the coldest regions of space, such as molecular clouds or protoplanetary disks. Photodesorption is also a process encountered in the development and running of the cryogenics parts of high energy accelerators and particle colliders, in which UV photons generated by synchrotron effect may induce molecular desorption from cryogenics walls, therefore limiting the vacuum performance of such systems [2].

In both cases, mechanisms of the photon-induced desorption, together with its absolute efficiency, must be known in order to either better understand molecular abundances in the interstellar medium, or to estimate and prevent its polluting action in the newest particle colliders, such as the FCC at the CERN.

These last years, we have developed an original experimental strategy which harnesses the high luminosity and tunability of the synchrotron radiation to quantitatively study the photodesorption from molecular ices. I will present the outcomes of these laboratory studies based on the use of the SOLEIL synchrotron facility – beamlines DESIRS and SEXTANTS – dedicated to understand and quantify the photodesorption processes in both the vacuum UV (7-13,6 eV) [3] and soft X-rays (500 – 1500 eV) [4] energy ranges respectively. The role played by the photon energy and of the molecular ice composition on the desorption yields will be highlighted, and I will present some outcomes of these studies on astrochemistry in the star- and planet-forming regions.

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HIGH-RESOLUTION FAR-INFRARED SPECTROSCOPY OF SPHERICAL-TOP MOLECULES USING SYNCHROTRON RADIATION

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Spherical-top molecules with tetrahedral or octahedral symmetry possess no permanent dipole moment and quite strict selection rules. As a consequence, some of their fundamental vibration bands are forbidden, in first approximation, in absorption spectroscopy; their purely rotational spectrum is very weak, being induced by centrifugal distortion or faint rovibrational interactions. Moreover, many of such molecules are quite heavy and consequently possess low-lying rovibrational state.

Far-infrared synchrotron radiation is thus an essential tool for the high-resolution absorption spectroscopy of such species, offering a high signal-to-noise ratio. In this presentation, we review the recent results obtained at the AILES Beamline of the SOLEIL Synchrotron facility concerning various species, especially some of atmospheric or planetary relevance: CF_4, SiF_4, SF_6 or GeH_4 (and some others). Such studies are essential in order to model low-lying states implied in hot band generation which are mandatory to provide quantitatively reliable line lists and databases for the atmospheric and astrophysical remote-sensing detection applications.

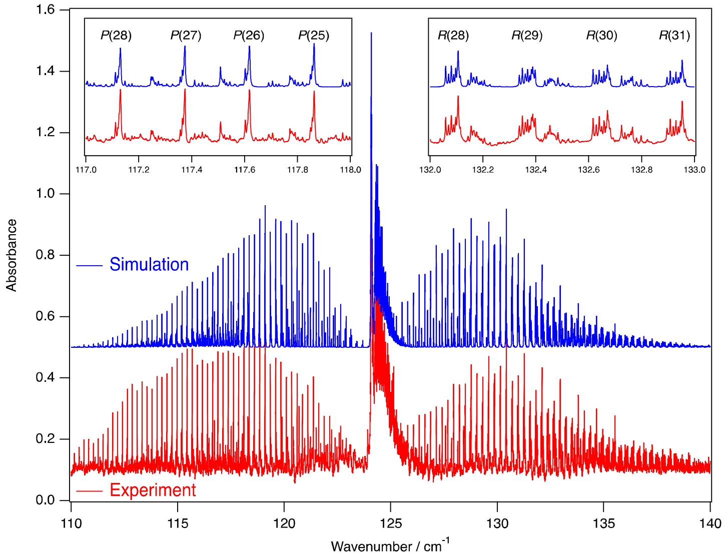

Figure 1: The ν_2–ν_4 difference band of SiF_4, in the far infrared.

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COMPETING ENERGY DISSIPATION PATHWAYS AT THE GAS-GRAIN INTERFACE: A STUDY OF ASTROPHYSICALLY-RELEVANT ICES

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The process of energy dissipation in solid water films is of key interest in the study of interstellar ices and their associated role in the development of molecular complexity in the interstellar medium. Icy interstellar grains are subjected to many forms of energetic processing, including cosmic ray bombardment, photon irradiation, thermal processing and surface reactivity. Ultimately all of these processes introduce energy into the grain which will then be dissipated, but the mechanisms involved are not yet fully constrained. To what extent does this energy modify the ice's structure and impact the ice surface's catalysis of atomic, radical and molecular reactivity?

Here, we provide an overview of recent experiments performed upon astrophysically-relevant amorphous and crystalline ices at the FELIX facility in the Netherlands. IR resonant vibrational excitation of stretching and bending modes in the molecular solid gives rise to competitive desorption and restructuring mechanisms, which we are beginning to unravel with the aid of molecular dynamics simulations.

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DE CURIE AU GANIL

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Femtosecond molecular dynamics at free-electron laser sources

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The recently developed free-electron laser (FEL) sources offer novel opportunities to investigate and even manipulate photoexcitation, photoionization and fragmentation dynamics in molecules. They provide ultraintense and ultrashort light pulses, which allows observing geometrical and electronic motion in molecules during radiation-induced structural changes on their natural timescale, e.g. femtoseconds.

Examples will be provided from experiments performed at different FELs. The focus will be on dynamics induced by multiphoton absorption, either in a pump-probe scheme or during a single pulse. Phenomena such as photoinduced structural deformation and radiation damage will be described.

The potential of the new FEL sources in obtaining information of unprecedented depth on molecular dynamics will be illustrated.

Tunable Free Electron Laser and IRMPD Spectroscopy: a perfect synergy to unravel the structure and reactivity of biomolecules in the gas phase

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Tandem mass spectrometry (MS/MS) is a key methodology to study biomolecules, with the electrospray ionisation (ESI) being one of the preferred ionization techniques [1]. It is well recognized as an efficient and highly versatile analytical tool [2], however its potential has long been limited by the structural information it can provide.

For this reason, the combination of tandem mass spectrometry with IR Multiple Photon Dissociation (IRMPD) spectroscopy has become a powerful tool for 3D structural characterisation of molecular ions in the gas phase [3].

Exploiting highly intense and widely tunable Free Electron Laser (FEL), IRMPD spectroscopy allows for the derivation of the vibrational fingerprint of molecular ions under tandem mass spectrometry (MS/MS) conditions [4]. Because resonant absorption of IR photons depends on molecular vibrations, the subsequent fragmentation event is highly structure specific, revealing characteristic functional groups of the molecule.

These kinds of experiments need to be performed with high power and widely tunable IR sources, i.e. free electrons lasers (FEL) at the FELIX (Free Electron Laser for Infrared eXperiment) facility in the Netherlands [5], and at the CLIO (Centre Laser Infrarouge d'Orsay) facility in France [6]. Their temporal structure and high brightness have been shown to be particularly suitable for inducing a rapid increase of the internal energy through an efficient resonant multiple photon absorption process [7]. Furthermore, they are easily tuneable in the mid-infrared region allowing for recording the IR spectra in the so-called IR fingerprint region.

Some examples of IRMPD spectroscopy performed at the CLIO Facility in Orsay are presented here to illustrate how IRMPD spectroscopy can be exploited to learn more about the molecules in space [8], to detect posttranslation modifications [9 and refs within] or to probe the structure of UV-Induced fragmentation products [10].

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APPLICATION OF NEAR EDGE X-RAY ABSORPTION MASS SPECTROMETRY FOR THE STUDY OF BIO-RELEVANT MOLECULES IN THE GAS PHASE.

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Over the past decades, biologically relevant macromolecules, such as peptides, proteins and oligonucleotides, have been investigated in the gas phase using state-of-the-art electrospray ionization sources, radiofrequency ion guiding and mass spectrometric techniques. These gas-phase experiments give the possibility to observe intrinsic properties in an isolated, solvent-free, environment. In order to obtain new insights into the electronic and structural properties of biomolecules, experimental approaches able to probe the electronic excitations, *e.g.* using VUV or soft X-ray photo-absorption, have been developed and carried out at synchrotron facilities, which offer a broad photon energy range and a high photon flux. In particular, Near-Edge X-ray Absorption Mass Spectrometry (NEXAMS), which is an action-spectroscopy technique based on fragment-resolved absorption upon resonant photoexcitation of core atomic levels, has been of growing interest in recent years for investigating the spatial and electronic structure of biomolecules. It has been used successfully to unravel various aspects of the photodissociation of peptides and to probe conformational features of proteins.

It is a current question to what extent the resonant photoabsorption spectra obtained by NEXAMS are sensitive to effects of conformational isomerism, tautomerism, and intramolecular interactions in gas-phase biomolecules. Additionally, in the soft X-ray regime, the high degree of localization of the deposited energy allows to obtain a deeper understanding on the dissociation processes. However, identifying products of site-selective dissociation in large biomolecules is challenging at the carbon, nitrogen, and oxygen edges because of the high recurrence of these atoms and related chemical groups. Probing a unique resonant excitation in a chemical bond or from an atom found only a single time within a biomolecule is a promising way to overcome this obstacle. I will present the principles of the NEXAMS technique as performed at the UE52_PGM Ion trap beamline (BESSY II, HZB, Berlin) as well as an overview of our recent results and current experimental and theoretical challenges.

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ACTIVATION AND SPECTROSCOPY OF MASS AND CHARGE SELECTED IONS STORED IN A LINEAR ION TRAP

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Gas phase spectroscopy offers the unique advantage of accessing intrinsic properties in the absence of solvent, and ultimately provides a mean to test theoretical methods. Biomolecules and large assemblies are fragile and difficult to bring intact in the gas phase and studies are usually limited to small building blocks and oligomers.

The so-called modern ionization techniques, such as electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) have demonstrated their potential to bring large, complex and fragile assemblies intact in the gas phase. However, direct absorption spectroscopy of ions is not trivial on such dilute targets while action spectroscopy offers a mean to circumvent the difficulties of measuring the attenuation of photon beams through ion clouds. Hence, mass spectrometry-based action spectroscopy provides unprecedented control over the target, such as the isotopic content and elemental composition, the charge, eventually the temperature, or the molecular shape/conformation in combination with ion mobility.

Action spectroscopy of bioorganic ions has been performed using synchrotron radiation in the VUV as an activation method. The targets are produced by ESI, stored and irradiated in the photon energy range of interest in an ion trap [1]. The products of the irradiation are monitored by measuring the mass spectrum after photon excitation. This method is sensitive to any changes of the mass-to-charge ratio of the product vs the precursor ion of interest, thereby allowing photoionization, photodetachment and photofragmentation dynamics to be studied.

In this talk, we will illustrate the potential of the method for analytical and structural chemistry as well as for gaining information on the electronic structure and the VUV photodynamic of a broad array of biomolecular targets.

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PHOTO- AND AUGER ELECTRON SPECTROSCOPIES OF PHTHALOCYANINES IN THE GAS PHASE

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Depuis leur découverte, les métallo-phthalocyanines (MPc) ont été extrêmement étudiées car ells présentent de ptentielles applications dans de nombreux domaines allant de la catalyse [1], l'optoélectronique [2] ou la photothérapie dynamique [3] pour en citer quelques uns. En utilisant le rayonnement synchrotron à SOLEIL, nous avons mesuré des spectres d'émission de la phthalocyanine de fer (FePc) en phase gazeuse sur une large gamme d'énergie nous permettant de répondre enfin à un débat vieux de plus de 60 ans [4] portant sur la caractérisation de son état fondamental électronique [5].

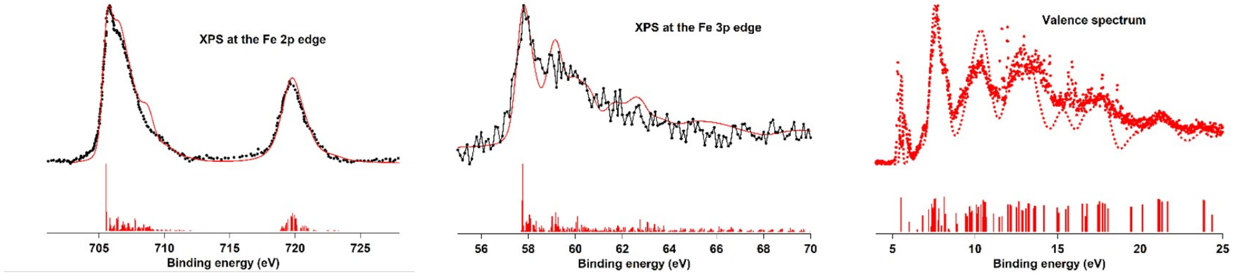

Figure 1: Spectres de photoelectrons de la phthalocyanine de fer mesurés à différentes énergies incidents et de liaisons, avec leurs spectres simulés respectifs par calculs DFT, pour le spectre de valence ou semi-empiriques basés sur la théorie des multiplets aux seuils 2p et 3p du fer.

Ces études sont un prérequis necessaire avant d'étudier des processus dynamiques résolus en temps dans des expériences pompe-sonde. Enfin, nous avons photoexcité FePc autour des résonances électroniques N 1s → OM* (Orbitale moléculaire non occupée) et observons, à l'énergie de liaison correspondant à un photoélectron 3p du fer, une augmentation de la section efficace au passage de ces résonances. Nous l'interprétons en terme de transfert d'excitation entre l'azote et le fer.

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IRRADIATION OF AN ISOLATED DNA DOUBLE HELIX BY CARBON IONS AT THE BRAGG-PEAK ENERGY

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Hadron therapy with protons and carbon ions is considered as a complementary therapy of conventional photon radiotherapy for cancer treatment, thanks to its advantages of precise targeting of the tumor, superior ballistic properties and biological efficiency to kill cells[1].These advantages are due to the physical processes playing a role in the interaction of MeV ions with biological tissues. The energetic ion beam deposits much of its energy at the end of its range (the Bragg peak), where the tumor is located. Cell death after tissue irradiation is believed to be mainly caused by DNA damage. Due to radical scavenging properties of the cell nucleus, around 50% of DNA nuclear damage *in vivo* is direct[2].

To obtain detailed mechanisms of direct DNA damage caused by ionizing radiation, many experiments have been done by using mass spectrometry to analyze the ionic products of isolated DNA building blocks[3] and nucleobase clusters[4], but only few reports exist on oligonucleotides[5,6]. Electron removal as well as fragmentation due to vibrational energy deposition have been found to occur. Herein, we report experimental results from the irradiation of an isolated DNA double helix by carbon ions at the Bragg peak energy. Non-dissociative single electron removal is the main process, but small fragments are also observed. The latter are less abundant than for the corresponding single strand: this is attributed to an increase of the size of the system. This is consistent with these fragments being formed after vibrational energy redistribution. Surprisingly, dissociation of the double helix into single strands is hardly observed, contrary to the case of collisions with a neutral gas at low kinetic energy in the CID experiments. Our results should have important implications for the physical and chemical mechanisms underlying hadrontherapy.

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PHOTOELECTRON CIRCULAR DICHROISM AS A PROBE FOR CONFORMATIONAL ISOMERISM IN 1-INDANOL

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Photoelectron circular dichroism (PECD) consists in a forward/backward asymmetry with respect to the light propagation axis in the photoelectron angular distribution after ionization of a chiral molecule by a circularly polarized light. PECD has shown a strong sensitivity to molecular conformations [1]. This is the reason why we applied this technique to a chiral flexible molecule: 1-indanol. Indeed, this molecule exists in one or two conformers in a supersonic beam, depending on the nature of the carrier gas (Figure 1)[2].

Figure 1: Conformations of the jet-cooled 1-indanol in argon (1_{eq}) and in helium (1_{eq} and 2_{ax})

Photoelectron spectra (PES) and PECD spectra of jet-cooled (S)-1-indanol and (R)-1-indanol were recorded in helium and argon at several photon energies on the DESIRS beamline at the SOLEIL Synchrotron. The PECD spectra exhibit a very good mirroring between the two enantiomers of 1-indanol in both carrier gases and show differences when changing the carrier gas (Figure 2) that we attribute to a clear conformational change.

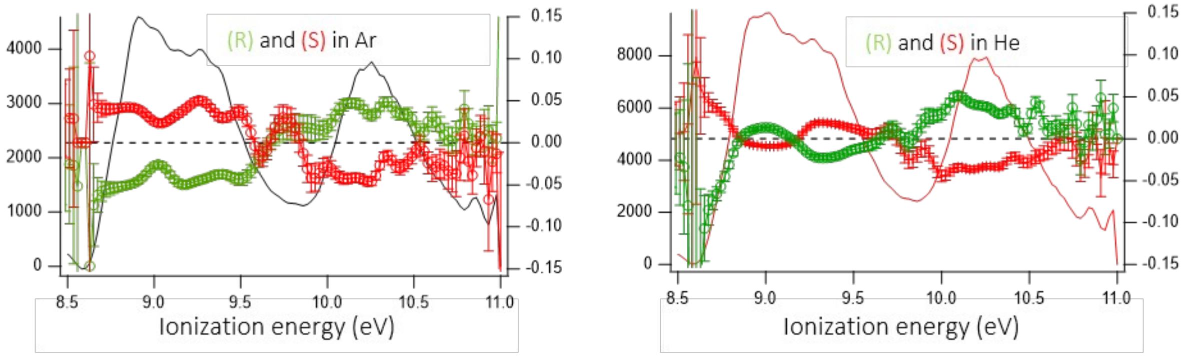

Figure 2: Photoelectron (left scale) and PECD (right scale) for 1-indanol in Ar and in He, at hν = 11.0 eV

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SURFACE CHEMISTRY OF GOLD NANOPARTICLES PRODUCED BY LASER ABLATION AND PERSPECTIVES AS PHOTOSENSITIZERS

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A promising nanoparticle (NPs) synthesis technique is based on laser irradiation of a solid target in a liquid environment. The Pulsed Laser Ablation in Liquids (PLAL) [1] method results in the formation of ligand-free NPs. These systems are well-suited for the development of technological applications [2] requiring subsequent surface functionalization or direct and controlled contact with an adjacent material. In addition, the surface chemical composition of the PLAL-generated NPs is expected to take part in the colloidal stability [3]. Their chemical characterization can be challenging since the environment or the probe itself can influence it. In this context, we develop an experimental study based on synchrotron radiation in free standing conditions, i.e. the NPs are analysed on the fly of a NPs beam. Using x-ray photoelectron spectroscopy, we probe their surface oxidation, the presence of adsorbed ions and their work function in order to answer to the following questions: (i) what is the origin of the colloidal stability despite the absence of any stabilizing agent? (ii) what is the role of the adsorbed ions? (iii) are there any ions in the volume of the NP? The results [4] collected at the PLEIADES beamline of the SOLEIL synchrotron facility will be presented as well as a perspective of the potential of these PLAL NPs for photovoltaic applications. Indeed, a precise knowledge and control of their surface chemical composition are of primary importance for driving their electronic properties.

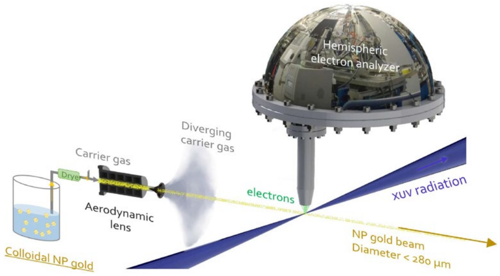

Figure 1: Experimental setup of the XPS chemical analysis of free-flying PLAL NPs at SOLEIL facility.

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PHOTOELECTRON ANGULAR DISTRIBUTIONS OF CHIRAL AEROSOL PARTICLES: CONDENSATION EFFECTS ON CHIRAL ASYMMETRIES

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Angle-resolved valence photoelectron spectroscopy is a valuable tool for the study of structural changes at the molecular level, occurring for example during the first steps of condensation. The photoelectron angular distribution can contribute additional information on the electronic orbital character and the kinetic energy-dependent scattering interaction of the photoelectron with the remaining ionic potential. For large molecular aggregates like aerosol particles, electron transport effects and the inhomogeneous light intensity distribution within the aerosol particle further affect the photoelectron angular distributions. I will present a study of the chiral angular asymmetries (photoelectron circular dichroism, PECD) in the photoemission of the amino acid serine, comparing the angular distribution of the isolated molecules with the angular distributions obtained for homochiral and racemic aerosol particles[1]. The latter still show a clear PECD distinguishable although other particle specific effects dominate the photoelectron angular distributions. The moderate reduction of the PECD between the gas phase and the particles is discussed in terms of various effects potentially affecting the angular distributions. In addition, I will discuss preliminary data on aerosol particles of the chiral amino acid tyrosine, which have been previously reported to show enhanced chiroptical effects, attributed to a chiral lattice effect[2].

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INVESTIGATION OF LIGAND ELECTRONIC EFFECTS ON IRON CYCLOPENTADIENYL COMPLEXES USING PHOTOELECTRON SPECTROSCOPY

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Organometallic complexes are key compounds in homogenous catalysis and their reactivity is closely related to the steric and electronic effects of the ligands within the complex. [1, 2] Photoelectron spectroscopy (PES) may be used as a fine probe of the electronic interaction between the ligand and the metal centre[3] . This method has been applied here to study tricarbonyl iron complexes of the type (Fe(CO)3L) with L being substituted cyclopentadiene ligands. Such complexes take part in hydrogen alkylation reactions[4] and reduction reactions[5].The experiments were carried out on the DESIRS beamline at the synchrotron SOLEIL facility, using e-/i+ coincidence techniques to obtain mass-selected PES of jet-cooled complexes. These spectra provide access to the ionisation energies and state-selected Fe-CO dissociation energies. Rationalization of the experimental results is further made using density functional theory and bond description methods to get information on the electronic structure of the complex and thus on the metal-ligand interaction.

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OVERVIEW OF NEUTRON SPECTROSCOPIC TECHNIQUES AND INSIGHT INTO THE MICROSCOPIC PROPERTIES OF WATER CONFINED IN NANOPORES

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Neutron scattering offers unique techniques for the study of molecular systems at the microscopic scale. Thanks to their wavelength and momentum, they provide a radiation that simultaneously probes the matter over atomic distances and energy of vibrational motions. It is therefore an ideal probe for structural studies but also spectroscopic ones, including vibrational and diffusive dynamics. I will present, in the first part of the talk, the specificities of neutrons techniques and their use in condensed and diluted systems.

I will then go deeper into the properties of water confined into different nanoporous materials: the soft polymeric membrane of Nafion and the crystalline metal organic framework ZIF-8.

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JET-COOLED FAR-INFRARED SPECTROSCOPY OF MOLECULES ON THE AILES BEAMLINE OF SOLEIL

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The "Jet-AILES" consortium brings together four laboratories, namely IPR Rennes, PhLAM Lille, MONARIS Paris 6, and AILES SOLEIL, with strong collaboration with ISMO Orsay. In 2009, our consortium equipped the AILES beamline with a supersonic jet facility. It was the first time that a beamline delivering far infrared radiation had benefited from such a device. There is currently no equivalent on the other third generation synchrotrons (Canadian Light Source, Swiss Light Source and Australian Synchrotron).

This supersonic jet apparatus, called Jet-AILES, is coupled to the high-resolution Fourier transform interferometer (Bruker IFS125HR) which equips the AILES beamline. It is used to obtain rotation-vibration absorption spectra of molecular species in the gas phase, at very low temperature (between 10 and 100 K) with a resolution down to 0.001 cm-1. The use of very low temperatures is essential to simplify the sometimes very complex spectral signature of polyatomic molecules, or to stabilize molecular van der Waals complexes, while far infrared reveals low lying vibrational modes characteristic to heavy molecules and weakly bound complexes (intermolecular modes).

This cooling process has proved to be very effective in disentangling the structures of the spectra of methoxyphenols [1], trans-butadiene [2], and especially of naphthalene (C10H8) [3], made up at room temperature of a tangle of overlapping cold and hot vibrational bands. It has also been applied to the study of the conversion of the nuclear spin of the water molecule in supersonic expansions [4], and to the determination of the conformational structure of amino-ethanol and its dimer [5]. The detection of molecular complexes with low non-covalent bond, stabilized by the very low temperatures reached in the adiabatic expansion, represents a further step in the experimental difficulty. However, we were able to form and to observe the (CH2)2O-H2O hetero-complex [6] and to differentiate unambiguously the absorption bands of the monomer and dimer of acetic acid [7] or formic acid. Finally, this is the first time that the planar cyclic structure of the HF trimer has been experimentally proven [8].

In this talk, I will discuss some advantages and limitations of the Jet-AILES set-up. The low density of the jet often limits the use of the synchrotron beam so that it is sometimes more judicious to use the internal light sources of the spectrometer to get a better signal-to-noise ratio. A new modulation concentration technique proposed by Gruet and Pirali [9] and adapted from an approach currently used in laser spectroscopy [10], should overcome such limitation.

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ON THE STRUCTURE AND ELECTRONIC SPECTRA OF EXCITED NEUTRAL ARGON RARE GAS CLUSTERS USING HOLE PARTICLE PSEUDOPOTENTIAL METHOD

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The structures of neutral excited Argon clusters are investigated using Hole-Particle Pseudopotential (HPP) [1] and compared with previous results [2] obtained using Diatomic-In-Molecules (DIM) method parametrized using CI potential energy curves [3].

The global minimum structures for excited Argon for N ≤ 13 are explored which differ from what was observed previously using diatomic-in-molecules approach. To parametrize DIM, the effect of diabatization is also investigated. The lowest energy isomer of trimer is observed to be linear anti-symmetric (C2v symmetry) instead of linear-symmetric (D∞h symmetry) as shown in figure 1.

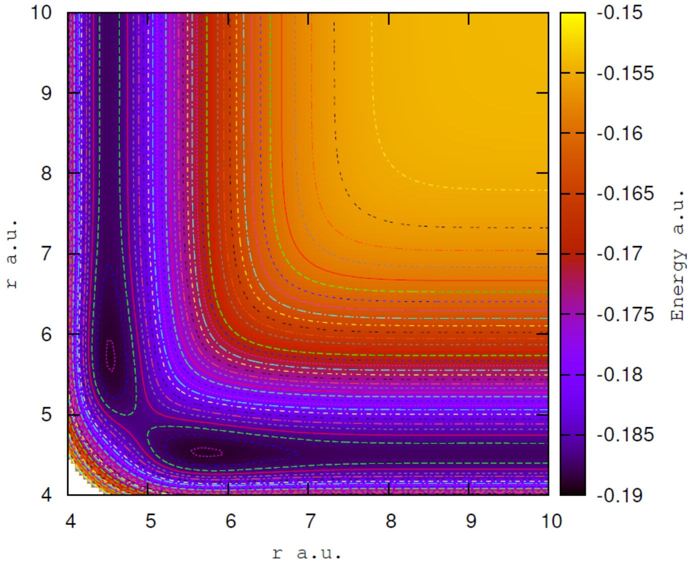

Figure 1: Potential Energy surface for excited Argon trimer linear system.

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Toward a better description of proteins electronic structure in a solvated state using electron spectroscopy

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Although widely studied, the interaction between high-energy ionizing radiations and matter remains of major interest as it underlies many fields from nuclear industry to medicine. The early stages of dose deposition processes have proven to be critical in terms of biological damage, as they initiate electron emission processes[1]. X-ray Photoelectron spectroscopy (XPS) has proven to be a powerful tool for studying surfaces. It is also emerging as a method of choice for the study of biological samples as it provides information on the chemical environment and thus helps to understand the composition and the chemical state of the biomolecules under study[2].

An under-vacuum liquid microjet set-up[3], with liquid collection capability, was here used to investigate the solvation of a protein, the bovine serum albumin (BSA). This set-up, presented in Figure 1, has shown to be a great tool for the elemental and chemical analysis of such fragile biomolecules embedded in water, without inducing structural damages. The XPS spectral structures of carbon and nitrogen were resolved and compared to charge distributions calculations. It demonstrated the great difficulty of assigning chemical contributions in complex systems in an aqueous environment state and highlighted the discrepancies in spectroscopic interpretations in the literature. This work also includes a thorough study of the valence band maximum and its position in relation to the Fermi level. Experimental results were compared to theoretical calculations to distinguish the elemental contributions in the electronic structure. All measurements were also conducted in the solid state (laboratory XPS analysis) in order to reveal solvation processes.

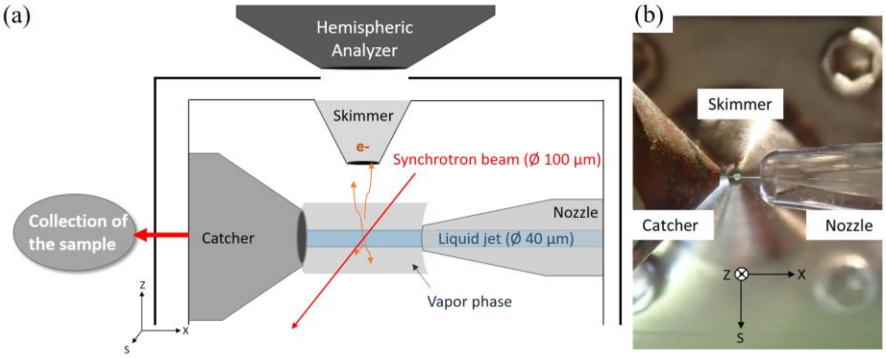

Figure 1:(a) Scheme of the under vacuum liquid-jet set-up used to perform electron spectroscopy experiment (b) Photography of the liquid jet assembly.

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