13th SOLEIL USERS' MEETING

JANUARY 18th & 19th, 2018

EDF Lab Paris-Saclay (Palaiseau) & SOLEIL (Saint-Aubin)

SCIENTIFIC COMITTEE

Marie d'ANGELO (Institut des Nanosciences de Paris)
Vincent BOUDON (Lab. Interdisciplinaire Carnot de Bourgogne, Dijon)
Noemi CARMONA-TEJERO (Université Complutense, Madrid)
Frédéric DATCHI (IMPMC - Paris)
Nicolas DELSUC (ENS Département de Chimie - Paris)
Jean-Sébastien GIRARDON (Unité de Catalyse et de Chimie du Solide - Lille)
Yann GOHON (Institut Jean-Pierre Bourgin - Versailles)
Renaud GUILLEMIN (LCPMR - Paris)
Thomas MAROUTIAN (Université Paris-Sud)
Rémi MARSAC (Université de Rennes 1 - Rennes)
Benoît MASQUIDA (IPCB - Plateforme de Biologie - Strasbourg)
Karine PROVOST (Institut de Chimie et des Matériaux de Paris-Est - Thiais)

Satellite Workshop

ivMX 2018
In vivo macromolecular crystallography: Advances and Perspectives
January 16th & 17th, 2018
SOLEIL (Saint-Aubin)

Information and registration:
www.synchrotron-soleil.fr/en/events/sum-2018

SOLEIL SYNCHROTRON

Welcome

The 13th SOLEIL Users' Meeting takes place on January 18th and 19th, 2018 at EDF Lab Paris-Saclay and at SOLEIL.

This invaluable forum for the synchrotron radiation users' community provides, the occasion to share scientific, technical and practical issues about the synchrotron radiation use.

The 3 plenary lectures deal with different aspects related to recent and future synchrotron sources evolutions:

- Diluted Matter
- Materials
- Cultural Heritage

A social programme with a buffet dinner is held at SOLEIL on the afternoon of January 19th in conjunction with the posters session, commercial exhibitions and visits of the following three beamlines:

- ANATOMIX
- NANOSCOPIUM
- PUMA

The Roger Fourme prize (student poster best prize) is awarded before the dinner buffet on January 18th.

Two tutoriols are organized at SOLEIL on Friday afternoon, January 19th, 2018:

- « FOXTROT software: from detector images to measurements, first steps after data acquisition in SWING beamline »
- « Processing of multi-modal x-ray imaging datasets on the NANOSCOPIUM beamline »

Bienvenue

Le 13ème Colloque des Utilisateurs de SOLEIL a lieu les jeudi 18 et vendredi 19 janvier 2018, à EDF Lab Paris-Saclay et à SOLEIL.

Ce rendez-vous incontournable pour la communauté des utilisateurs du rayonnement synchrotron est le lieu pour échanger sur les aspects scientifiques, techniques et pratiques de l'utilisation du rayonnement synchrotron.

Les **3 conférences plénières** abordent différents thèmes de recherche de la communauté des utilisateurs de SOLEIL :

- Matière Diluée
- Matériaux
- Patrimoine

Un temps de convivialité et de discussion est organisé à SOLEIL le jeudi 18 janvier après-midi avec la séance posters, les stands d'entreprises, la visite des lignes suivantes :

- ANATOMIX
- NANOSCOPIUM
- PUMA

La remise du prix Roger Fourme (Prix de meilleur poster étudiant) a lieu avant le buffet dinatoire le 18 janvier.

Deux formations pratiques sont organisées à SOLEIL le vendredi 19 janvier 2018 après-midi :

- « FOXTROT : des images du détecteur aux mesures, premiers pas du traitement des données sur la ligne SWING »
- « Traitement de données d'imagerie X multi-modale sur la ligne NANOSCOPIUM »

SOLEIL Users' Meeting

January 18th - 19th, 2018

EDF Lab Paris-Saclay – France & Synchrotron SOLEIL, Saint-Aubin - France

Summary

- Programme
- Plenary Session
- Parallel Sessions:
  - Ancient & New Materials
  - Dynamic, Reactivity & Chemical analysis Diluted Matter
  - Life & Earth Sciences
- Posters Session
  - List of Student Posters
  - List of other posters
- Tutorials
- List of Industrial Exhibitors
- Companies Advertisements

EDF Lab Paris-Saclay – France
&
Synchrotron SOLEIL, Saint-Aubin - France

Programme

Thursday, January 18th

EDF Lab PARIS-SACLAY

09:00 - 10:00	Registration & coffee
10:00 - 10:10	Welcome / Introduction ***Jean-Sébastien Girardon*** *- ORGUES Chairperson*
10:10 - 10:20	The word of SOLEIL General Director ***Jean Daillant***
10:20 - 11:05	Materials : Molecular semimetallic hydrogen and high temperature superconductivity ***Mikhail Eremets*** *- Max Planck Institute for Chemistry, Mainz, Germany*
11:05 - 11:50	Cultural heritage : Tri-modal (X-ray fluorescence, reflectance and molecular fluorescence imaging spectroscopy) investigation of works of art ***John K. Delaney*** *- National Gallery of Art, Washington DC, USA*
11:50 - 12:10	Peer Review Committee Chairman 3 (5mn) – ***René Guinebretière*** Peer Review Committee Chairman 4 (5mn) – ***Fabienne Testard*** Questions 10mn
12:10 - 13:45	*Lunch*
	Parallel sessions (see the detailed programme below)
13:45 - 15:15	• Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces) • Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry) • Life & Earth Sciences (Biology / Health & Environment / Geoscience)

15:15 - 15:45 *Coffee break*

Parallel sessions (see the detailed programme below)

15:45 - 17:15
- Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces)
- Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry)
- Life & Earth Sciences (Biology / Health & Environment / Geoscience)

Transfer to SOLEIL (17h30)

17:45 - 20:00 Posters session / Commercial exhibition / ORGUES and AFURS Booth

18:30 - 20:00 Visit of 3 Beamlines (ANATOMIX / NANOSCOPIUM / PUMA)

19:30 - 21:00 *Buffet /* Award of the best student poster

Friday, January 19th

EDF Lab PARIS-SACLAY

9:00 - 09:45
Diluted matter:
VUV Synchrotron radiation: A precious tool for unrevealing the properties of cosmic PAHs
Christine Joblin *- IRAP, Université de Toulouse, France*

Parallel sessions (see the detailed programme below)

9:50 - 10:50
- Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces)
- Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry)
- Life & Earth Sciences (Biology / Health & Environment / Geoscience)

10:50 - 11:20 *Coffee break*

Parallel sessions (see the detailed programme below)

11:20 - 12:50
- Ancient & New Materials (Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces)
- Dynamic, Reactivity & Chemical analysis (Diluted Matter & Chemistry)
- Life & Earth Sciences (Biology / Health & Environment / Geoscience)

Synthesis and discussion with SOLEIL Management

12:55 - 13:10 Conclusion

13:10 - 14:30 *Lunch*

Transfer to SOLEIL (14h45)

2 tutorials (reserved to registered participants)

15:00 - 18:00
- « FOXTROT *software: from detector images to measurements, first steps after data acquisition in SWING beamline* »
- « Processing of multi-modal x-ray imaging datasets on the NANOSCOPIUM beamline »

Parallel Sessions Schedule

Ancient & New Materials
(Cultural heritage / Structure / Electronic Properties /Surfaces & Interfaces)

Chairpersons:
Marie d'Angelo, Karine Provost, Noemie Carmona-Tejero,Thomas Maroutian & Frédéric Datchi

Thursday, January 18th

AUDITORIUM - EDF Lab PARIS-SACLAY

13:45 - 14:15 (25'+5')	Probing a microelectronic device's active atoms through operando experiments at SOLEIL ***Martin Bowen -*** *Institut de Physique et Chimie des Matériaux de Strasbourg, France*
14:15 - 14:35 *(15'+5')*	In-situ X-ray diffraction studies on piezoelectric thin films ***Thomas Cornelius -*** *IM2NP, Marseille, France*
14:35 - 14:55 *(15'+5')*	Amorphous - crystalline transition mechanism of phase change materials: GeTe thin films ***Manon Gallard –*** *Synchrotron SOLEIL, Gif-sur-Yvette and IM2NP, Marseille, France*
14:55 - 15:15 *(15'+5')*	Reversible strain alignment and reshuffling of nanoplatelet stacks confined in a lamellar block copolymer matrix ***Emmanuel Beaudoin*** *- Laboratoire de Physique des Solides, Orsay, France*
15:15 - 15:45	*Coffee break*
15:45 - 16:15 (25'+5')	Nanoparticle-based resistive strain Gauges: Fabrication and characterization by small angle X-ray scattering coupled with in-situ electromechanical measurements ***Laurence Ressier -*** *LPCNO, Université de Toulouse, France*
16:15 - 16:35 *(15'+5')*	Investigation by X-ray natural linear dichroism (XNLD) and X-ray magnetic circular dichroism (XMCD) towards magnetic properties of 6nm $CsNiCr(CN)_6$ nanoparticles single layer assembled on graphite ***Luqiong Zhang*** *- ICMMO, Orsay and IMPMC, Paris, France*
16:35 - 16:55 *(15'+5')*	Chemical nature and beam sensitivity of photochromatic images investigated by Ag K-edge quick spectroscopy ***Victor de Seauve*** *- Centre de recherche sur la conservation, Paris, France*
16:55 - 17:15 *(15'+5')*	Time resolved X-ray diffraction for stress measurements during ultrasonic fatigue tests ***Nicolas Ranc*** *- PIMM, Paris, France*

Parallel Sessions Schedule

Ancient & New Materials
(Cultural heritage / Structure / Electronic Properties /Surfaces & Interfaces)

Chairpersons:
Marie d'Angelo, Karine Provost, Noemie Carmona-Tejero,Thomas Maroutian & Frédéric Datchi

Friday, January 19th

AUDITORIUM - EDF Lab PARIS-SACLAY

09:50 - 10:10 (15'+5')	Structural and magnetic phase diagram of magnetocaloric $Y_{0.9}$ $Gd_{0.1}$ Fe_2H_y hydrides ***Valérie Paul-Boncour*** *- ICMPE, Thiais, France*
10:10 - 10:30 (15'+5')	Phase diagram of ammonia monohydrate at high pressure and temperature ***Haiwa Zhang*** *- Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Paris (France)*
10:30 - 10:50 (15'+5')	Spectroscopic evidence of a new scale for superconductivity in H_3S ***Benjamin Langerome*** *- Synchrotron SOLEIL, Gif-sur-Yvette, France*
10:50 - 11:20	*Coffee break*
11:20 - 11:50 (25'+5')	Interfacing magnetic oxides – Insights by photoelectron spectroscopy ***Martina Müller*** *- Centre de recherche de Jülich & T. Univ. Dortmund, Germany*
11:50 - 12:10 *(15'+5')*	Electronic structure of two-dimensional WS_2/Graphene van der Waals heterostructures ***Julien Rault*** *- Synchrotron SOLEIL, Gif-sur-Yvette, France*
12:10 - 12:30 *(15'+5')*	Increasing the magnetic anisotropy through onion-like magnetic nanoparticles ***Kevin Sartori*** ***-*** *IPCMS, Strasbourg and Synchrotron SOLEIL, Gif-sur-Yvette, France*
12:30 - 12:50 (15'+5')	Direct measurement of lateral correlations under controlled nano-confinement: The long-range attraction between hydrophobic surfaces ***Patrick Kékicheff*** *- Institut Charles Sadron, Strasbourg, France*

Parallel Sessions Schedule

Dynamic, Reactivity & Chemical analysis
(Diluted Matter & Chemistry)

Chairpersons:
Jean-Sébastien Girardon, Nicolas Delsuc, Vincent Boudon and Renaud Guillemin

Thursday, January 18th

AMPHIS 1& 2 - EDF Lab PARIS-SACLAY

13:45 - 14:15 *(25'+5')*	Study of electrochemical mechanisms in batteries: Contribution and limits of X-ray absorption spectroscopy ***Lorenzo Stievano*** *- Institut Charles Gerhardt, Montpellier, France*
14:15 - 14:35 *(15'+5')*	Decoupling cationic–anionic redox processes in lithium-ion battery cathodes via operando XAS ***Gaurav Assat*** *- Collège de France, Paris, France*
14:35 - 14:55 *(15'+5')*	Electrochemical and spectroscopic study of Eu(III)/(II) redox couple in the ehtylmethylimidazolium bis(trifluromethanesulfonyl)imide ionic liquid ***David Bengio*** *- CEA Marcoule, Bagnols-sur-Cèze, France*
14:55 - 15:15 *(15'+5')*	Shape-controlled nanoparticle assembly mediated by electrostatic complexation with long polyelectrolyte chains ***Florent Carn*** *– Laboratoire Matière et Systèmes Complexes, Paris, France*
15:15 - 15:45	*Coffee break*
15:45 - 16:15 *(25'+5')*	Creation of double K-shell vacancies with a single photon: How and why? ***Francis Penent*** *- Laboratoire de Chimie Physique-Matière et Rayonnement, Paris, France*
16:15 - 16:35 *(15'+5')*	Multistep ultrafast dissociation and its control by hard X-ray photons ***Oksana Travnikova*** *- LCPMR, Paris and Synchrotron SOLEIL, Gif-sur-Yvette, France*
16:35 - 16:55 *(15'+5')*	Structural study of uranyl bisphosphonate-based ligands as potential uranium decorporation agents ***Gaoyang Ye*** *- CNRS-IN2P3, Orsay, France*
16:55 - 17:15 *(15'+5')*	Approaching the limits of cationic and anionic electrochemical activity with the Li-rich layered rocksalt Li_3IrO_4 ***Antonella Iadecola*** *- RS2E, Amiens and Synchrotron SOLEIL, Gif-sur-Yvette, France*

Parallel Sessions Schedule

Dynamic, Reactivity & Chemical analysis
(Diluted Matter & Chemistry)

Chairpersons:
Jean-Sébastien Girardon, Nicolas Delsuc, Vincent Boudon and Renaud Guillemin

Friday, January 19th

AMPHIS 1& 2 - EDF Lab PARIS-SACLAY

09:50 - 10:10 *(15'+5')*	XAS study of Rh-based catalysts for the hydrogenation of butadiene ***Claudia Zlotea*** *- Institut de Chimie et des Matériaux Paris-Est, Thiais, France*
10:10 - 10:30 *(15'+5')*	Tailoring the reactivity of oxide-supported Pd-based nanoparticles ***Alina Vlad*** *– Synchrotron SOLEIL, Gif-sur-Yvette, France*
10:30 - 10:50 *(15'+5')*	Evidencing the Mo/W regioselectivity at the pentagonal motifs within giant polyoxometalates ***Emmanuel Cadot*** *- Institut Lavoisier de Versailles,France*
10:50 - 11:20	*Coffee break*
11:20 - 11:50 *(25'+5')*	Multimodal imaging of lipids and metals on liver tissue sections ***François Le Naour*** *– Hôpital Paul Brousse, Villejuif, France*
11:50 - 12:10 *(15'+5')*	Labeling of hyaluronic acids with a re-tricarbonyl tag and percutaneous penetration into human skin studied by multimodal imaging ***Lucas Henry*** *- Laboratoire des Biomolécules, Paris, France*
12:10 - 12:30 *(15'+5')*	Exploring the surface and reactivity of copper nanoparticles with in situ FT-IR ***Xavier Frogneux*** *- Laboratoire de Chimie de la Matière Condensée de Paris, France*
12:30 - 12:50 *(15'+5')*	Electronic effects of phosphines bound to molybdenum complexes ***Héloïse Dossmann*** *- Institut Parisien de Chimie Moléculaire, Paris, France*

Parallel Sessions Schedule

Life & Earth Sciences
(Biology / Health & Environment / Geoscience)

Chairpersons:
Benoît Masquida, Yann Gohon, and Remi Marsac

Thursday, January 18th

ROOMS A1.116-A1.140 - EDF Lab PARIS-SACLAY

13:45 - 14:15 (25'+5')	Structural model of PRORP2-tRNA complex interaction build it by the combination of crystal, in solution structures with biophysical characterization ***Pablo Fernandez-Millan*** *– Autonomous univeristy of Barcelona, Cerdanyola del Vallès, Spain*
14:15 - 14:35 *(15'+5')*	Structure and regulation of a GTPase system that regulates bacterial motility ***Christian Galicia*** *– Laboratoire de Biologie et Pharmacologie Appliquée, Cachan, France*
14:35 - 14:55 *(15'+5')*	Soft X-ray imaging and spectroscopy for biological samples on HERMES beamline ***Camille Rivard*** *– Soleil Synchrotron, Saint-Aubin, France*
14:55 - 15:15 *(15'+5')*	Determinants of neuroglobin plasticity highlighted by high pressure crystallography and crystallography under moderate gas pressure ***Nathalie Colloc'h*** *– ISTCT CNRS UNICAEN CEA Normandie univ., CERVOxy team, centre Cyceron, Caen, France*
15:15 - 15:45	*Coffee break*
15:45 - 16:15 (25'+5')	Exploring the speciation of thallium in soil using synchrotron-based X-ray (micro)spectroscopies ***Andreas Voegelin*** *– Eawag, Dübendorf, Switzerland*
16:15 - 16:35 *(15'+5')*	Structure and oxidation of moderately volatile elements (Sn and Zn) in natural silicate melts ***Paolo Sossi*** *– Institut de physique du globe, Paris, France*
16:35 - 16:55 *(15'+5')*	Magnetotactic bacteria studied with scanning transmission X-ray microscopy ***Lucas Le Nagard*** *– McMaster University, Hamilton, Canada*
16:55 - 17:15 *(15'+5')*	Overcoming radiation artifacts In X-ray cryomicrospectroscopy: Case study of thallium speciation in soil manganese concretions ***Francesco Femi Marafatto*** *– Paul Sherrer Institut , Villigen, Switzerland*

Parallel Sessions Schedule

Life & Earth Sciences
(Biology / Health & Environment / Geoscience)

Chairpersons:
Benoît Masquida, Yann Gohon, and Remi Marsac

Friday, January 19th

ROOMS A1.116-A1.140 - EDF Lab PARIS-SACLAY

09:50 - 10:20 *(25'+5')*	The archaeal acetoacetyl-CoA-thiolase/HMG-CoA-synthase complex channels the intermediate via a fused CoA-binding site ***Tristan Wagner** –Max Planck Institute for Terrestrial Microbiology, Marburg, Germany*
10:20 - 10:50 (25'+5')	Structural basis for alternate substrate recognition and processing by a bifunctional viral protease/deubiquitinase ***Stéphane Bressanelli** - Institute for Integrative Biology of the Cell, Gif-sur-Yvette, France*
10:50 - 11:20	*Coffee break*
11:20 - 11:50 (25'+5')	The ascent of sap and xylem vessel (dis)content: 4 centuries of debate ***Sylvain Delzon** –Université de Bordeaux,Talence, France*
11:50 - 12:10 *(15'+5')*	Structure-function analysis of the R2TP cochaperone complex, recruiting HSP90 for macromolecular complex assembly. ***Julien Henri** – Institut de Biologie Physico-Chimique, Paris, France*
12:10 - 12:30 *(15'+5')*	Membrane-active properties of an amphitropic peptide from the CyaA toxin translocation region ***Alexis Voegele** – Institut Pasteur, Paris, France*
12:30 - 12:50 *(15'+5')*	Multimodal analysis from the DUV to the NIR of the endogenous fluorescence of brain tumor biopsies ***Fanny Poulon** – Imagerie et Modellisation en Neurobiologie et Cancerologie, Orsay, France*

PLENARY SESSION

PLENARY SESSION

Thursday, January 18th

PT-01	Materials : Molecular semimetallic hydrogen and high temperature superconductivity ***Mikhail Eremets*** *- Max Planck Institute for Chemistry, Mainz, Germany*
PT-02	Cultural heritage : Tri-modal (X-ray fluorescence, reflectance and molecular fluorescence imaging spectroscopy) investigation of works of art ***John K. Delaney*** *- National Gallery of Art, Washington DC, USA*

Friday, January 19th

PT-03	Diluted matter: VUV Synchrotron radiation: A precious tool for unrevealing the properties of cosmic PAHs ***Christine Joblin*** *- IRAP, Université de Toulouse, France*

Molecular Semimetallic Hydrogen and High Temperature Superconductivity

M. I. Eremets

Max-Planck-Institut fur Chemie, Hahn-Meitner Weg 1, 55128 Mainz, Germany

ABSTRACT

Studies of metallic hydrogen and hydrogen-dominant materials will be reviewed based mostly on the results of our group.

More than 80 years ago Wigner and Hungtinton [1] predicted that insulating molecular hydrogen will dissociate to atomic metallic hydrogen at a high pressure. Another less known possible way of metallization is in the molecular state, through gradual overlapping of electronic bands [2]. Current calculations are not precise enough to predict which way of metallization is actual. Our experiments [3] indicate that hydrogen transforms to metal in the molecular state at a pressure of about 350 GPa when reflection of the sample significantly increases. At this pressure, hydrogen has poor electrical conductivity while showing metallic temperature dependence. With increasing pressure, electrical conductivity measured up to 440 GPa strongly increases. At the same time the molecular state persists. At higher pressures up to 480 GPa, the Raman spectra of the molecular hydrogen disappear indicating further transformation to a good molecular metal or to an atomic state.

Our conclusion that the molecular hydrogen is semimetal at pressures above ~350 GPa is consistent with the recent theoretical works [4-6] showing that the metallization happens through closing of an indirect band gap in molecular hydrogen at pressure of ~350 GPa, and the system starts behaving as a bad metal. With the increase of the band overlap, the electrical conductivity gradually increases to a typical metallic value. This process occurs over a range of pressures of ~200 GPa, Thus a predicted high temperature superconductivity in hydrogen [7] can be found likely at pressures of >~500 GPa.

Before the pure hydrogen, the high temperature superconductivity was found in a hydrogen-dominant material [8] with record T_c=203 K in H_3S [9]. The superconductivity has been well established experimentally with the aid of different techniques. In particular, the infrared studies were done at SOLEIL. This conventional superconductivity was analyzed in numerous theoretical works. In particular, it was shown that the major input (~90%) in the superconductivity is from hydrogen part of the phonon spectrum, and therefore H_3S can be considered as doped atomic metallic hydrogen. Prospects of reaching room temperature superconductivity will be discussed too.

REFERENCES

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Tri-modal (X-ray Fluorescence, Reflectance and Molecular Fluorescence Imaging Spectroscopy) Investigation of Works of Art

J.K. Delaney, and K.A. Dooley

National Gallery of Art, Washington DC, USA

ABSTRACT

Combining site-specific results from different analytical methods provides a higher level of confidence in the identification of artist materials. Analyzing an area using techniques such as x-ray fluorescence imaging spectroscopy (XRF-IS) and reflectance imaging spectroscopy (RIS), plus molecular fluorescence imaging spectroscopy (FIS) is the logical next step, and extends the data collection to two spatial dimensions. Here we describe a novel tri-modal scanner along with case studies showing the utility of having such data sets. The scanner system operates by moving the artwork on a two-axis computer-controlled easel in front of a series of stationary sensors. This allows for a variety of imaging sensor modules to be used. The easel provides three scan modes: raster, line, and step/stare over a 1.5 m^2 collection area. Novel registration software allows the spatial alignment of the resulting spectroscopic images with the reference color images and x-radiographs.

Case studies of artwork in the National Gallery of Art's collection, such as paintings and works on paper, will be presented that show the utility of having such registered multimodal data. Concepts for using the hyperspectral reflectance and fluorescence camera systems on the micro-scale with synchrotron light sources will be presented as well.

Bio: John K. Delaney, Ph.D. is the Senior Imaging Scientist at the National Gallery of Art, where his research focuses on the application of remote sensing methods to assist in the study of works of art.

VUV Synchrotron Radiation: A Precious Tool for Unrevealing the Properties of Cosmic PAHs

C. Joblin

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ABSTRACT

For astronomers, polycyclic aromatic hydrocarbons (PAHs) are very small dust particles that play a key role in the chemical and physical evolution of star-forming regions from the small scales of protoplanetary disks to the large scales of galaxies.

Cosmic PAHs and related species such as C_{60}, are observed by their emission features in the mid-infrared, following the absorption of VUV photons. Over than radiative cooling, the interaction with VUV photons can trigger ionisation and unimolecular dissociation. These processes impact the charge and hydrogenation states as well as the survival of PAHs in cosmic environments [1]. VUV processing of very small carbonaceous grains was also proposed as a possible top-down mechanism to produce PAHs in the gas-phase at the UV-irradiated surface of molecular clouds [2].

In my presentation, I will discuss how this subject has greatly benefited from the availability of VUV tunable synchrotron radiation. I will summarize the results of experiments that were mainly obtained on the DESIRS beamline at SOLEIL. Both imaging photoelectron photoion coincidence spectroscopy (PEPICO) and ion trap techniques were used to study the interaction with VUV photons of PAHs [3-6], C_{60} [7] and PAH clusters as models of carbonaceous nanograins [8]. I will also describe coming exciting perspectives. These include observations with the James Webb Space Telescope [9] but also experiments on new types of C-nanograins analogues such as the ones synthetized in the Nanocosmos Stardust machine in Madrid [10]. The molecular analysis of these samples [11], combined with that of extraterrestrial samples such as meteorites, is expected to provide new insights into chemical pathways leading to the formation of cosmic PAHs. I will illustrate how these analytical experiments could also benefit from the use of VUV radiation.

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PARALLEL SESSIONS

PARALLEL SESSION

Ancient & New Materials
(Cultural heritage / Structure / Electronic Properties /
Surfaces & Interfaces)

AUDITORIUM - EDF Lab Paris-Saclay

Thursday, January 18th

Chairpersons:

Marie d'Angelo, Karine Provost, Noemie Carmona-Tejero,
Thomas Maroutian & Frédéric Datchi

IT-01	Probing a microelectronic device's active atoms through operando experiments at SOLEIL *M. Bowen*
OC-01	In-situ X-ray diffraction studies on piezoelectric thin films *T.Cornelius*
OC-02	Amorphous - crystalline transition mechanism of phase change materials: GeTe thin films *M. Gallard*
OC-03	Reversible strain alignment and reshuffling of nanoplatelet stacks confined in a lamellar block copolymer matrix *E. Beaudoin*
IT-02	Nanoparticle-based resistive strain Gauges: Fabrication and characterization by small angle X-ray scattering coupled with in-situ electromechanical measurements *L. Ressier*
OC-04	Investigation by X-ray natural linear dichroism (XNLD) and X-ray magnetic circular dichroism (XMCD) towards magnetic properties of 6nm $CsNiCr(CN)_6$ nanoparticles single layer assembled on graphite *L. Zhang*
OC-05	Chemical nature and beam sensitivity of photochromatic images investigated by Ag K-edge quick spectroscopy *V. de Seauve*
OC-06	Time resolved X-ray diffraction for stress measurements during ultrasonic fatigue tests *N. Ranc*

PARALLEL SESSION

Ancient & New Materials
(Cultural heritage / Structure / Electronic Properties / Surfaces & Interfaces)

AUDITORIUM - EDF Lab Paris-Saclay

Friday, January 19th

Chairpersons:

Marie d'Angelo, Karine Provost, Noemie Carmona-Tejero,
Thomas Maroutian & Frédéric Datchi

OC-07	Structural and magnetic phase diagram of magnetocaloric $Y_{0.9}$ $Gd_{0.1}$ Fe_2H_y hydrides *V. Paul-Boncour*
OC-08	Phase diagram of ammonia monohydrate at high pressure and temperature *H. Zhang*
OC-09	Spectroscopic evidence of a new scale for superconductivity in H_3S *B. Langerome*
IT-03	Interfacing magnetic oxides – Insights by photoelectron spectroscopy *M. Müller*
OC-10	Electronic structure of two-dimensional WS_2/Graphene van der Waals heterostructures *J. Rault*
OC-11	Increasing the magnetic anisotropy through onion-like magnetic nanoparticles *K. Sartori*
OC-12	Direct measurement of lateral correlations under controlled nano-confinement: The long-range attraction between hydrophobic surfaces *P. Kékicheff*

Probing a Microelectronic Device's Active Atoms through Operando Experiments at SOLEIL

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ABSTRACT

Large instrument facilities such as the synchrotron have historically played a materials science support role regarding device studies, which are typically performed separately. To improve the relation of causality between these separate studies**, 'materials-centric' operando studies aim to probe the materials properties of a device after it has been placed in a given state**. This approach is widely used across such diverse device types as batteries, solar cells, p-n junctions, etc…. We will illustrate this materials-centric operando approach by showing how to electrically tune[1] the magnetic properties of a ferromagnetic metal/molecule interface[2] using an underlying ferroelectric layer[3].

However, the atoms within a given device do not necessarily contribute equally to its operation. It is therefore desirable to focus the materials science technique onto those atoms that drive a device's response and performance. To do so, **in a 'device-centric' operando approach, the materials science technique excitation is implemented, but the readout is performed within device operation.**

To demonstrate this 'device-centric' operando technique, we considered magnetic tunnel junctions (MTJs), a spintronic microelectronic device with industrial penetration toward next-generation memories[4] and bio-inspired computing[5]. Because current flows through nanoscale hotspots defects in the device's MgO tunnel barrier (due to e.g. oxygen vacancies[6]), this macroscale device operates using a minute subset of active atoms. To focus on solely these atoms, we examined how the device current is altered when the MTJ's oxygen atoms absorb soft X-rays at beamline DEIMOS[7]. Our results link, as a fact, device operation with Fe-O bonds at the MTJ's interfaces.

Performing such operando experiments at Synchrotron SOLEIL can, thanks to its unique materials science capabilities, not only generate more efficient fundamental science, but can also greatly accelerate the pace of industrial R&D, and thus represents an important financial opportunity for SOLEIL to secure long-lasting industrial contracts. The resulting financial boon would be a win-win for both fundamental research and SOLEIL operations. The implication is that **Synchrotron SOLEIL further enhance its device operando studies culture** at the machine, beamline and user levels (e.g. an on-site wire bonder, streamlined/fast-tracked Tango integration of device measurement apparatus, on-site know-how to track/eliminate EM noise/spikes, etc…). We will describe the present implementation[8] on beamline DEIMOS, and future developments on both beamlines DEIMOS and HERMES within the context of a joint SOLEIL/IPCMS/IJL PhD project.

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In-situ X-ray Diffraction Studies on Piezoelectric Thin Films

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ABSTRACT

Within the last decade, the properties of ferroelectrics have been extensively studied. Several important devices, such as Ferroelectric Random Access Memories (FeRAMs) and Dynamic Random Access Memory (DRAM), are manufactured based on ferroelectric thin films [1,2]. With the crescent and continuous demand for portability in consumer electronics, the understanding of the effects of miniaturization on the properties of ferroelectric thin films becomes increasingly important. Although continuous improvements in conventional semiconductor designs are implemented, the basic physics of the size effects is, however, poorly understood. It is well known that the crystallite size plays an important role in tailoring ferroelectric properties.

The piezoelectric properties of $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) and $Pb_{1-y}La_y(Zr_{1-x}Ti_x)O_3$ (PLZT) thin films of different compositions consisting of few tens of nanometer sized grains were studied by *in-situ* local probe X-ray diffraction at the DiffAbs beamline at Synchrotron SOLEIL [3]. For this purpose, gold electrodes of 0.3 mm in diameter were deposited on top of the thin film of which one was contacted electrically with a thin wire. Constant electric fields as well as alternating ones with frequencies ranging from 0.01 Hz to 31 kHz were applied. The diffraction signal from an area beneath the electrically contacted electrode was monitored as a function of the applied electric field. From the shift of the position of the Bragg peak induced by the applied potential, the piezoelectrically generated strain was determined revealing “butterfly loops” [4] which are a clear signature of the piezoelectric hysteresis. Asymmetric “butterfly loops” found for PZT thin films with $x = 0.5$ indicate the presence of a self-polarization which tends to disappear for PZT thin films with $x = 0.47$ [5]. These findings are supported by piezoelectric force measurements revealing an asymmetry of the hysteresis loops towards positive electric fields which are a clear signature of a macroscopic self-polarization effect in the studied PZT films. For PLZT thin films the piezoelectric coefficient was found to be increased with a maximum for films with 3% La. For both types of films (PZT and PLZT) the butterfly loops are less pronounced for AC frequencies > 1 Hz and the piezoelectric response was found to be smaller than for DC electric fields. In addition, a linear behavior of the piezoelectrically induced strain as a function of the applied electric field was found for PLZT thin films instead of butterfly loops.

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Amorphous - Crystalline Transition Mechanism of Phase Change Materials: GeTe Thin Films

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ABSTRACT

Phase Change Materials such as Ge-Sb-Te ternary alloys are used in data storage devices like PCRAM (Phase-Change Random Access Memory). The memory mechanism is based on the quick and reversible transition from amorphous to crystalline state [1-3]. During this transition, the optical reflectivity and the electrical resistivity exhibit a huge variation which is accompanied by a densification of 7% of the material [4]. This last one contributes to stress and fatigue that leads to defects, potentially leading to failure in memory device. This points out the importance for a better understanding of crystallisation processes and its consequences, in a first step done for model (simplified) samples consisting of continuous thin GeTe films, as function of film thickness.

The model samples consisted of 100 nm down to 5 nm thick GeTe thin films , capped with 10 nm of TaN to prevent oxidation [5] deposited on 100 µm thick Si(001) substrates. Samples were characterised using a unique set-up installed on DiffAbs beamline (Synchrotron SOLEIL) allowing, during *in situ* annealing of the sample, the combination of X-ray Diffraction (XRD), X-ray Reflectivity (XRR) and optical curvature measurements (MOS, Multi-beam Optical Sensor). These coupled measurements give access to complementary information such as the evolution of microstructure, densification, stress and strain, during *in situ* thermal annealing. For example, lattice parameters (XRD), film thickness (XRR) and macroscopic strain evolution (MOS) are extracted and will be shown. Sample behaviour during annealing and crystallisation process will be detailed and discussed for different film thickness (confinement).

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Reversible Strain Alignment and Reshuffling of Nanoplatelet Stacks Confined in a Lamellar Block Copolymer Matrix

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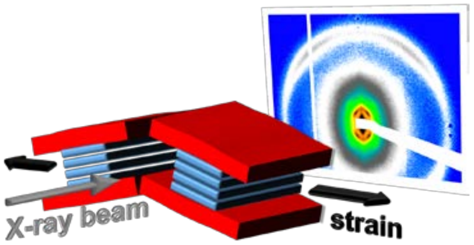
ABSTRACT

A promising strategy for obtaining new materials consists in dispersing nanoparticles with interesting properties within a medium that is easy to shape and manipulate. in such nanocomposites, the main difficulty is controlling the aggregation state of the particles, as well as their position and orientation. We have shown that all these parameters can be tuned by reversibly stretching a thermoplastic elastomer composite.

Our composite consists in anisotropic CdSe nanoplatelets, eight atoms thick and fifteen times as wide, dispersed in a matrix of SBS (polystyrene-polystyrene-polybutadiene) block-copolymer. The platelets assemble together spontaneously in small stacks, confined in the polybutadiene domains of the lamellar microstructure of SBS. Using an in-situ traction device, the material is submitted to controlled strain, while being exposed to the strong X - ray beam produced by the SWING of the Soleil synchrotron beamline. The scattering pattern recorded thus provides information on the evolution of the microstructure and the platelet stacks of lamellar.

In agreement with literature results on these systems, we observe a reorientation of the lamellar domains under strain. The surprising result is that this motion destabilizes the platelet stacks, shears and tilts them on the side, as if cutting a deck of cards in smaller ones. The evolution is reversible since, after releasing the stress, the stacks return to their original size and orientation. Moreover, the process can be inhibited by reinforcing the interaction between platelets in the stack using excess oleic acid, the molecule that renders them compatible with the matrix.

This discovery not only raises fundamental questions on the interaction of nano-objects with their environment, but also suggests new ways of designing and processing composite materials with original properties. Application can be found in opto-mechanical devices. For example, our composite displays strongly anisotropic fluorescence emission under strain.



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Nanoparticle-based Resistive Strain Gauges: Fabrication and Characterization by Small Angle X-ray Scattering Coupled With In-situ Electromechanical Measurements

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ABSTRACT

This talk presents the fabrication of high-sensitivity resistive strain gauges based on electron tunneling in assemblies of gold colloidal nanoparticles and their characterization by coupling Small Angle X-ray Scattering (SAXS) with in-situ electromechanical measurements.

The active area of these strain gauges consists in well-defined arrays of parallel, few micrometer wide wires of close-packed gold nanoparticles. These nanoparticle wires are obtained by convective self-assembly on flexible substrates, without any lithographic pre-patterning.

Microstructural changes (mean interparticle distance variations) within these nanoparticle wires under uniaxial stretching, estimated by SAXS, are correlated to the simultaneously measured macroscopic electrical resistance of the strain gauges. The obtained results allow a fine understanding of the electromechanical behavior of such nanoparticle-based sensors, extremely promising for integration into micro-electromechanical systems, high resolution strain mapping or wireless sensor network applications.

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Investigation by X-ray Natural Linear Dichroism (XNLD) and X-ray Magnetic Circular Dichroism (XMCD) towards Magnetic Properties of 6nm CsNiCr(CN)$_6$ Nanoparticles Single Layer Assembled on Graphite

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ABSTRACT

From previous work by Mallah *et al.*[1-4], we have synthesized bimetallic cyanide-bridged networks of Prussian Blue Analogues (**PBAs**) under the form of nanoparticles (**NPs**) of general formula Cs[Ni^{II}Cr^{III}(CN)$_6$]. The present work investigates the magnetic properties of these **NPs** with 6 nm diameters assembled as single layer on Highly Oriented Pyrolytic Graphite（**HOPG**）substrate. Comparing to Prado's work[4], a combination of angular dependent X-ray absorption spectroscopy(**XAS**) and advanced theoretical analysis using Ligand Field Multiplet (**LFM**) calculations[5-6] has been carried out, which allows us to determine the local structural distortion around Ni^{II} and the corresponding magnetic anisotropy.

In this work, all spectra have been recorded on **DEIMOS** beamline at Synchrotron **SOLEIL**. These data elucidate the relations among X-ray Natural Linear Dichroism (**XNLD**) and X-ray Magnetic Circular Dichroism (**XMCD**) spectra recorded at the Cr^{3+} and Ni^{2+} L$_{2,3}$ edges concerning structural and magnetic information. **XNLD** experimental data and the associated theoretical analysis show that the Ni local environment is not cubic but an elongation along the C$_4$ axis of the octahedral coordination sphere of nickel ions. The analysis of the **XMCD** data coupled to the atomic magnetization curves allow the determination of the magnetic anisotropy that is fully consistent with the geometric environment determined by **XNLD**. We conclude that the **NPs** possess an easy plane of magnetization parallel to the plane of the monolayer.

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Chemical Nature and Beam Sensitivity of Photochromatic Images Investigated by Ag K-edge Quick Spectroscopy

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ABSTRACT

In 1848 Edmond Becquerel developed the very first colour photographic process and was able to record the solar spectrum with its own colour, basing himself on Seebeck's works on silver chloride [1]. The support is a silver plate similar to those used for daguerreotypes that underwent a sensitization step and the positive colour image is directly formed onto the sensitized plate. The exposure times were quite long and the resulting *photochromatic images* could not be fixed which is why this invention was not widely used.

If this process was the first response to the problem of colours in photography, the origin of colours in these images motivated a debate between scientists in the 19th century [2], [3], issue that is still not solved in the 21th century [4], [5]. In order to investigate the nature of these colours, we try to relate the sub-microstructure of the silver and chlorine-based sensitized layer to its optical properties.

In this context, several model and real samples of photochromatic image that we created in the lab were analysed by Ag K-edge X-ray Absorption Spectroscopy (XAS) at the ROCK beamline. In this talk, we will focus on three aspects of the results we obtained. Firstly, thanks to the ROCK's quick monochromator, we studied the sensitivity to the X-ray of the samples intrinsically photon-sensitive and found conditions to measure them. Secondly, we will show the self-absorption issues that we had to face while working at grazing or normal incidence. And lastly, we will compare the signals obtained on real and model sensitized and coloured samples of the photochromatic image. The chemical nature of the photochromatic image will be discussed; in particular, the resemblance of the EXAFS signal of the sensitized layer to that of the Ag/AgCl composite will be discussed [6].

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Time Resolved X-ray Diffraction for Stress Measurements during Ultrasonic Fatigue Tests

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ABSTRACT

Ultrasonic machines are useful experimental devices to study the fatigue properties of metallic alloys in the gigacycle fatigue domain. The main difficulty of this technique is the quantification of the stress amplitude applied to the specimen. Generally, the maximum stress in the center of the specimen is estimated from the displacement amplitude of the edge of the horn which is obtained after a calibration of the ultrasonic fatigue machine. The stress amplitude is then determined by a harmonic calculation based on the assumption of a purely elastic response of the material. In this communication, this assumption will be discussed. We propose a new method for stress determination, based on time resolved X-ray diffraction, for which no assumption about the specimen response is necessary. In this last method the stress is estimated from the displacement of diffraction Bragg peaks measured in-situ at synchrotron SOLEIL (France) thanks to synchronization of the 2D X-ray detector and the strain gauge. Due to the large loading frequencies (typically 20kHz) of the ultrasonic machine, a temporal resolution of about one microsecond or even less was necessary. The signal to noise ratio of diffraction pattern was then reduced by cumulating X-ray acquisition over a large number of cycles, for ~5 sec. The stress values determined by the X-Ray diffraction technique were compared with the classical and were discussed.

Structural and Magnetic Phase Diagram of Magnetocaloric $Y_{0.9}Gd_{0.1}Fe_2H_y$ Hydrides

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ABSTRACT

Classical refrigeration technologies are using refrigerants which deplete the ozone layer and contribute to global warming, and will be therefore forbidden by different climate protocols. Alternative refrigerants present also various drawbacks (flammable, toxic). Therefore, it is worth to develop new refrigeration technologies without environmental problems such as magnetic refrigeration based on the magnetocaloric effect (MCE). Development of efficient magnetocaloric materials (MCM) has become challenging since the discovery of a giant MCE near room temperature (RT) in $Gd(Ge,Si)_5$ compounds[1]. Interesting magnetocaloric effects have been discovered in $YFe_2(H,D)_{4.2}$ compounds around a ferromagnetic-antiferromagnetic transition (F-AF) due to the itinerant electron metamagnetic behavior of the Fe sublattice[2]. A significant magnetic entropy variation (ΔS_M) has been observed in monoclinic $YFe_2H_{4.2}$ at T_{F-AF} = 130 K[3]. T_{F-AF} is highly sensitive to any volume change induced by applying an external pressure, but also by replacing H by D[3] (giant isotope effect) or by chemical substitution of Y by another rare earth element. The full substitution of Y by Gd allows to increases T_{F-AF} near 200 K, but it is not sufficient for RT magnetic refrigeration[5]. Another way to increase the magnetic ordering temperature is to vary the H content as it has been observed in $Y_{0.9}Gd_{0.1}Fe_2H_y$ hydrides[4]. However, determining the best hydride in term of transition temperature and MCE requires a fine knowledge of the structural and magnetic properties of $Y_{0.9}Gd_{0.1}Fe_2H_y$ hydrides versus hydrogen content ($3 \le y \le 4.6$). At RT, it has been observed that the hydrides crystallize into different structures: two phases with monoclinic structures and one with orthorhombic structure separated by cubic phases with intermediate cell volumes. Each phase exists in a narrow range of H content and several two phase ranges are therefore observed. All these structures are derived from the cubic C15 of the pristine compound and the lowering of crystal symmetry is related to hydrogen order into interstitial sites. Upon heating these phases undergo order-disorder transitions with complex structural transformations. In order to solve all these structural changes, high resolution is required and we have performed powder diffraction experiments using synchrotron radiation of SOLEIL on the CRISTAL beam line. Analysis of the XRD patterns has allowed us not only to study the phase transformations due to H order-disorder, but also to find the existence of superstructures and of magnetostrictive effects correlated to magnetic transitions. Resulting phase diagrams showing the strong interplay between magnetic and structural properties will be presented. Magnetic ordering temperatures near RT were found for hydrides with $y < 4$.

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Phase Diagram of Ammonia Monohydrate at High Pressure and Temperature

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ABSTRACT

Water and ammonia are considered major components of the interiors of the giant icy planets and their satellites. The phases formed by their mixtures under temperature and pressure conditions of these giant planets are significant for understanding observable properties like magnetic field, gravitational moments and atmospheric composition. The present study focuses on the 1:1 compound, ammonia monohydrate (AMH). Our previous work [1] has shown that AMH transforms at room temperature and above 8 GPa to a mixture of a partially ionized bcc phase, previously reported as the DMA phase [2], and a fully ionic P4/nmm phase [3]. Here we investigate the phase diagram of ammonia monohydrate at high P-T by using Raman spectroscopy, synchrotron radiation and infrared (IR) absorbance spectroscopy up to 40 GPa at temperatures from 296 K to 700 K. A phase transition to a simple bcc structure is observed upon heating, and the phase line is drawn from our data set. Another phase is recovered upon cooling, with complex structure. We also report melting line measurements up to 10 GPa, 690 K.

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Spectroscopic Evidence of a New Scale for Superconductivity in H_3S

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ABSTRACT

In material sciences, particular attention is given to superconducting compounds, a phenomenon characterized by two main effects: expulsion of a magnetic field and absence of electrical resistance. Regarding this last characteristic, applications are numerous, most notably for energy and electricity, and the repercussions are colossal. However, superconductivity is often induced at low or even very low temperatures, which deeply limits the conditions for its exploitation.

In that context, the discovery in 2015 of a H_3S phase, superconducting at a record temperature of 200 Kelvins [1], is a breakthrough toward high temperature superconductivity. This metallic phase is formed by compressing hydrogen sulfur (H_2S) up to 150 GigaPascals (more than 6 order of magnitude higher than ambient pressure) in a diamond anvils cell. However, the compound remains to be carefully characterized in particular regarding the determination of the energy scale of the involved charges.

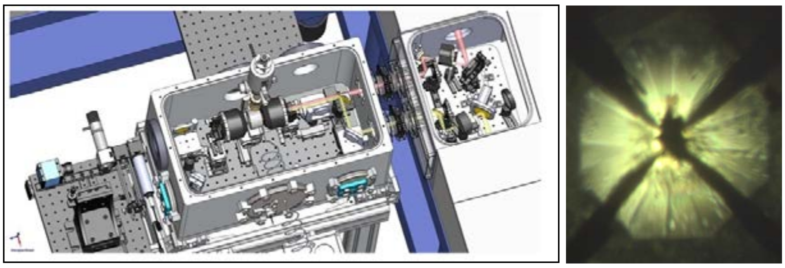

Fig. 1: Left panel: Schematic view of the high pressure – low temperature setup. Right panel: Optical microscope image of the sample with the four electrodes used to measure resistivity

In that purpose, we performed an optical study by infrared spectroscopy which evidences that the high temperature superconductivity in this compound is driven by the electron – phonon interaction, thus confirming that H_3S is a conventional superconductor [2]. In view of the complexity of the measurement, several problems had to be overcome. Firstly, the experimental setup used had to combine a control of the temperature just as the one of the pressure (Fig.1) [3]. Moreover, because of the use of a high pressure cell, the formed metallic sample is of the order of 50 micrometers. It implies that the spectroscopic study in reflectivity had to be made on a sample with a micrometric size. Finally, the expected spectral signatures being of the order of 3% of measured intensity, the system had to present a sufficient stability of measurement.

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Interfacing Magnetic Oxides – Insights by Photoelectron Spectroscopy

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ABSTRACT

Functional metal oxides are at the heart of such diverse research areas as nano, spin- and opto-electronics. An exciting prospect in the field of oxide spintronics is the implementation of magnetic oxides into novel hybrid systems with semiconductors or oxides – in order to generate highly spin-polarized currents, to create confined electron systems or tune the magnetic exchange. Spectroscopic insights into the interrelations between magnetic and electronic properties allow to finally control spin functionalities in magnetic oxide heterostructures [1].

In ferro(i)magnetic oxides - such as 4f Heisenberg rare earth systems and 3d transition metal ferrites – the spin functionality largely relies on the thermodynamic properties which in turn determine growth, interface chemistry and magnetic properties. We employ hard X-ray photoelectron spectroscopy (HAXPES) as a powerful nondestructive and element-sensitive probing technique which enables the chemical depth profiling of heterostructures and interfaces, and to follow oxygen-related mechanisms driven by redox processes. In particular, we investigate the chemical processes at the interfaces of the prototypical all-oxide hybrid EuO/ITO and show, that ITO virtual substrates act as thermally activated, additional source of oxygen during reactive MBE growth. Generally, the oxygen conductivity turns out to be a major criterion for carefully choosing materials and synthesis temperatures. [2][3].

Moreover, two-dimensional electron systems (2DESs) in functional oxides have gained strong interest as a novel state of matter with fascinating and exotic interface physics. The prospect of creating and manipulating a macroscopic magnetic ground state in oxide-based 2DESs is of enormous interest, as this would pave the route towards oxide spintronic applications. We create a 2DES with magnetic functionalities at the interface between EuO, a ferromagnetic insulator, and $SrTiO_3$ - a transparent non-magnetic insulator considered the bedrock of oxide-based electronics by a controlled *in situ* redox reaction. We find that EuO can be tuned from paramagnetic to ferromagnetic-depending on the Eu metal coverage- and show, using angle-resolved photoemission spectroscopy (ARPES), that the integrity of the 2DES is preserved [4].

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Electronic Structure of Two-dimensional WS_2/Graphene van der Waals Heterostructures

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ABSTRACT

In two-dimensional semiconducting transition metal dichalcogenides (TMDs), exciting electronic phenomena such as tunable band gap and strongly bound excitons emerge from strong many-body effects beyond spin-orbit coupling. Combining single-layer TMDs with graphene layer in van der Waals heterostructures offers an intriguing means of controlling the electronic properties through these many-body effects via engineered interlayer interactions. Here, we report the electronic properties of transferred single layer WS_2 on epitaxial graphene using Angle-resolved photoemission spectroscopy measurements (ARPES) and Density Functional Theory (DFT) calculations. The valence band maximum (VBM) at the K point is found to be significantly higher than at the Γ point and located at about -1.8 eV relative to the Fermi level (n-type doping), see Figure 1. Strong spin-orbit coupling leads to a large spin-splitting of the bands in the neighborhood of the K points, with a maximum splitting of 0.44 eV (Fig. 1). By comparing our DFT results with local and hybrid functionals, we find the top valence band of the experimental heterostructure is a close to the calculations for suspended WS_2 monolayer. Moreover, we determined the interface band alignment using x-ray photoemission spectroscopy, our results provide an important reference for future studies of electronic properties of WS2 and its applications in valleytronic devices.

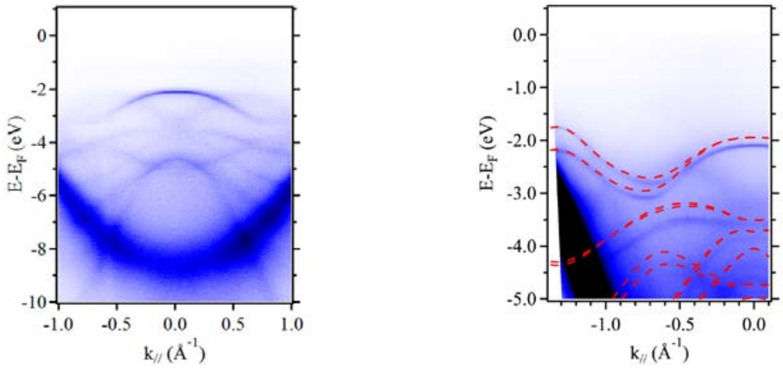

Figure 1: ***E*** vs ***k*** curves around Γ (left) and K (right) points in the first BZ of WS_2 (hv = 50 eV). Red dotted lines are theoretical bands obtained with DFT calculations.

Direct Measurement of Lateral Correlations under Controlled Nano-confinement: The Long-range Attraction between Hydrophobic Surfaces

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ABSTRACT

The origin and nature of the interaction between hydrophobic macroscopic substrates across water and aqueous solutions[1] has been in debate for the last 30 years.[2] Here, atomically smooth mica surfaces are rendered hydrophobic and charge neutral by immersion in cationic surfactant solutions at low concentrations.[3] Lateral correlations along the hydrophobic surfaces whose separation can be varied continuously down to contact are measured by X-ray scattering using a modified Surface Force Apparatus coupled with synchrotron radiation, named SFAX. A weak isotropic diffuse scattering along the equatorial plane is revealed.[4] The peak corresponds to a lateral surface correlation length of about 12 nm, without long-range order. Remarkably the scattering patterns remain stable for gap widths larger than the lateral period, but change as soon as the separation becomes smaller than the correlation length. This evolution codes for a redistribution of counterions (counterion release from antagonistic patches) and the associated new X-ray labelling of the patterns. The redistribution of counterions is the key mechanism to the long-range electrostatic attraction between similar, overall charge-neutral walls, measured directly by the Surface Force Apparatus[5]. Thus, the SFAX provides the ultimate experimental missing clue for explaining not only the origin of the long-range attraction between macroscopic hydrophobic substrates, but also confirms[4] the electrostatics nature of that interaction proposed earlier.[5]

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Increasing the Magnetic Anisotropy through Onion-like Magnetic Nanoparticles

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ABSTRACT

Bulk iron oxide (Fe3O4) is ferrimagnetic at room temperature, while for size smaller than 30 nm, the Fe3O4 nanoparticles become superparamagnetic[1]. However, several applications (like data storage) need nanoparticles size as small as possible with high magnetic anisotropy. Several works have already been reported as an example, on ferromagnetic cobalt nanoparticles that are shelled by antiferromagnetic cobalt oxide (CoO)[2] which allows the spin momentum from the ferromagnetic cobalt core to ordinate in one direction, removing the spin canting effect at its surface and providing exchange coupling between spins at the FM and AFM interface[3]. In this kind of materials, the interfacial crystallinity is crucial: the better it is, the higher the anisotropy will be. So, the chosen materials have to be one ferro or ferrimagnetic and the other one antiferromagnetic with anisotropy constants separated by at least one order of magnitude and high epitaxial relationship. Therefore, iron oxide (Fe3O4) and cobalt oxide (CoO) are good candidates as they are respectively featured by 10^5 and a 10^6 erg.cm-3 anisotropy constants and 8,4 and 4,3 Å cubic cell parameters[4]. Despite a high crystallinity interfacial phase Fe3O4@CoO nanoparticles remain superparamagnetic at room temperature, because of the Néel temperature (TN = 290 K) of CoO. Within this framework, our effort deals with extending shell numbers to increase the FiM/AFM interface and so, to enhance dramatically the magnetic anisotropy of nanoparticles. In order to achieve this goal, several advanced characterization techniques will be combined to study the core@shell@shell structure of nanoparticles by electronic transmission microscopy (EFTEM, EELS, …). We will focus on the chemical nature of the interface which is a critical parameter regarding to the enhancement of magnetic anisotropy. The possible diffusion of species will be investigated by XMCD measurements to observe the environment of each atom. Polarized small angle neutron scattering (PSANS) will bring also precious information on the electronic and magnetic structure of nanoparticles.

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PARALLEL SESSION

Dynamic, Reactivity & Chemical analysis

(Diluted Matter & Chemistry)

AMPHIS 1&2 - EDF Lab Paris-Saclay

Thursday, January 18th

Chairpersons:

Jean-Sébastien Girardon, Nicolas Delsuc, Vincent Boudon and Renaud Guillemin

IT-04	Study of electrochemical mechanisms in batteries: Contribution and limits of X-ray absorption spectroscopy *L. Stievano*
OC-13	Decoupling cationic–anionic redox processes in lithium-ion battery cathodes via operando XAS *G. Assat*
OC-14	Electrochemical and spectroscopic study of Eu(III)/(II) redox couple in the ehtylmethylimidazolium bis(trifluromethanesulfonyl)imide ionic liquid *D. Bengio*
OC-15	Shape-controlled nanoparticle assembly mediated by electrostatic complexation with long polyelectrolyte chains *F. Carn*
IT-05	Creation of double K-shell vacancies with a single photon: How and why? *F. Penent*
OC-16	Multistep ultrafast dissociation and its control by hard X-ray photons *O. Travnikova*
OC-17	Structural study of uranyl bisphosphonate-based ligands as potential uranium decorporation agents *G. Ye*
OC-18	Approaching the limits of cationic and anionic electrochemical activity with the Li-rich layered rocksalt Li_3IrO_4 *A. Iadecola*

PARALLEL SESSION

Dynamic, Reactivity & Chemical analysis
(Diluted Matter & Chemistry)

AMPHIS 1&2 - EDF Lab Paris-Saclay

Friday, January 19th

Chairpersons:

Jean-Sébastien Girardon, Nicolas Delsuc, Vincent Boudon and Renaud Guillemin

OC-19	XAS study of Rh-based catalysts for the hydrogenation of butadiene *C. Zlotea*
OC-20	Tailoring the reactivity of oxide-supported Pd-based nanoparticles *A. Vlad*
OC-21	Evidencing the Mo/W regioselectivity at the pentagonal motifs within giant polyoxometalates *E. Cadot*
IT-06	Multimodal imaging of lipids and metals on liver tissue sections *F. Le Naour*
OC-22	Labeling of hyaluronic acids with a re-tricarbonyl tag and percutaneous penetration into human skin studied by multimodal imaging *L. Henry*
OC-23	Exploring the surface and reactivity of copper nanoparticles with in situ FT-IR *X. Frogneux*
OC-24	Electronic effects of phosphines bound to molybdenum complexes *H. Dossmann*

Study of Electrochemical Mechanisms in Batteries: Contribution and Limits of X-ray Absorption Spectroscopy

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ABSTRACT

X-ray absorption spectroscopy (XAS) can be very efficiently used in the study of modern batteries. In fact, the use of highly penetrating x-rays in the 4-35 KeV range makes XAS an ideal technique for *in situ* and *operando* studies of electrode materials under reaction conditions. Moreover, since XAS probes short-range order in matter, it can be used to study amorphous and nanometric materials, usually not easily measurable by long range techniques such as X-ray diffraction. In the last years, its application, mainly using the *operando* approach via specifically developed electrochemical cells, has helped unraveling the electrochemical mechanism of many positive and negative electrode materials in lithium and post-lithium batteries.

In this presentation, we will provide a few representative examples of how such technique can contribute to the understanding of the electrochemical mechanisms in batteries, focusing both on the understanding of the redox processes in crystalline materials as well as in the identification of amorphous species formed during more complicate processes, such as conversion reactions. In particular, the comparison of *operando* results with *ex situ* measurements on the same materials will show the importance of using real-time investigation tools in the study of electrochemical reactions.

Finally, the recent application of chemometric tools for the interpretation of whole sets of *operando* XAS data will be highlighted. It will be in particular shown how this approach allows the unbiased extraction of all possible information from the *operando* data, defining in some cases also the limits of this technique in its ability to identify sluggish intermediate phases.

Decoupling Cationic–anionic Redox Processes in Lithium-ion Battery Cathodes via *Operando* XAS

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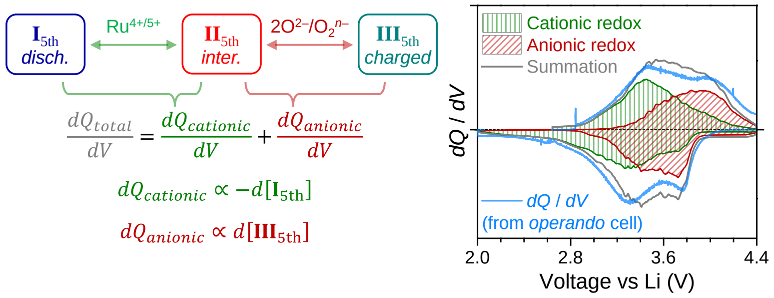
ABSTRACT

A sustainable transition towards renewable energy and electrified transportation is being facilitated by rechargeable lithium-ion batteries – an important thrust area being the energy density of their cathode materials [1]. Conventional cathodes are limited by cationic redox of transition metals for storing energy, but the recent demonstration of reversible anionic redox in lithium-rich layered oxides has revitalized the search for higher energy battery cathodes [2]. To facilitate the success of such materials, the fundamentals of the promising anionic redox mechanism need to be further advanced.

Through this oral communication, we will focus on the cationic–anionic redox processes in $Li_2Ru_{0.75}Sn_{0.25}O_3$ – a "model" lithium-rich layered cathode in which Ru (cationic) and O (anionic) are the only redox-active sites [3]. We will lay out its charge compensation mechanism and local structural evolutions, as revealed via *operando* (and complementary *ex situ*) X-ray absorption spectroscopy (XAS) performed on the ROCK beamline of SOLEIL synchrotron. We will also present several interesting local effects discovered by EXAFS modelling, e.g., the anionic-oxidation-driven distortion of oxygen network around Ru atoms. We will complement these findings by presenting a direct proof of lattice oxygen's reversible redox reactivity, as revealed via hard-X-ray photoelectron spectroscopy (HAXPES) performed on the GALAXIES beamline of SOLEIL synchrotron [3,4].

We will demonstrate a spectroscopy-driven visualization of electrochemical reaction paths, which was achieved through a chemometric approach for *operando* XAS data analysis based on principal component analysis (PCA). This enabled us to neatly decouple the individual cationic–anionic contributions on the *dQ*/*dV* electrochemical curve (see Figure). We hence successfully established the redox and structural origins of all electrochemical features, and further demonstrated the vital role of anionic redox in the practically-important properties of hysteresis and kinetics [3].

Cationic–Anionic redox deconvolution via PCA and MCR-ALS analyses



These fundamental insights about lithium-rich systems are crucial for improving the existing anionic-redox-based cathodes and for evaluating the ones being discovered rapidly.

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Electrochemical and Spectroscopic Study of Eu(III)/(II) Redox Couple in the Ehtylmethylimidazolium Bis(triflurommethanesulfonyl)imide Ionic Liquid

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ABSTRACT

Ionic liquids (ILs) are molten salts composed of an organic cation that are liquid below 100 °C. They demonstrate unique physico-chemical properties such as good conductivity, negligible vapor pressure and non-flammability.[1] As a consequence; they are often regarded as green solvents and could become an alternative to the use of both high-temperature molten salts and volatile organic solvents in rare-earth elements processing and recycling.[2] The diversity of interactions existing in an ionic liquid allows the solubilization of both polar and apolar compounds. Moreover, coordinating functions on their composing ions can lead to stabilization of some species.

For instance, in non-aqueous media, europium exists in the oxidation state +2 which is not stable in aqueous solutions.[3] Understanding the mechanism of Eu(III) reduction to Eu(II) and the stabilization of Eu(II) species in IL media could be of major interest for the development of innovative recycling processes. Consequently, reduction of Eu(III) to Eu(II) and stability of Eu(II) in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIm][NTf_2]) was studied on MARS beamline thanks to a XAS-spectro-electrochemistry set up. The latter was used to follow *in situ* the evolution of the XANES spectrum around the L_3 edge of Eu during electrolysis.

A method is presented to obtain the XANES spectrum of Eu(II) after non-exhaustive electrolysis. EXAFS spectra were recorded in order to get an insight into the structures of the different complexes formed in the IL. The different models tested to fit these spectra were adapted from the crystallographic structures obtained for crystalized $[La(NTf_2)_3(H_2O)_3]$ [4] and $[Bmpyr]_2[Ln(NTf_2)_5]$.[5]

These results were completed by using transient electrochemistry and UV-Vis spectroscopy in order to get valuable information on the redox behavior of the Eu(III)/(II) couple. This couple is found to be quasi-reversible and under inert conditions, a good stability of Eu(II) is observed.

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Shape-controlled Nanoparticle Assembly Mediated by Electrostatic Complexation with Long Polyelectrolyte Chains

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ABSTRACT

The complexation of long polyelectrolyte chains with oppositely charged nanoparticles (NPs) could leads to the formation of stable finite size clusters of NPs on a wide range of sizes, shapes and inner structures. Despite a large interest, the formation of such NPs multiplets with a given structure and their interactions is still missed understood. From the experimental point of view, the lack of structural studies employing non-distorting techniques and well characterized building blocks is detrimental. In this context, we studied the structure of electrostatic complexes obtained by simple mixing of inorganic NPs (silica[1,2,3] and gold[4]) of different radius (R) with polyelectrolyte chains (chitosan, hyaluronan, poly-l-lysine, polystyrene sulfonate) of different persistence length (Lp).

I will present a detailed structural study performed by combining SANS, SAXS, light scattering and cryo-TEM in the different regions of the different state diagrams. Then, I will point the pivotal role of Lp/R on this NPs' organization and the mechanism of multiplet formation based on time resolved SAXS measurements combined with stop-flow.

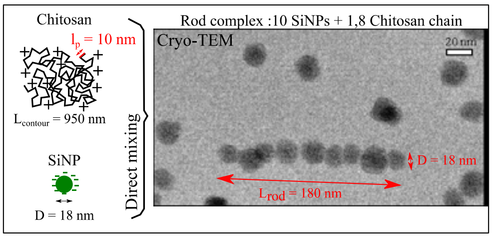

Figure 1 Naïve representation of individual components (left) before complexation and cryo-TEM picture (right) of a stable nanorod complex obtained after mixing in water.

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Creation of Double K-shell Vacancies with a Single Photon: How and why?

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ABSTRACT

Since a few years, double core-hole states (DCHs) have been the subject of many studies on synchrotron [1] and XFEL [2] to explore the potential of their chemical sensitivity [3].

With synchrotron radiation, only a single x-ray photon is absorbed and, although the dominant ionization process is single K-shell ionization (K^{-1}), due to electron correlations, well-known shake-up ($K^{-1}V^{-1}V'$) or shake-off ($K^{-1}V^{-1}$) processes are observed involving a valence electron. Much less probable (~1‰ of K^{-1}) is the process where the *shaken* electron is another K-shell electron: we have here ***super***-shake-up (leading to $K^{-2}V$ states) or ***super***-shake-off (leading to K^{-2} states) processes. With two K-shell vacancies, these states further decay by emission of two successive characteristic Auger electrons.

With a magnetic bottle electron spectrometer, it is possible to detect **all** these electrons in coincidence. In this way, one has access to the spectroscopy of DCH states and to their peculiar Auger decay [1, 4].

The $K^{-2}V$ process presents another great interest [4-6] because two different pathways are possible: 1- K-shell **ionization** with shake-**up** of the other K-shell electron *(direct pathway)* and, 2- K-shell **excitation** with shake-**off** of the other K-shell electron *(conjugate pathway).* Since only one photoelectron is emitted, the process can also be studied with a high resolution electron analyzer [5-7]. Those direct and conjugate shake-up processes populate states with different symmetries and open the field of a new spectroscopy that combines both advantages of XPS and NEXAFS spectroscopies [4]. The different photon energy dependence of the two pathways is also of great interest [5] and implies studies with different experimental approaches: electron coincidence experiments with a magnetic bottle at lower photon energies (<1.5 keV) on SEXTANTS beamline, and high resolution electron spectroscopy on GALAXIES at higher photon energy (>2.3 keV).

I will present the last development of our studies on different atomic and molecular systems.

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Multistep Ultrafast Dissociation and its Control by Hard X-ray Photons

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ABSTRACT

Hard X-rays create deep electron vacancies, which have very rich relaxation decay dynamics. We describe a mechanism of multi-step ultrafast dissociation, using the example of HCl following Cl $1s \rightarrow \sigma^*$ excitation. Furthermore, we demonstrate that by tuning the photon energy multi-step ultrafast dissociation can be controlled on a subfemtosecond timescale.

Absorption of hard x-ray photons leads to creation of deep core holes, which have a very short lifetime ($t \leq 1$fs). The decay of a deep electron vacancy is very complex, and occurs via a series of subsequent relaxation steps. We studied in detail [1, 2] the dominant *KLL*-decay path in HCl, in the course of which 3 *Auger* electrons are ejected sequentially:

$$\mathrm{HCl}^*[1s^{-1}\sigma^*] \xrightarrow[\sim 1\,fs]{KLL} \mathrm{HCl}^+[2p^{-2}\sigma^*] + e_{\mathrm{Auger}} \xrightarrow[\sim 3\,fs]{LMM1} \mathrm{HCl}^{2+}[2p^{-1}(V\sigma^*)^{-2}] + 2e_{\mathrm{Auger}} \xrightarrow[\sim 8\,fs]{LMM2} \mathrm{HCl}^{3+}[(V\sigma^*)^{-4}] + 3e_{\mathrm{Auger}}$$

In general, intermediate states with one or multiple holes in the shallower core electron 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 is sufficiently low. This phenomenon was called multistep ultrafast dissociation (MUST UFD) [1] to distinguish it from the single-step ultrafast dissociation (UFD) induced by soft X-rays. UFD was extensively investigated in a number of molecular systems since its discovery in 1986 [3] (see e.g. [4, 5]).

Moreover, MUST UFD can be controlled by tuning the photon energy. This is the heart of the well-known core-hole clock method, which has been successfully applied to the studies of UFD in soft x-ray energy regime [6]. In the present case (a multistep process), we control the dynamics of the overall Auger cascade by manipulating the effective duration time of the very first step corresponding to the decay of the Cl $1s^{-1}\sigma^*$ state, which is the shortest part ($\tau \sim 1$ fs) of the overall MUST UFD process (6–20 fs). Remarkably, this leads to drastic changes in nuclear dynamics, which are observed on the hundreds of attoseconds timescale [2]. Energy dependent molecular fragmentation is observed and explained by a strong interplay between the core-hole-clock and the topology of the potential energy curves, involved in the Auger-cascades.

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Structural Study of Uranyl Bisphosphonate-based Ligands as Potential Uranium Decorporation Agents

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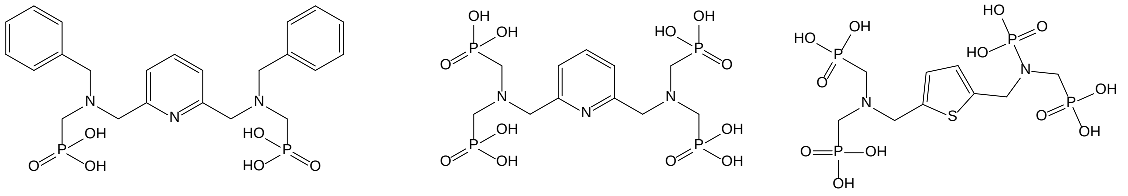
ABSTRACT

Because of the widely use of uranium in fuel cycle, the environmental and occupational exposure opportunities has increased. Although uranium has very limited radioactive dose impact, its chemical toxicity still need to be considered (e.g. U(VI) is a chemical kidney poison). The only way to remove or prevent the internally deposited uranium is by using decorporation agents to accelerate excretion. It is known that phosphonate group has a really strong affinity to complex U(VI). Three new bisphosphonate-based ligands, synthetized in Strasbourg, were tested for their uranium-binding properties.



L1 L2 L3

Fig.1 structure of bisphosphonate-based ligands

The three bisphosphonate-based ligands /uranyl complexes prepared under pH 3 and 7.4 had been studied using IR and SAX technics.

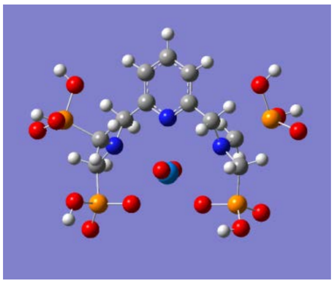


Fig.2 Minimum energy conformation obtained from DFT calculations (B3LYP) in aqueous solution for the [$UO_2(H_6L2)$] system

The IR measurements indicate a strong bonding between the uranyl ion and the phosphonate groups for the three ligands and the first EXAFS data analysis showed clearly that the uranyl ion is linked with the ligands L1 and L2 as shown on the figure 2.

Approaching the Limits of Cationic and Anionic Electrochemical Activity with the Li-rich Layered Rocksalt Li_3IrO_4

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ABSTRACT

The Li-rich rocksalt oxides Li_2MO_3 (M = 3d/4d/5d transition metal) are promising positive-electrode materials for Li-ion batteries, displaying capacities exceeding 300 mAh g^{-1} thanks to the participation of the oxygen non-bonding O(2p) orbitals in the redox process[1-4]. Understanding the oxygen redox limitations and the role of the O/M ratio is therefore crucial for the rational design of materials with improved electrochemical performances. To probe the effect of increasing the O/M ratio to reach higher anionic extra capacities, we searched for Li_3MO_4 compounds relying on the transition metal M having a partially filled d-band. The Li_3IrO_4 compound (O/M = 4) can reversibly take up and release 3.5 electrons per Ir and possesses the highest capacity ever reported for any positive insertion electrode[5].

O*perando* X-ray absorption spectroscopy (XAS) experiments at Ir L_3-edge were performed on the ROCK beamline of SOLEIL synchrotron to monitor the evolution of the Ir oxidation state as well as the local structural changes occurring during the Li insertion/extraction. A chemometric approach based on Principal Component Analysis (PAC) and Multi-variate Curve Resolution Alternating-Least Square (MCR-ALS) has been used to extract information on the reaction processes involved in both oxidation and reduction.

Combining *operando* XAS to *in situ* X-ray diffraction, *ex situ* electron paramagnetic resonance (EPR), pressure measurements and density functional theory (DFT) calculations, we show that the Li_3IrO_4 phase can be either oxidized ($Li_3IrO_4 \rightarrow$ 'IrO_4') or reduced ($Li_3IrO_4 \rightarrow Li_5IrO_4$), with this amphoteric character being nested in redox processes involving anions on oxidation ($x < 3$) and cations on reduction ($x > 3$).

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XAS Study of Rh-based Catalysts for the Hydrogenation of Butadiene

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ABSTRACT

Carbon supported Rh-based catalysts with an average size of 1.0 nm have been synthesized by a simple liquid impregnation method followed by reduction under hydrogen at 175 °C (Fig 1 A).[1] Two Rh-based nanocatalysts were tested for the hydrogenation of butadiene : the hydride RhH_x (as-synthesized nanoparticles) or the metal Rh (as-synthesized nanoparticles pre-treated at 300 °C under He).

Laboratory catalytic tests were performed for the hydrogenation of butadiene for different gas feed compositions and temperatures. They proved that the Rh hydride nanocatalysts are more active than the metal counterpart, irrespective of reaction condition (Fig 1B). However, the apparent activation energies and the selectivities to products are almost identical for both Rh and RhH_x catalysts, suggesting similar reaction mechanism.

In order to highlight the local structure of both Rh and RhH_x nanocatalysts, XAS experiments in *operando* conditions were carried out on the ROCK beam line. The EXAFS analyses confirmed that the Rh-based catalysts do not change throughout the reaction at room temperature: neither hydrogen depletion from the hydride phase nor hydride formation from metal phase were observed over the period of 2 hours (Fig 1C).

The reaction mechanisms may be similar for both metal and hydride nanocatalysts, but the stabilization of Rh-H bonds at the surface in the presence of subsurface hydrogen, as previously suggested theoretically[2], might reasonably elucidate the higher activity of the hydride phase relative to the metal catalyst.

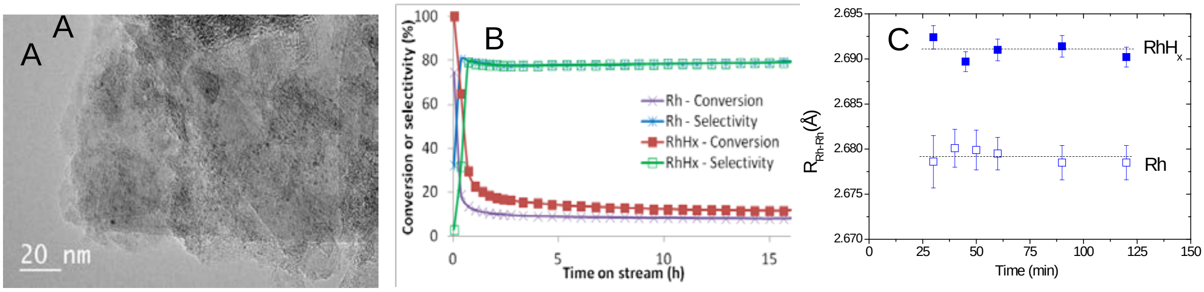

Figure 1. TEM image of 1.0 nm Rh-based nanocatalysts (A), conversion of butadiene and selectivity to butenes during the laboratory catalytic tests (B), time variation of nearest neighbor distance (R_{Rh-Rh}) for Rh and RhH_x catalysts, as obtained by EXAFS (C).

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Tailoring the Reactivity of Oxide-supported Pd-based Nanoparticles

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ABSTRACT

Pd-based nanoparticles (NPs) have been extensively studied for their high catalytic activity in CO oxidation reaction. We investigated the interaction of oxygen and the CO oxidation activity of Pd-based nanocatalysts for the CO oxidation reaction. In particular, 3 and 5 nm $Au_{1-x}Pd_x$ (x = 0, 0.25, 0.5, 0.75, 1) nanoparticles were prepared on SiO_x/Si(100) substrates via micelle nanolithography, a technique well adapted to yield minimal size distribution of nanoparticles. This synthesis method implies a plasma treatment - either oxygen or hydrogen - as a last step in order to form the NPs and to decompose the polymer matrix. The effect of the plasma on the oxidation kinetics and CO oxidation activity was studied by means of surface-sensitive x-ray scattering experiments performed at SixS Beamline, Synchrotron SOLEIL. We combined in-situ grazing incidence x-ray diffraction with mass spectrometry in order access both the structural and chemical information on our catalysts using a diffraction - compatible portable flow reactor (Leiden Probe Microscopy, The Netherlands). The observed lattice constants were found to depend on the composition of nanoparticles as expected by the Vegard's law. Altering slightly the synthesis route allows us to tune the morphology and the reactivity of the catalysts.

Evidencing the Mo/W Regioselectivity at the Pentagonal Motifs within Giant Polyoxometalates

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ABSTRACT

Polyoxometalates (POMs) are discrete anions usually described as soluble molecular oxides.[1] Their unrivalled structural and chemical diversity are sparking in numerous domains of science ranging from catalysis to biology. Besides, this class of molecular objects reaches in size the frontiers of the nanoworld with a set of spectacular giant species, highly useful to develop sophisticated supramolecular chemistry.[1] Even these species could differ in their topology, they contain in their metal-oxo framework pentagonal motifs $\{M_6O_{21}\}$ (with M = Mo or W), as common structural invariant.[2] Besides, these striking pentagons were found also in many multi-element layered oxides that behave as efficient catalysts in selective oxidation processes.[3]

In this communication, we report that mixed $\{WMo_5O_{21}\}$ pentagon can be formed through regioselective condensation processes. This mixed pentagonal core was found in a series of giant polyoxometalates that differ in their topology and in their conditions of formation. For these mixed Mo-W compounds, single X-ray diffraction analysis revealed a single Mo/W distribution, rather consistent with W atom at the center of the pentagon and Mo atoms distributed on the five peripheral sites. In such a distribution, W atoms exhibit an heptacoordinated geometry while the Mo atoms are exclusively hexacoordinated. Furthermore, EXAFS spectroscopy at the tungsten L_{III}-edge was used to investigate more deeply the local geometry of the W atoms. For each case, the EXAFS spectrum, recorded on the SAMBA beamline, evidences the W•••O and W•••Mo shells with fitted parameters highly consistent with a $\{WO_7\}$ core and usual W-O bond lengths. Besides, experimental observations are nicely supported by DFT calculations which reveal that the Mo/W regioselectivity process at the pentagon is both thermodynamically and kinetically driven.

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Multimodal Imaging of Lipids and Metals on Liver Tissue Sections

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ABSTRACT

Liver is subject to various chronic pathologies, progressively leading to cirrhosis, which is associated with an increased risk of hepatocellular carcinoma. There is an urgent need for diagnostic and prognostic markers of chronic liver diseases and liver cancer. Spectroscopy-based approaches can provide an overview of the chemical composition of a tissue sample offering the possibility of investigating in depth the subtle chemical changes associated with pathological states. In this study, we have addressed the potential of spectroscopy-based approaches for diagnosis of Wilson disease as well as for investigating the composition and quantification of steatosis.

Wilson's disease (WD) is a rare autosomal recessive disease due to mutations of the gene encoding the copper-transporter ATP7B. The diagnosis is hampered by the variability of symptoms induced by copper accumulation, the inconstancy of the pathognomonic signs and the absence of a reliable diagnostic test. We investigated the diagnostic potential of X-ray fluorescence (XRF) that allows quantitative analysis of multiple elements. XRF experiments were first performed using synchrotron radiation to address the elemental composition at the cellular level. High-resolution mapping of tissue sections allowed measurement of the intensity and the distribution of copper, iron and zinc while preserving the morphology. Investigations were further conducted using a laboratory X-ray source for irradiating whole pieces of tissue. XRF on whole formalin-fixed paraffin embedded needle biopsies allowed profiling of the elements in a few minutes. The intensity of copper related to iron and zinc significantly discriminated WD from other genetic or chronic liver diseases with high specificity and sensitivity. This study established a definite diagnosis of Wilson's disease based on XRF. This rapid and versatile method can be easily implemented in a clinical setting.

Steatosis is one of the most important factors affecting liver allograft function. The gold standard to assess hepatic steatosis in liver grafts during the transplantation procedure is the histologic examination of frozen sections by a pathologist. The major issue is that assessment of hepatic steatosis on histologic sections is an imperfect and not reproducible method. We addressed the potential of Fourier transform-infrared (FTIR) microspectroscopy for grading steatosis on frozen tissue sections. The use of the bright infrared source emitted by synchrotron radiation allowed the investigation of the biochemical composition at the cellular level. We demonstrated that the progression of steatosis corresponds not only to the accumulation of lipids but also to dramatic changes in the qualitative composition of the tissue. We observed that dramatic biochemical changes occur in the non-steatotic part of the tissue despite its normal histological aspect, suggesting that the whole tissue reflects the grade of steatosis. We further developed a method for the quantification of lipid content on tissue section. This rapid method that takes only 1 minute has been implemented on laboratory instrument. Thus, the method can be easily used at the hospital for reliable assessment of graft quality control in liver transplantation.

Labeling of Hyaluronic Acids with a Re-tricarbonyl Tag and Percutaneous Penetration into Human Skin Studied by Multimodal Imaging

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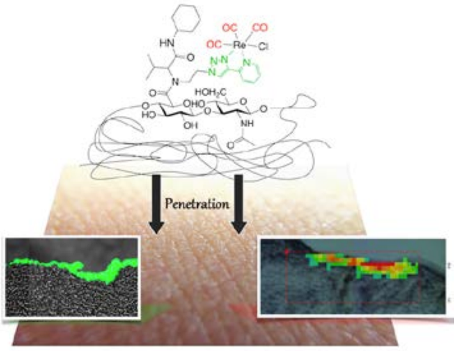
ABSTRACT

Recently, we demonstrated that $Re(CO)_3$ compounds can be used as Single Core Multimodal Probe for Imaging (SCoMPI) for the labelling of molecules of interest and their imaging in biological environment (cell, skin biopises…).[1-4] The aim of the present study is to use the same correlative approach to study the penetration of a widely used cosmetic agent: hyaluronic acid (HA). HA is a carbohydrate naturally present in the human body that is commonly used as a wrinkle filler in cosmetic applications.[5] Although HA is often injected into the dermis, it can be applied at the surface of the skin. In order to estimate the penetration after topical application, hyaluronic acids of different molecular weights (MW) were labelled with a SCoMPI and their penetration was studied into human skin using both IR microscopy and fluorescence imaging.



After a 7-hour exposure, the low MW HA was localized at some hotspots in the *stratum corneum* (SC) whereas the high molecular weight HA was not detected at the surface of the skin. After a 24-hour exposure, the low MW HA was homogeneously distributed in the *stratum corneum* but was not detected in deeper layers of the skin whereas the high MW HA was only located at some spots in the SC. We could not see any change in the IR-signature of lipids or amides where the HA was located.

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Exploring the Surface and Reactivity of Copper Nanoparticles with *in situ* FT-IR

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ABSTRACT

A LOVE STORY BETWEEN PHOSPHINE AND COPPER NANOPARTICLES: FORMATION OF ACTIVE CLUSTERS IN HYDROSILYLATION REACTION

The synthesis of metallic nanoparticles has known a tremendous progress for the last two decades. New properties of these nano-objects were unveiled for a large area of applications (electronic, medical imaging, cosmetic, textile, catalysis, etc.).[1] More particularly, for copper nanoparticles, in spite of their sensibility to oxidation, variations on the surface/ligand system, or deposition on various supports has allowed the development of robust catalytic systems on a large area of reactions (click-chemistry, C-N and C-O cross-couplings, etc.).[1b]

In our project, copper nanoparticles of 25-50 nm diameters are synthesized by reducing the copper precursor with oleylamine[2] and are used as catalysts for the hydrosilylation of benzaldehyde as a model reaction.[3] It appeared that this system was particularly active in the presence of a phosphine as additional ligand (*e.g.* P(*n*Bu)$_3$). In order to investigate the nature of the ligands on the surface of the copper nanoparticle, FT-IR measurements were conducted at the Soleil synchrotron (SMIS beamline) in a taylor-made ATR FT-IR cell to identify the nature of the species at the surface of the copper.[4]

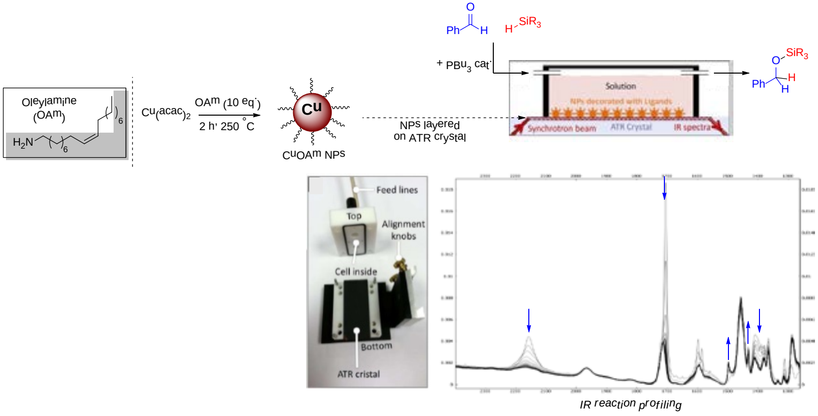

Figure 1 - Taylor-made ATR FT-IR cell, decorated with Cu NPs for reaction profiling

The IR analysis provided unexpected clues about the real nature of the ligand at the surface of the nanoparticles. The reaction was followed with this IR cell at the time-scale of the minute, allowing us to obtain reaction profiles (Figure 1). These showed the fast reaction of the hydrosilane and the benzaldehyde in contact with the ligand-covered nanoparticles. Kinetic analysis is underway to verify the absence of an induction time in this reaction.

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Electronic Effects of Phosphines Bound to Molybdenum Complexes

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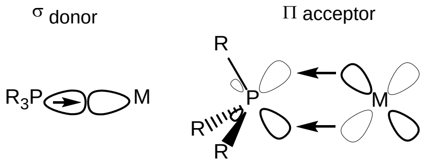
ABSTRACT

An important feature of metal-based catalysts lies in the crucial role of ancillary ligands on the electronic structure of the metal center.[1] Determining how those ligands affect the reactivity of the metal center and quantifying these effects is thus of great importance. Various methods have been proposed to evaluate the electronic influence of ligands; the most popular and easy-to-use method is the Tolman Electronic Parameter (TEP), initially developed for phosphine ligands. It is based on the observation of the IR stretching frequency of the carbonyl ligand(s) in a complex such as $Ni(CO)_3L$ or $LW(CO)_5$.[2] This approach suffers however from some limitations. In particular it does not give access to the relative contributions of the ligand by means of σ-donation and π-back donation effects as described by the Dewar-Chatt-Ducanson (DCD) model (Scheme 1).[3]



Scheme 1. The M-P bond as described by the DCD model.

In this context and within the frame of a collaborative network from various fields (organometallic chemistry and catalysis, theoretical chemistry, mass spectrometry), we have performed experiments on the DESIRS beamline using VUV-spectroscopy. Our objective is to explore new approaches to describe and rationalize electronic properties of ligands bound to a given metal. A serie of Molybdenum complexes, $Mo(CO)_5L$, with L = PR_3 (R = alkyl, Me_xPh_y or Pyr_xPh_y) has been studied by means of photoelectron spectroscopy. This method enables to probe the electronic configuration of a system by measuring its ionization energies which are related to discrete energy levels of molecular orbitals.[4] For the Mo complexes, interpretation of the photoelectron spectra was made with the help of density-functional-theory (DFT) calculations. Results indicate that a detailed description of the σ-donor and π-acceptor characters of the phosphine ligands is accessible with this approach.

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PARALLEL SESSION

Life & Earth Sciences
(Biology / Health & Environment / Geoscience)

ROOMS A1.116-A1.140 - EDF Lab Paris-Saclay

Thursday, January 18th

Chairpersons:

Benoît Masquida, Yann Gohon, and Remi Marsac

IT-07	Structural model of PRORP2-tRNA complex interaction build it by the combination of crystal, in solution structures with biophysical characterization *P. Fernandez-Millan*
OC-25	Structure and regulation of a GTPase system that regulates bacterial motility *C. Galicia*
OC-26	Soft X-ray imaging and spectroscopy for biological samples on HERMES beamline *C. Rivard*
OC-27	Determinants of neuroglobin plasticity highlighted by high pressure crystallography and crystallography under moderate gas pressure *N. Colloc’h*
OC-28	Exploring the speciation of thallium in soil using Synchrotron-based X-ray (micro)spectroscopies *A. Voegelin*
OC-29	Structure and oxidation of moderately volatile elements (Sn and Zn) in natural silicate melts *P. Sossi*
OC-30	Magnetotactic bacteria studied with scanning transmission X-ray microscopy *L. Le Nagard*
OC-31	Overcoming radiation artifacts In X-ray cryomicrospectroscopy: Case study of thallium speciation in soil manganese concretions *F.F. Marafatto*

PARALLEL SESSION

Life & Earth Sciences
(Biology / Health & Environment / Geoscience)

ROOMS A1.116-A1.140 - EDF Lab Paris-Saclay

Friday, January 19th

Chairpersons:

Benoît Masquida, Yann Gohon, and Remi Marsac

IT-08	The archaeal acetoacetyl-CoA-thiolase/HMG-CoA-synthase complex channels the intermediate via a fused CoA-binding site *T. Wagner*
IT-09	Structural basis for alternate substrate recognition and processing by a bifunctional viral protease/deubiquitinase *S. Bressanelli*
IT-10	The ascent of sap and xylem vessel (dis)content: 4 centuries of debate *S. Delzon*
OC-32	Structure-function analysis of the R2TP cochaperone complex, recruiting HSP90 for macromolecular complex assembly. *J. Henri*
OC-33	Membrane-active properties of an amphitropic peptide from the CyaA toxin translocation region *A. Voegele*
OC-34	Multimodal analysis from the DUV to the NIR of the endogenous fluorescence of brain tumor biopsies *F. Poulon*

Structural Model of PRORP2-tRNA Complex Interaction Build it by the Combination of Crystal, in Solution Structures with Biophysical Characterization

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ABSTRACT

The family enzymes named protein-only RNase P (PRORP) achieves the reaction of t-RNA precursor maturation removing 5' leader sequences, like ribozyme RNase P. PRORP have a double localization commonly in eukaryotes: organelle and nucleus carrying out ribonuclease activity.

Our study is focused on Arabidopsis nuclear PRORP2 and its interaction with tRNA substrates. The comparison of PRORP2 structure by X-ray crystallography with by small-angle X-ray scattering in solution showed the dynamics of pentatricopeptide repeat motifs. PRORP2-tRNA precursor complex structure in solution was modelled by small-angle X-ray scattering. Additional biochemical, biophysical and affinity analyses confirmed our structural data, suggesting conformational changes in PRORP2 to accommodate its substrate and defined the contribution of each motif. The combination of all these results provides the first structural model of a PRORP–tRNA complex, and illustrates the binding mechanism.

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Structure and Regulation of a GTPase System that Regulates Bacterial Motility

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ABSTRACT

Small GTPases regulate multiple cellular functions through an switch-like mechanism by alternating between a GDP-bound state (inactive) and a GTP-bound state (active), influenced by regulatory proteins[1]. One group of such regulators are GTPase-activating proteins or GAPs, which stimulate the hydrolysis of bound GTP to convert the GTPase back to its inactive state. In the bacteria *Myxococcus xanthus* the GTPase MglA and its GAP, MglB, are located at opposite poles of the cell. Together they modulate cellular motility by responding to the bacteria's chemosensory system and acting on the motility machinery when MglA is in its active state[2,3]. The positions of MglA and MglB form a polarity axis that determines the direction in which the bacteria moves[3,4]. How the kinetics and conformational changes of the GDP/GTP cycle of MglA control this process has remained mysterious.

To get insight into this question, we studied the activity of the MglA / MglB system using biochemical and structural approaches. To measure the kinetics of GTP hydrolysis, we established a new GAP assay based on an engineered protein that becomes fluorescent upon binding inorganic phosphate [5]. Using this technique we characterized the efficiency of MglB and uncovered self-regulating effects never observed in canonical GTPases. We determined crystal structures of MglA, MglB and the MglA/MglB complex that recapitulate the entire GDP/GTP cycle. These include a crystal of MglB containing 20 subunits in the asymetric unit, which could be located by molecular replacement using a low resolution electron density from another space group combined to density modification. Overall, these results points towards a atypical GTPase cycle in which MglA and MglB perform a function different than that of canonical eukaryotic GTPases and GAPs.

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Soft X-ray Imaging and Spectroscopy for Biological Samples on HERMES Beamline

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ABSTRACT

This talk will introduce three recent studies aiming at developing soft X-ray microscopy methods for studying biological and organic samples. Soft X-ray microscopy offers nowadays a unique approach for studying biological samples by combining imaging and spectroscopy methods, especially in the so-called water window energy. We took advantage of the opportunity offered by the STXM microscope at HERMES beamline to explore three kind of biological samples.

At first we have determined the subcellular changes and the mechanism of cell death that take place in *Trypanosoma bruce*i conditional mutants for the proteins TbRRP44 and TbUTP24 which are two potential endonucleases involved in ribosome biogenesis. Mutant parasites were compared to the wild type. Single image acquisitions were recorded with 50 nm spatial step at 500 eV to enhance organic molecules contrast.

Carbon K-edge spectroscopy was used to determine the spatial distribution of starch, lipids and proteins in maize endosperm. Indeed, starch and proteins are heterogeneously deposited leading to the formation of vitreous (periphery) and floury regions (center of the endosperm). To improve maize breeding for vitreousness, it is necessary to get a better characterization of the different C gradients within vitreous and floury endosperms as well as within starch granules located in these regions. Stacks of images around C K-edge were recorded from 270 to 350 eV, with 75 nm spatial step. Spectra were thereafter extracted, compared to references and species maps reconstructed using Mantis software.

A third preliminary study was conducted on cell infected by modified Rabies Virus to characterize the formation of “Negry Bodies” which are specialized intracellular compartments known as viral factories. The physico-chemical nature of those factories being so far poorly understood, a correlative approach combining UV-visible fluorescence microscopy with soft X-ray spectroscopy at carbon K-edge has been undertaken.

Crucial aspects for successful experiments specifically related to biological samples, such as specific sample preparations (methodology and tools and instruments available at SOLEIL), radiation damages aspects, carbon contamination will also be addressed during the presentation.

Determinants of Neuroglobin Plasticity Highlighted by High Pressure Crystallography and Crystallography under Moderate Gas Pressure

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ABSTRACT

Protein dynamics and plasticity are intrinsically correlated to functional efficiency. Internal cavities present within proteins facilitate conformational transitions between conformers and are crucial for conformational flexibility. On one hand, pressure promotes high energy conformers of lower volumes, and thus becomes an ideal tool to study conformational fluctuations and relationships between local rigidity and overall flexibility. On the other hand, noble gas labelling is the best way to map hydrophobic cavities and tunnels.

Combining high hydrostatic pressure crystallography performed on CRISTAL beamline and crystallography under moderate gas pressure (10 – 100 bar) performed on FIP/BM30 beamline allow to determine the most flexible and the most rigid parts of neuroglobin in relation with cavity modifications. This combined approach allows us to identify a mechanical nucleus around which neuroglobin hinges during its conformational transition induced by gaseous ligand to achieve its coordination through the heme sliding mechanism. Moreover, this study highlights on one hand the role of this mechanical nucleus to host NO during its scavenging process and on the other hand the significance of the intrinsic flexibility of a loop to drive the heme sliding mechanism (1,2).

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Exploring the Speciation of Tl in Soil using Synchrotron-based X-ray (micro)Spectroscopies

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ABSTRACT

Thallium (Tl) is commonly known for its high toxicity. The biogeochemical behavior of Tl, however, has been studied to a lesser extent to date than of other toxic trace elements, and only few studies used X-ray (micro)spectroscopies to determine the speciation of Tl in environmental samples.

Our work on Tl was initially motivated by the discovery of a site in the Swiss Jura mountains where soils with high Tl contents developed from carbonate rock hosting a Tl-As-Fe-sulfide mineralization. Using micro-focused X-ray absorption near-edge structure spectroscopy (XANES) at the Tl L_{III}-edge to characterize Tl in selected soil thin sections, we identified four major Tl species: (i) Avicennite (Tl_2O_3) and (ii) Tl(I)-substituted jarosite as weathering products of the primary mineralization; (iii) Tl(III) associated with Mn-concretions and (iv) Tl(I) bound to illite as pedogenic Tl species. Using bulk XANES spectroscopy on topsoil and subsoil samples with a hundred to thousands of mg/kg of Tl, we quantified the importance of these species for Tl sequestration. In combination with chemical extractions, our results highlighted the key role of illite (and probably other micaceous phylloscilicates) for the sequestration of high levels of Tl in soil via adsorption and fixation [1].

In subsequent laboratory experiments, we studied the adsorption of Tl(I) onto purified Illite du Puy in different background electrolytes, derived a quantitative adsorption model, and used XANES spectroscopy to assess variations in the mode of Tl uptake by illite as a function of Tl loading. Our results confirmed that Tl(I) has a very high affinity for adsorption at the frayed edges of illite platelets by coordination in siloxane cavities [2]. In continuation of this work, we aim to also take advantage of information contained in Tl L_{III}-edge EXAFS spectra to unravel the coordination of Tl adsorbed onto different clay minerals at various loadings. In further laboratory work, we aim to use XAS to assess variations in the mode of Tl uptake by different polymorphs of birnessite (MnO_2) over relevant chemical conditions via oxidative and non-oxidative mechanisms.

Ongoing (cryo)microspectroscopic X-ray analyses on natural soil samples are aimed at elucidating the structure of a yet unidentified Tl(III)-phase in samples from our field site, and at studying variations in the mode of Tl sequestration in Mn-concretions as a function of the type of Mn-oxide and Tl loading, in order to complement our laboratory studies on pure sorbents with field-based evidence.

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Structure and Oxidation of Moderately Volatile Elements (Sn and Zn) in Natural Silicate Melts

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ABSTRACT

Moderately volatile elements are those that are sub-equally partitioned into the vapour- and condensed phases under the conditions that prevail during planetary formation. These elements, and their isotopes, yield insight into how and when the volatile budgets of the inner rocky planets and meteorites were accreted[1]. Their importance notwithstanding, the ability to infer temperature, pressure, and oxygen fugacities (fO_2) that typify planetary formation hinges upon knowledge of the oxidation and co-ordination environment of these moderately volatile elements in silicate melts.

Two of the key elements used to determine planetary volatile element budgets are Sn and Zn. The former has two oxidation states in silicate melts, Sn^{2+} and Sn^{4+}, and is therefore a powerful indicator of fO_2, by the reaction $SnO + ½O_2 = SnO_2$. However, the equilibrium constant for this reaction in natural silicate melts is unknown, and hence the oxidation state of Sn in natural magmas (such as basalts and granites) remains unconstrained. Although Zn is solely divalent in silicate liquids, it has a fully occupied valence $3d^{10}$ electron shell, meaning it often exists in tetrahedral co-ordination with oxygen, in contrast to other divalent transition metal cations.

The aim of the study is two-fold; 1) to determine at which fO_2 the transition from Sn^{4+} to Sn^{2+} occurs and 2) how Zn is co-ordinated by oxygen in silicate melts and whether it changes with melt composition (from komatiite, MgO-rich; to granite, MgO-poor).

To do so, Sn L_3-edge XANES spectra were acquired at the LUCIA beamline, SOLEIL, to identify diagnostic features that vary with oxidation state. The intensity of the pre-edge feature at 3932 eV is demonstrated to be particularly sensitive to the Sn^{2+}/Sn^{4+} ratio, which is quantified using linear combination fitting as a function of fO_2. We show that Fe has a significant effect in stabilising tetravalent tin in natural silicate melts.

For Zn, K-edge EXAFS spectra were collected at the SAMBA beamline, SOLEIL. Fitted spectra show a systematic difference between the Zn-O bond lengths in MgO-rich and MgO-poor compositions, which can be linked to its structural role in silicate melts.

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Magnetotactic Bacteria Studied with Scanning Transmission X-ray Microscopy

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ABSTRACT

Magnetotactic bacteria (MTB) are species that use interactions with the earth's magnetic field to their advantage. They synthesize magnetosomes (<50 nm sized, magnetic single domain, magnetite crystals surrounded by a lipid membrane) through a genetically controlled process. These organelles confer to the cells a permanent magnetic moment that passively aligns the cells in external magnetic fields. Therefore MTB cells behave as micro-compasses that swim along magnetic field lines. We use scanning transmission X-ray microscopy (STXM) to study the chemical and magnetic properties of several MTB species. X-ray absorption spectromicroscopy recorded at the Fe 2p, C 1s, O 1s and S 2p edges provides insight about the cell biochemistry with high spatial (30 nm) and energy (0.1 eV) resolution. Individual magnetosomes can be resolved, their spectroscopy is now well understood [1], and the ability to investigate cytoplasmic Fe species as well as magnetosomes inside an individual cell has been demonstrated [2].

Our current goal is to understand how magnetotactic bacteria synthesize these crystals. To do so we perform time-course experiments in which the morphology and chemical state of iron in individual MTB cells actively growing magnetosomes is studied at different stages of the biomineralization process. We also study the magnetism of the developing magnetosome chain using X-ray magnetic circular dichroism (STXM-XMCD). Our results show that subchains inside single cells can have opposite magnetic polarities [3], which decreases the total magnetic moment of the chain. This raises questions about the widely accepted model that assumes that magnetotactic bacteria try to maximize their magnetic moment. This work is carried out at Soleil on the HERMES-STXM beamline, as well as at CLS and ALS.

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Overcoming Radiation Artifacts in X-ray Cryomicrospectroscopy: Case Study of Thallium Speciation in Soil Manganese Concretions

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ABSTRACT

Thallium is a highly toxic trace metal. In the environment, Tl occurs in the oxidation states Tl(I) and Tl(III). Relatively soluble monovalent Tl(I) can sorb onto clay minerals and mineral oxides1, whereas less prevalent trivalent Tl(III) precipitates as Tl2O3 or sorbs onto Mn-oxides2. Given these differences, speciation information is of primary importance to evaluate the mobility and potential toxicity of Tl in the environment.

Synchrotron based X-ray absorption spectroscopy (XAS) provides information on the redox state and speciation of trace elements, with up to micrometric spatial resolution when using a micro-focused X-ray beam. However, third-generation synchrotrons are characterized by increasingly higher photon flux density, which raises concerns about beam-induced chemical changes due to the breaking of chemical bonds and/or promoting the formation of radical species3. A number of studies have shown that the rate of radiation-induced damage in some systems can be slowed down at low (cryogenic) temperatures. Additionally, sample exposure to the beam can be reduced by collecting energy maps at discrete energies across X-ray absorption edges that allow discriminating relevant chemical species. With the combination of low sample exposure and temperature, we can obtain spatially-resolved speciation information on dilute samples with minimal instrumental artifacts.

In recent work, we confirmed that both reduction in sample temperature and X-ray exposure diminish beam-induced Tl speciation changes in reference samples. By measuring thin-sections of geogenically Tl-contaminated soil at cryogenic temperatures (10 K) and reducing sample exposure through chemical redox mapping at discrete energies, we were able to resolve the heterogeneity of Tl redox speciation associated with soil Mn concretions, which was previous not accessible1. Our results point to complex redox dynamics, where Tl speciation is probably linked to Tl loading and the type of Mn oxide2. This relationship will be further explored in ongoing cryo-microspectroscopy work.

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The Archaeal Acetoacetyl-CoA-thiolase/HMG-CoA-synthase Complex Channels the Intermediate Via a Fused CoA-binding Site

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ABSTRACT

Many reactions within a cell are thermodynamically unfavorable. To efficiently run some of those endergonic reactions, nature evolved intermediate-channeling enzyme complexes, in which the products of the first endergonic reactions are immediately consumed by the second exergonic reactions (1). Based on this concept, we studied how archaea settle the unfavorable first reaction of isoprenoid biosynthesis (2); the condensation of two molecules of acetyl-CoA to acetoacetyl-CoA catalyzed by acetoacetyl-CoA thiolases (thiolase). We natively isolated for the first time an enzyme complex made of the thiolase and HMG-CoA synthase (HMGCS) from a fast-growing methanogenic archaeon *Methanothermococcus thermolithotrophicus*. HMGCS catalyzes the second reaction in the mevalonate pathway, the exergonic condensation of acetoacetyl-CoA and acetyl-CoA to 3-hydroxy-3-methylglutaryl-CoA, which will be then converted in mevalonate by another enzyme.

The first structure of the physiological thiolase/HMGCS complex has been solved on the beamline Proxima-2A at SOLEIL. The newly developed Tb-Xo4 phasing agent (3) was used in combination with a single-wavelength anomalous diffraction at the Tb L_{III} absorption edge.

The 380-kDa crystal structure revealed that both enzymes are held together by a third protein with so far unknown function (DUF35 protein). The active-site clefts of thiolase and HMGCS formed a single fused CoA-binding site, which enables the pantetheinyl-arm of CoA to swing from one active site cavity to the other; thus, the endergonic thiolase reaction can be directly coupled with the exergonic HMGCS reaction. The tripartite complex is found in almost all archaeal genomes and in some bacterial ones. In addition, the DUF35 proteins are also essential for polyhydroxyalkanoate (PHA) biosynthesis most probably by functioning as a scaffold protein that connects thiolase with 3-ketoacyl-CoA reductase.

This natural and highly conserved enzyme complex offers great potential to improve isoprenoid and PHA biosynthesis in biotechnologically relevant organisms (4).

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Structural Basis for Alternate Substrate Recognition and Processing by a Bifunctional Viral Protease/deubiquitinase

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ABSTRACT

Ubiquitylation is a posttranslational event that features in many viral infections. For instance, the host cell can tag viral proteins with ubiquitin to target them towards proteasome for degradation. Thus, many viruses encode deubiquitinases (DUBs) that edit or remove the resulting poly-ubiquitin chains. Furthermore, viruses with particularly compact genomes, such as single-stranded, positive-sense RNA (RNA+) viruses, use proteases to process their own proteins into mature products. The RNA+ virus *Turnip yellow mosaic virus* (TYMV) encodes an ovarian tumor (OTU)-like protease/deubiquitinase (PRO/DUB) protein domain that is involved in both processes. Such a duality of functions allows further compaction of the genome, but how a single, 150-residue enzyme domain switches between substrates has been a longstanding puzzle.

We have solved the crystal structures of TYMV PRO/DUB in three states: In a free form[1 2], in complex with a protease substrate[3], and now with ubiquitin (Fieulaine et al, in preparation). Our results show how PRO/DUB uses overlapping recognition patches to alternately bind completely different protein surfaces. The interface with ubiquitin is quite unusual in its layout (especially as compared to known ubiquitin-DUB interfaces) and mobility (as confirmed by molecular dynamics simulations) and distributed in two parts: On the DUB side, it involves both the core OTU DUB fold and the *Tymoviridae*-specific N-terminal lobe. On the ubiquitin side, the two major recognition patches are engaged simultaneously. Furthermore, our results highlight an idiosyncratic PRO/DUB mobile loop that participates in reversibly constricting its unusual catalytic site. The more closed conformations also correlate with a reordering of the TYMV PRO/DUB catalytic dyad, that then assumes a classical, yet still unusually mobile, OTU DUB alignment.

These results allowed us to design mutants that specifically impair DUB activity while retaining full PRO function. Introduction of mutations into the viral genome revealed that the DUB activity contributes to the extent of viral RNA accumulation both in single cells and in whole plants. Such mutants now provide powerful tools with which to study the specific roles of reversible ubiquitylation in viral infection.

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The Ascent of Sap and Xylem Vessel (dis)content: 4 Centuries of Debate

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ABSTRACT

The mechanism of sap ascent in trees and the content of xylem vessels have been the subject of intense debates over the age. Trees are capable of rapidly transporting water to leaves by a transport system that relies on water sustaining a tensile force. However, this transport mechanism comes with its own set of problems, most notably that water under tension is in a metastable state and prone to embolism. In the first part of my talk I will put this debate into an historical perspective. More recently, a lot of studies had concluded that plants and trees seemed to be highly vulnerable to embolism, leading to a high level of xylem embolism, but with recovery on a daily basis. However, thanks to direct observation of the xylem content, recent advances in plant hydraulics have demonstrated that, contrary to what was previously believed, embolism and repair may be far from routine in trees. Finally, I will discuss the validity of the current destructive standard techniques to measure embolism resistance in trees and compare then to direct observations of embolism on intact plants performed using synchrotron-based X-ray microCT, a non-invasive imaging technique. For instance, our findings provide evidence that grapevine is unable to repair embolized xylem vessels under negative pressure, but its hydraulic vulnerability segmentation provides a significant protection of the perennial stem.

Vitis vinifera Grew (1674)

Structure-function Analysis of the R2TP Cochaperone Complex, Recruiting HSP90 for Macromolecular Complex Assembly

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ABSTRACT

Box C/D small nucleolar ribonucleoparticles, phosphatidyl-inositol 3-kinase-related kinases, telomerase and RNA polymerases are essential eukaryotic molecular machines. Biogenesis of these macromolecular complexes requires the intervention of the R2TP-HSP90 chaperone machinery. The Hsp90 molecular chaperone is responsible for the conformational activation and assembly of proteins that are essential for cell signaling and regulation. Many of these client proteins control functions involved in malignant transformation and the chaperone has attracted considerable interest as anticancer target. Maturation of client proteins is an ATP-dependent phenomenon where the chaperone conformational changes are coupled to the binding and hydrolysis of the nucleotide. This Hsp90 ATPase/chaperone cycle is regulated by a set of cochaperones proteins. The human R2TP cochaperone complex is composed of RUVBL1 and RUVBL2 AAA+ ATPases, PIH1D1 interacting platform and RPAP3 adaptator. RPAP3 cochaperone contains tetratricopeptide repeats (TPR) domains anchoring HSP70 and HSP90 to R2TP.

We focused our attention on the mechanisms of chaperones regulation by the RPAP3-PIH1D1 cochaperones and observed a modulation of Hsp90 activity by RPAP3. This modulation is correlated with the stabilizing interactions between the HSP90 dimer and RPAP3 as evaluated by FRET experiments. PIH1D1 associates with RPAP3, and both cochaperones closely interact with the HSP90 dimer. Finally, we integrated 3D structures, SAXS measurements and biochemical assays into a global model that supports an iterative mechanism of client complex assembly by the RPAP3-coordinated action of Hsp90.

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Membrane-active Properties of an Amphitropic Peptide from the CyaA Toxin Translocation Region

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ABSTRACT

The adenylate cyclase toxin CyaA is involved in the early stages of infection by *Bordetella pertussis*, the causative agent of whooping cough. CyaA intoxicates target cells by a direct translocation of its catalytic domain (AC) across the plasma membrane and produces supraphysiological levels of cAMP, leading to cell death. The molecular process of AC translocation remains largely unknown, however. We have previously shown that deletion of residues 375–485 of CyaA selectively abrogates AC translocation into eukaryotic cells. We further identified within this “translocation region” (TR), P454 (residues 454–484), a peptide that exhibits membrane-active properties, i.e., is able to bind and permeabilize lipid vesicles. Here, we analyze various sequences from CyaA predicted to be amphipatic and show that although several of these peptides can bind membranes and adopt a helical conformation, only the P454 peptide is able to permeabilize membranes. We further characterize the contributions of the two arginine residues of P454 to membrane partitioning and permeabilization by analyzing the peptide variants in which these residues are substituted by different amino acids (e.g., A, K, Q, and E). Our data shows that both arginine residues significantly contribute, although diversely, to the membrane-active properties of P454, i.e., interactions with both neutral and anionic lipids, helix formation in membranes, and disruption of lipid bilayer integrity. These results are discussed in the context of the translocation process of the full-length CyaA toxin.

Multimodal Analysis from the DUV to the NIR of the Endogenous Fluorescence of Brain Tumor Biopsies

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ABSTRACT

The main challenge of brain tumor surgeries nowadays is to keep improving patients' quality of life after the operation. A key factor to equilibrate the onco-functional balance of a patient after the surgery is to control the extent of resection, measured by Simpson grading system, while preserving surrounding eloquent brain areas is necessary [1]. Developing a tool able to increase the accuracy of tissue analysis and that will be able on long term to deliver an immediate diagnostic on tumor, could drastically improve actual surgeries and patients survival rates, our group is working on the realization of such an endomicroscope[2]. However, to achieve such performances the construction of a complete optical database on autofluorescence signature is required. An excitation ranging from ultraviolet to infrared and four different contrasts was were used: 1) spectral analysis covering the deep-ultraviolet (DUV) to near-infrared (NIR) range, 2) two photon fluorescence lifetime imaging 3) second harmonic generation imaging[3,4]and 4) Fluorescence imaging using DUV to IR, by one and two photon excitations. In all those measurements, we excite and collect the endogenous fluorescence of tissues to avoid any bias and further clinical complication due to exogenous markers. Thereafter, all the different modalities are then crossed to build a matrix of criteria to discriminate tumorous tissues, some of the indicators are shown in the Figure 1. The results of multimodal optical analysis on human biopsies were also compared to the gold standard histopathology in order to validate our analysis.

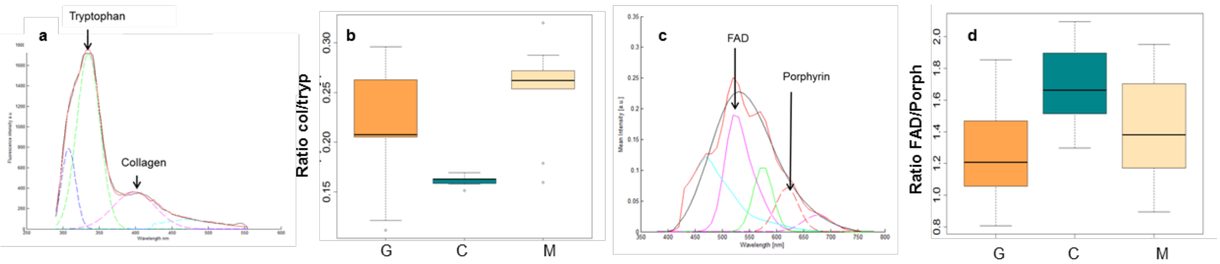

Figure 1. Quantitative analysis with DUV excitation (a,b) and NIR excitation (c,d) on three groups of tissue : Glioblastoma (G), Metastasis (M) and Controls (C).

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POSTERS SESSION

List of Student Posters

PO-AN-01	Emergent high-spin state above 7 GPa in superconducting FeSe *B.W. Lebert*
PO-AN-02	Atomic layer deposition of hafnium oxide on a Si(111) surface followed by NAP-XPS *L. Pérez Ramírez*
PO-AN-03	The stability hierarchy of the trimorphic system L-Tyrosine ethyl ester as a function of pressure and temperature *I.B. Rietveld*
PO-AN-04	Vertical epitaxy mechanisms of ultrathin and highly strained nickel nanowires embedded in $SrTiO_3$ *X. Weng*
PO-DR-05	VUV photoionization of methylisocyanate: vibronic structure and dissociative ionization channels *O. Harper*
PO-DR-06	Multiple Auger decay of the potassium 2p holes and its satellites *M.A. Khalal*
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PO-DR-08	XAS time-resolved phase speciation of Cu-based LDH to ethanol dehydrogenation *R. Santos*
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PO-LH-10	Biophysical characterization of a two component system response regulator, ParR *K. Housseini*
PO-LH-11	Monitoring food structure in plant protein solutions and gels during digestion using small angle scattering and imaging techniques *J. Pasquier*
PO-LH-12	Identification and mapping of metallic ions and phenols in fleshy fruit by cryo-methods *K. Vidot*

Emergent High-spin State above 7 GPa in Superconducting FeSe

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ABSTRACT

The local electronic and magnetic properties of superconducting FeSe have been investigated by Kβ x-ray emission (XES) and simultaneous x-ray absorption spectroscopy (XAS) at the Fe K-edge at high pressure and low temperature [1]. Our results indicate a sluggish decrease of the local Fe spin moment under pressure up to 7 GPa, in line with previous reports [2], followed by a sudden increase at higher pressure which has been hitherto unobserved. The magnetic surge is preceded by an abrupt change of the Fe local structure as observed by the decrease of the XAS pre-edge region intensity and corroborated by ab-initio simulations. This pressure corresponds to a structural transition, previously detected by x-ray diffraction [3], from the *Cmma* form to the denser *Pbnm* form with octahedral coordination of iron. Finally, the near-edge region of the XAS spectra shows a change before this transition at 5 GPa, corresponding well with the onset pressure of the previously observed enhancement of the superconducting critical temperature [4]. Our results emphasize the delicate interplay between structural, magnetic, and superconducting properties in FeSe under pressure.

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Atomic Layer Deposition of Hafnium Oxide on a Si(111) Surface followed by NAP-XPS

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ABSTRACT

Continued miniaturisation of integrated circuits (IC) is central to their technological advancement. Given that metal-oxide-semiconductor field-effect transistors (MOSFETs) are the basic building blocks of ICs, further downscaling can be achieved by reducing the thickness of their gate oxide[1]. Silicon dioxide (SiO_2) has been the preferred material as gate insulator since the early 1960s. However, for SiO_2 films thinner than 1.5 nm, leakage current due to tunnelling effects reaches unacceptable levels. Therefore the need to develop high-k dielectrics to replace SiO_2. Since 2007, hafnium oxide (HfO_2) appeared as a good candidate[2]. Not only it has a relative dielectric constant six times greater than that of SiO_2, but it also has relatively large energy band gap and a good thermal stability as compared to Si, which allows a higher capacitance and reduces leakage current[3].

The use of synchrotron-based radiation x-ray photoelectron spectroscopy (XPS) is widely extended in surface science, it has been employed for many years to study chemical composition, due to its surface sensitivity and chemical specificity. However, XPS is limited to vacuum conditions which often make it a post-mortem technique. Relatively recent development has allowed the adaptation of XPS to elevated pressures, in the order of mbar range. Near ambient pressure-XPS (NAP-XPS) allows the characterisation of a sample in a gaseous environment, which means it is possible to perform measurements at the surface during a chemical reaction. In this work, HfO_2 ALD on a native Si(111) oxide substrate was performed using alternating exposures of tetrakis(ethylmethylamido)hafnium(IV) ($Hf(EtMeN)_4$) and H_2O as precursors. The HfO_2 growth mechanism was studied by NAP-XPS.

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The Stability Hierarchy of the Trimorphic System L-Tyrosine Ethyl Ester as a Function of Pressure and Temperature

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ABSTRACT

Many organic molecules crystallize in different crystal structures, which is known as polymorphism. In particular for the pharmaceutical industry, it is important to establish which of the crystalline phases is the most stable one. The stability hierarchy can be determined with a straightforward, so-called topological, approach involving calorimetric and volumetric (by X-ray) measurements, the Le Chatelier principle and the Clapeyron equation resulting in a pressure – temperature phase diagram. For known crystalline phases, it is often not even necessary to carry out measurements under pressure. Once a phase diagram has been constructed for a dimorphic system, additional crystalline phases can be incorporated in the stability hierarchy, by constructing pressure – temperature phase diagrams for each combination of two crystalline phases. By superposition of these diagrams (and effectively of the Gibbs energy), the complete phase diagram can be constructed with stable and metastable solid phases.

This method will be illustrated using the case of l-tyrosine ethyl ester, which possesses two crystalline phases under ordinary conditions and one additional phase (III), which apparently only appears under pressure.

It will be shown how the stability hierarchy between phases I and II can be determined using calorimetric data obtained under ordinary pressure and density measurements as a function of temperature by X-ray diffraction. Form II is stable under ambient conditions, but it changes with increasing temperature into form I, which melts. It is shown using thermodynamic arguments that with increasing pressure, form II becomes the more stable form and thus the system becomes in principle monotropic at higher pressure.[1]

When form I is subjected to high pressure measurements a third crystalline form appears (form III) and when form II is subjected to high pressure, no trace of form III is observed.[2]

It is shown using thermodynamic arguments that among the three polymorphs, form II is the stable high-pressure form. Moreover, under ordinary conditions, without applying pressure, all three phases have a stable temperature domain and the system is fully enantiotropic under these conditions. Increasing the pressure, the stability domains of forms I and III cease to be stable. Thus at higher pressure form II is the only remaining stable phase and the system has become fully monotropic.

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Vertical Epitaxy Mechanisms of Ultrathin and Highly Strained Nickel Nanowires Embedded in $SrTiO_3$

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ABSTRACT

Metallic nanowires (NWs) vertically epitaxied in a planar oxide matrix constitute a new class of composite materials. In these hybrid systems, the large interface and coupling between the NWs and matrix can give rise to unexpected optical, magnetic, electrical or mechanical properties, which deviate from the bulk ones.

In this study, we present results on ultrathin Ni NWs in a $SrTiO_3$ matrix with diameters in the range from 6 down to 2 nm. The NWs axial tensile strain depends strongly on the diameter: it increases from 2.3 up to 3.6%, with decreasing NWs diameters. Magnetic measurements have shown that such NWs do not display the usual behavior expected when considering only their shape and large aspect ratio. We therefore used XRD (beamline SixS) and XAS (beamline Samba) to analyze the Ni NWs crystalline structure and the local atomic order. Along the NWs [001] axis, XRD patterns sketch a structural picture of connected coherent domains of about 15 nm height. Along a NW, the strain and the rotation of lattice planes evolve together in a correlated way. More precisely, the strain relaxes when the lattices planes rotate around Ni fcc [100] or [010] axis. The important feature here is that the relaxation ends at around 1.3% axial strain and a rotation of approximately 4.2 degrees, until achieving a (101) lattice plane match between the NWs and matrix. XANES spectra are bulk-like for slightly strained and thick NWs (diameter 6 nm), while unusual and striking structural anisotropy was observed by linear dichroism for highly strained and ultrathin NWs (diameter 2 nm). Upon further reduction of the diameter (~1.7 nm), a spectrum characteristic of quasi-amorphous metallic nickel is observed. EXAFS spectra confirm the trend that the atomic structural disorder increases with decreasing NWs diameters and increasing strains.

Results obtained allow us to establish the strain field inside the ultrathin Ni NWs, revealing strain relaxation mechanisms in the vertical epitaxy. They will be correlated to the properties of ultrathin and highly strained Ni NWs, such as the peculiar magnetic anisotropy.

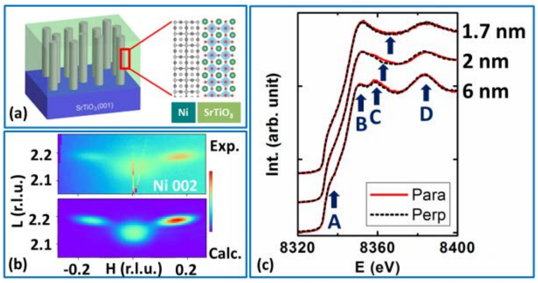

Figure: (a) Scheme of Ni NWs in $SrTiO_3$. (b) XRD patterns: measured and calculated Ni 002 spot. (c) XANES parts of linear-dichroic XAS spectra with the x-ray polarization parallel (red solid lines) or perpendicular (black dashed lines) to the NWs: i) bulk-like Ni NWs of 6 nm diameter, with the characteristic Ni bulk peaks indicated by A, B, C and D arrows; ii) dichroic NWs of 2 nm diameter; iii) quasi-amorphous metallic Ni NWs of 1.7 nm diameter.

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VUV Photoionization of Methylisocyanate: Vibronic Structure and Dissociative Ionization Channels

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ABSTRACT

Methylisocyanate, CH_3NCO, is an organic molecule belonging to the isocyanate family involving two consecutive double bonds (N=C=O). It has been detected in Space in the hot core of a giant molecular cloud Sgr B2(N) and in the Orion clouds [1,2]. It is also one of the most abundant species detected very recently on the surface of comet 67P/Churyamov-Gerasimenko thanks to the COSAC mass spectrometer on board Rosetta's Philae lander [3]. This molecule is a common example of methyl-distorted linear system resulting in a complex rotational structure. The rotational spectrum of this asymmetric top species has been investigated by several mm-wave laboratory experiments. Concerning the cation, only photoelectron spectra at low resolution are available [4,5]. In Space, this compound can be ionized by the vacuum-ultraviolet (VUV) local radiation field and its resulting cation in the gas phase can play a role in the chemical evolution of these media.

Experiments performed on the DESIRS beamline of SOLEIL with the DELICIOUS III double imaging spectrometer have allowed to investigate the vibronic structure of the electronic ground state of the cation, $^2A''$, and to measure accurately the first ionization potential (10.59 ± 0.01 eV). This value is in very good agreement with theoretical calculations. Using the vibrational energies of the neutral methyl isocyanate and *ab initio* calculations, we were able to assign all the observed vibrational structures in the vicinity of the $X^+\,^2A'' \leftarrow X\,^1A_1$ photoionizing transition of the experimental photoelectron spectrum.

In addition, photoionization yields of the various cationic fragments formed through dissociative ionization have been recorded between 10.3 and 20.5 eV at lower resolution. These spectra do enable the identification of various fragments and their corresponding formation channels. In particular, we were able to extract appearance energies for several fragments, in very good agreement with quantum chemical calculations. To our knowledge, it is the first time that the photon-induced dissociative ionization of CH_3NCO is studied.

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Multiple Auger Decay of the Potassium 2p Holes and its Satellites

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ABSTRACT

Auger decay is the predominant pathway in the de-excitation of the inner-shell vacancies in light atoms. It is a non-radiative transition where the core-hole is filled by a valence electron and one or several Auger electrons are ejected leading thus to the formation of a multiply charged ion [1,2].

We investigate the Auger decay processes following the 2p inner shell ionization of atomic potassium. The experiment was carried out at the PLEIADES beamline of the SOLEIL synchrotron facility. Our spectrometer, a magnetic bottle with a 2m long time-of-flight tube [3], allows the efficient collection of almost all electrons in 4π solid angle. The detection efficiency of the electron allows the detection of up to four electron in coincidences. Relative abundances of K^{2+}, K^{3+} and K^{4+} ions that follows respectively single, double and triple Auger decay are determined (figure 1). These results are compared with the decay of Ar 2p holes to point out the role of the 4s external electron in the decay mechanism of potassium [4].

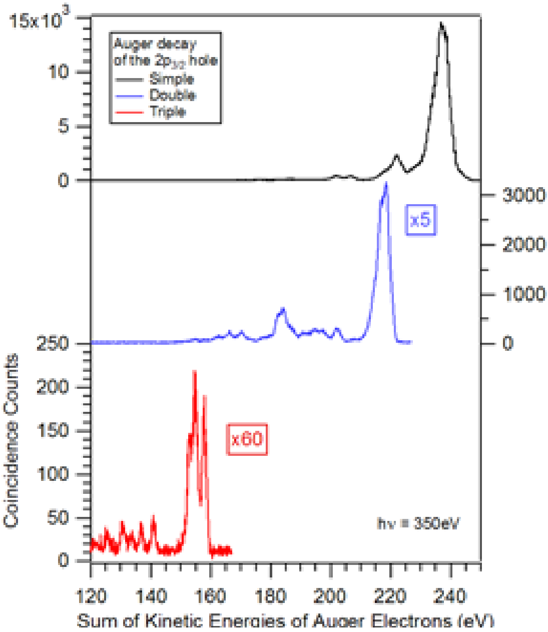

Figure 1. Auger spectra for the Auger decay of a K 2p hole by emission of one, two or three Auger electrons.

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Validation of a Capillary Reactor to Characterize In-situ the Liquid Sulfidation of Hydrotreatment Catalysts by Quick-XAS

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ABSTRACT

Improvement of hydrotreatment catalysts to obtain cleaner fuels requires the development of more efficient cobalt-promoted MoS_2 catalysts supported on alumina. One way to achieve this is the addition of chelating agents such as citric acid in order to postpone the sulfidation of promotor compared to molybdenum. A deeper understanding of the activation step, i.e. the sulfidation of cobalt and molybdenum, is necessary to explain the origin of a better activity for additivated catalysts. At the industrial scale, high pressure (30 bar) sulfidation is performed under hydrogen and diesel feed additivated with a sulfiding agent such as dimethyl disulfide. To achieve this harsh condition, a new reactor was developed to study catalysts under industrial conditions at the lab scale by X-ray absorption spectroscopy. Improvement of the catalysts requires a better insight into the sulfidation mechanism and the identification of the intermediate species involved.

As recently shown[1], the Quick X-ray Absorption Spectroscopy (Quick-XAS) available at the ROCK beamline at the SOLEIL synchrotron is a powerful technique to probe the local structure and electronic environment at both cobalt and molybdenum K-edges. The new designed cell is composed of 2 parts, a fluid distribution system and a bracket which holds the capillary reactor and the heating system. This reactor is a glassy carbon tube with an inner diameter of 2.1mm, an outer diameter of 6mm and a length of 150mm. The reaction area (around 30mm) in the tube was filled with crushed catalyst (30-40µm) diluted in diamond powder (30-40µm). This set up was used to study a CoMoP catalyst and an additivated one with citric acid. For each catalyst, the sulfidation was recorded at the Co K-edge and the Mo K-edge simultaneously using the edge jumping operation mode which allows us to alternate 5 min measurements at each edge during the 30 hours of activation carried out on a single sample. The data were analysed by Principal Component Analysis and Multivariate Curve Resolution by Alternating Least Square minimization in order to determine the concentration profiles of the species involved during activation and the XAS spectra of these pure species. The combination of time resolved data collected at both edges with chemometric analysis allowed us to give a first insight into the liquid sulfidation mechanism with and without citric acid and to determine the different chemical species involved.

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XAS Time-resolved Phase Speciation of Cu-based LDH to Ethanol Dehydrogenation

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ABSTRACT

Nowadays, the search for higher yields and lower energy costs in chemical transformations increases the research for nanocatalysts. Nanocatalyst characteristics combine advantages of both heterogeneous and homogeneous catalysis, with the ease of handling, separation and recycling of heterogeneous catalysts, together with the higher activities and selectivity of the homogeneous catalysts. In this sense, nanocatalysts derived from the thermal decomposition of layered double hydroxides (LDH) can be used in different reactions, presenting high dispersion of the active phase, low costs and high catalytic yields. LDH are described by the expression: $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]_{\text{layer}}\ [A^{n-}_{x/n}\cdot zH_2O]_{\text{interlayer}}$, where M^{2+} and M^{3+} are metal cations occupying the octahedral interstices of sheet, while A^{n-} represents anions. Upon thermal treatment and reduction, LDH lead to highly dispersed and stable metallic nanoparticles strongly interacting with the mixed oxide matrix.[1]

In this work, a CuZnAl-LDH system containing 10%wt copper and a M^{2+}: M^{3+} ratio of 0.8:1 was synthesized *via* coprecipitation method and applied in the ethanol dehydrogenation reaction (EDR). *Operando* quick-XAS characterization during the activation and EDR were carried out at the ROCK beamline of the SOLEIL Synchrotron. The time-resolved normalized Cu-K edge XAS dataset was analysed by Principal Component Analysis (PCA) and Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) fitting analysis in order to identify and quantify the copper species formed upon activation and reaction.[2] Initially the LDH was calcinated at 450 °C in air atmosphere, forming exclusively nano-CuO species. Two activation methods were studied: classical activation (reduction in H_2 atmosphere at 350°C) and self-activation (reduction during the reaction with ethanol itself starting at 200°C with gradual increase of the temperature by 50°C every 45 min).

On the one hand, the self-reduction occurs slowly at 200 °C, forming an intermediate Cu^+ oxidic species. When the temperature increases, the Cu^0 species comes up, as the H_2 production is greater, reaching around 95% at 250°C, 98% at 300 °C and 100% at 350 °C. On the other hand, the classically activated catalyst quickly reaches 100% of Cu^0 during the activation and does not change during the whole reaction carried out between 250 and 350°C using isothermal steps of 50 °C with 45 min at each temperature. The results show that despite the energy savings of the H_2 reduction step, the self-activated catalyst was less active than the classically activated one. Even though the Cu^+ species or an optimal Cu^+:Cu^0 ratio has been shown in some recent studies more efficient than Cu^0 species,[3] it appears quite difficult to maintain this ratio during the EDR conditions used herein. Namely, upon ethanol feed, the H_2 product immediately reduces the Cu^+ species to Cu^0.

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Charge Transfer and Nuclear Dynamics after Methyl Iodide Core Ionization following Single Photon Absorption

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ABSTRACT

The aim of this study is to investigate experimentally photoionization and photodissociation processes in gas-phase of Methyl iodide (CH_3I) by tender X-ray photons. This molecule can be considered as a prototype of small organic molecules containing a heavy halogen atom. Core ionization of iodine lead to multiple charge transfers in the molecule during the electronic relaxation. Several experiments have been done on this molecule using multi-photon absorption [1][2][3]. Our measurements were obtained by single photon absorption on the GALAXIES beamline at SOLEIL. We have measured the momentum vector of the ionic fragments using a double time of flight spectrometer, CELIMENE [4], after ionization of Iodine at the 2s and 2p edges. We also applied electron – ions coincidence techniques (PE3PICO) to elucidate the fragmentation mechanisms.

We demonstrate that photoabsorption of iodine in deep inner-shell (2p and 2s) followed by multiple Auger decay leads to the creation of highly charged ionic states up to 14+. Moreover, we observe the dissociation of the molecule by concerted explosion.

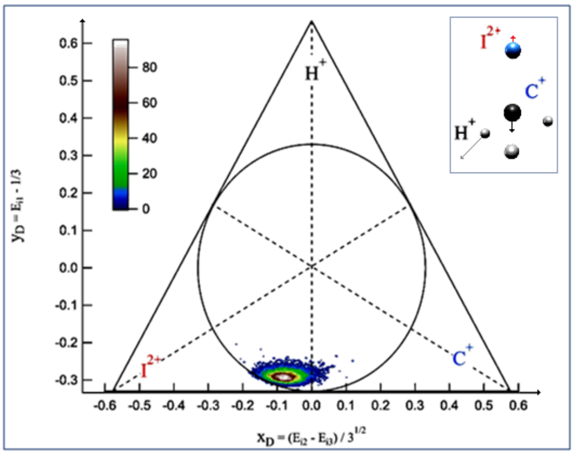

Fig.: Experimental Dalitz Plot, for three ions: (H^+, I^{2+} and C^+), located in one area correspond to the direct ionization process.

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Biophysical Characterization of a two Component System Response Regulator, ParR

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ABSTRACT

Pseudomonas aeruginosa is one of the most important infectious agents, which affects approximately 80% of cystic fibrosis (CF) patients associated with severe pulmonary exacerbations, accelerated loss of lung function and increased mortality. The mechanisms by which *P. aeruginosa* adapts to the CF airway and maintains prolonged residence are not completely understood. Both large genome variability and frequent mutations facilitate selection of adaptive mutants, including the development of antibiotic resistance, which contribute to the multidrug resistance phenotype (MDR). One of the most important mechanisms is the expression of multidrug efflux (Mex) pumps that diminish antibiotic concentration in the periplasm. Nowadays, twelve *P. aeruginosa* efflux pumps are characterized and four of them are involved in the MDR phenotype. Among them, MexXY-OprM specifically transport aminoglycosides (AG) in addition of β-lactams and quinolones families.

This work focusses on the mechanisms behind the expression regulation of those pumps. Two majors regulation pathways are described for MexXY-OprM pump: one consist of a canonical repressor/activator system and the other one includes a two-component system (TCS); both of them activate expression of MexXY-OprM under different situations. On one hand, the canonical system comprises a repressor (MexZ) and an activator (ArmZ). Although it is known that this system is engaged by ribosome-targeting agents such as AG,,it is still not clear how MexZ is modulated by ArmZ. On the other hand, the interaction of antimicrobial peptides (polymixins B and E) with lipopolysaccharide (LPS) triggered an uncharacterized signal detected by a sensor Histidine Kinase (HK) ParS which autophosphorylates its cytosolic domain on a conserved Histidine residue. A phospho-relay allows the activation of the response regulator ParR by transferring the same phosphate group. Once ParR is activated, the expression of different operons is induced including the *mexXY* operon.

In this study, we aim at characterizing the activation of the efflux pump MexXY by solving the structure of the phosphorylated regulator ParR in complex with the DNA operator of *mexXY* operon. I will present biochemical study of ParR showing a monomeric inactive protein. Structural data with SAXS (Small Angle X-ray Scattering) support a protein with 2 domains associated by a flexible linker.

Monitoring Food Structure in Plant Protein Solutions and Gels During Digestion using Small Angle Scattering and Imaging Techniques

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ABSTRACT

Objectives: We aim at exploring on a wide scale range how enzyme efficiency and consequently gastric and intestinal phases of digestion are influenced by food microstructure. We use UV fluorescence imaging and Small Angle Scattering, from X rays (SAXS) at Synchrotron SOLEIL, and from Neutron radiation (at LLB), best suited for gels hosting also fat. After work on dairy gels[1], we now introduce model plant protein solutions/gels coming from rapeseed.

Methods: Rapeseed proteins have been extracted and purified at BIA-INRA, Nantes. Napin is a monomeric protein very similar to the lysozyme. On the contrary, cruciferin is a more complex system with six sub-units stabilized by weak interactions. Gels modulus, pH, can vary on a wide range, and protein inner conformation can be affected too. Given these structure-related properties, we expect different digestion profiles. We submit pure solutions as well as gels to gastric and intestinal enzymes and study the kinetics of evolution of the structure. Secondly, we will introduce fat and monitor the interactions between these two nutrients along digestion.

Results: SAS enables us to identify proteins and differently structured aggregation. We will be able to relate the compactness of the system and its accessibility for the digestive enzymes at different scales. Results can be linked with data obtained during in vitro digestion on the same samples in UMR GMPA (biochemical analyses, rheology, light scattering), or LLB (water diffusion).

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Identification and Mapping of Metallic Ions and Phenols in Fleshy Fruit by Cryo-methods

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ABSTRACT

Metallic cations and polyphenols nature and distribution are poorly known in plant. They play a major role in plant organ physiology, and particularly in fruit ripening with impacts on food processing and consumer preference[1],2. A better understanding of the nature and variability of metallic cations and phenols would contribute to innovative strategies for cultivar varietal selection, and for the development of production and post-harvest practices. A final aim would be to enhance the fruit quality in industrial food processes and consumers habits. To achieve this goal, the nature, location and quantity of metallic cations (Mg, K, Ca, Mn and Fe) of two texture-contrasted apple varieties have been investigated by scanning X-ray fluorescence imaging (XRF) at LUCIA SOLEIL beamline (energy: 7.2 keV focused beam:3x3 μm^2).From the same specimen preparation, tannins and phenolic acids were also analysed by micro-spectroscopy using their auto-fluorescence under deep UV excitation at 275 nm at DISCO beamline. A particular attention was paid to check sample preparation routes and environmental conditions of these analyses: a combination of cryo-fixation, cryo-sectionning and cryo-observations were used to fix ions and metabolites diffusion in apple cortex. On LUCIA a liquid nitrogen cryostat was used and on DISCO, a specific home-made cryo-setup3 was adapted for the full field inverted microscope TELEMOS. The first results reveal that Ca, Mn, Fe were mainly found in the epidermal and outer cortex cell layers. Moreover, evolution of the Ca and Fe distributions were depending on the fruit softening. With regard to phenolics, variations in tissue auto-fluorescence emission were observed in different cell layer and fruit variety. Combining cryo-methods and the two synchrotron light beam revealed gradient distributions of ions and phenolics are function of genetical and developmental characteristics. Images analysis will help establishing relation between these gradients that may impact fruit processing and consumer perception. These results open the way to further studies at the cellular and subcellular scale to identify specific ions and phenolics locations and environments in the context of fruit quality elaboration.

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List of Other Posters

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PO-14	Utility of scanning transmission X-ray microscopy for determining the dimensions of core-shell nanoparticles *S. Swaraj*
PO-15	LUCIA. A multidisciplinary beamline *D. Vantelon*

HC_5N^+ Vibronic Structure Investigated by VUV Photoelectron-spectroscopy and *ab initio* Calculations

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ABSTRACT

Cyanobutadiyne H-C≡C-C≡C-C≡N, a molecule of astrophysical interest, is a member of the cyanopolyyne family which requires complex organic synthesis in the lab [1], yielding very small quantities that are usually redhibitory for conducting high-consumption gas-flow experiments. The recent implementation of an effusive beam source coupled with the DELICIOUS III spectrometer on the DESIRS beamline has opened new perspectives in studying rare or/and expensive compounds with the double-imaging photoelectron/photoion technique in coincidence. This development allowed us to perform a complete TPEPICO photoionization study of HC_5N between 10.4 and 14.8 eV (see Figure 1 below).

The vibronic structure of the four lowest electronic states has been observed and accurate values of the adiabatic ionisation energies have been measured, which significantly improve the only values derived from low-resolution He(I) photoelectron spectroscopy in 1980 [2]. In addition, the HC_5N^+ ion yield has been recorded for the first time in the range 10.4-19.8 eV, revealing sharp autoionization structures.

The spectral analysis of the vibronic bands and the complex electronic state manifold has been supported by high-level *ab initio* calculations [3]. These new data will be of great help to analyze the high-resolution VUV absorption spectrum of HC_5N that we have recorded with the VUV FTS instrument of the DESIRS beamline. In particular, the new information obtained on the cation vibronic states will help to identify the neutral Rydberg states and their vibrationally excited components.

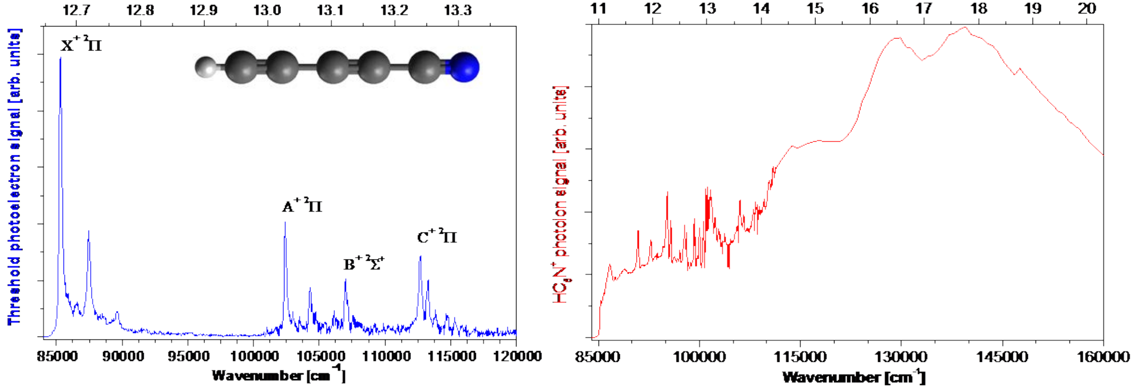

Fig. 1: Overview of the HC_5N TPEPICO spectrum and photoionization yield recorded on the DESIRS beamline

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Heterodyne Receivers Optimized for Synchrotron Sources (HEROES)

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ABSTRACT

The goal of the HEROES project is to develop a new high-resolution spectroscopic set-up in the far infrared (FIR), using a heterodyne detection scheme. A FIR optically-pumped gas laser[1] will be used as the local oscillator (LO), SOLEIL synchrotron as the source and a hot electron bolometer (HEB) as the mixer (Fig. 1). The combination of the excellent spectral coverage of the AILES beamline (1-10 THz) and an unprecedented series of LO will able to cover several new frequency channels with a resolution of 10 kHz and should pave the way to obtain an ultra-high resolution and wide range spectrometer.

We present here preliminary results. A multiplier chain is used as the LO in the heterodyne detection scheme. This first experiment at the AILES beamline allowed to obtain the detection of the D_2O absorption line $^{R}Q(4)_{0,4}$ at low pressure around 0.78 THz with a resolution better than 1 MHz (Fig. 2). This resolution is typically thirty times better than the resolution of the Fourier transform spectrometer of AILES[2].

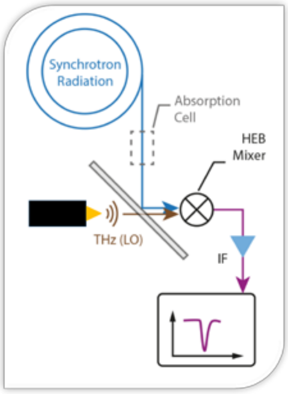

Fig. 1. Heterodyne detection scheme

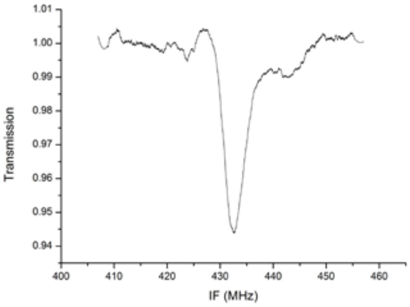

Fig. 2. Absorption line of D_2O with sub-MHz resolution. LO frequency: 782.0388 GHz, T = 293 K, P = 50 µbar.

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Structure of Co/C_{60}/Co(0001)

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ABSTRACT

Due to their long spin relaxation time and the possibility to functionalize them at will, the use of organic materials is a promising way for the development of new spintronic applications, especially for the realization of vertical spin valves in which the non-magnetic spacer is made of an organic film. Promising results have already been obtained on C_{60} based spin-valve presenting a magneto-resistance at room temperature [Gobbi2011]. The magnetoresistance is strongly affected by the interface structure [Barraud2010] and the organic layer organization, thus, it is crucial to study both of them.

We studied the first C_{60} monolayer to investigate the structure of the bottom interface, and showed that it organizes in an hcp lattice with 4x4 reconstruction with respect to the Cobalt substrate. In this work, we present the study of the structure of the C_{60} crystal grown in-situ on a Co(0001) single crystal under UHV conditions, before, during, and after deposition of Cobalt on top of it. To achieve this, we used different X-rays scattering tools at SIXS beamline of SOLEIL synchrotron : reflectivity, grazing incidence diffraction and small angle scattering.

We were able to show that the C_{60} layer on Co(0001) fully crystallizes in two fcc lattices without interface relaxation. The C_{60} crystal is strongly affected by the Cobalt deposition as we evidenced a diffusion of the Cobalt in the entire C_{60} layer, occupying interstitial sites.

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Fermi Surface of the Metallic Diamond Investigated by ARPES

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ABSTRACT

Doping pure diamond thin films with boron atoms induces a phase transition towards a metallic state. The boron doping lifts the top of the diamond valence band above the Fermi level, and makes this metallic phase easily measurable by photoemission spectroscopy [1]. High resolution ARPES experiments reveal a small Fermi surface centered at the center of the Brillouin zone. The Fermi surface consist of three different hole sheets as observed by rotating the polarization of the SR light in several directions. The experimental data are compared with the theoretical Fermi surface obtained using the k.p model.

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Crystallography Platform at the Institut Pasteur

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ABSTRACT

The goal of the crystallography platform is to provide research teams working in the field of macromolecular crystallography at Institut Pasteur with the expertise and technology for high throughput crystallization, X-ray diffraction measurements, and crystallographic computing as a core facility. Our second mission is to offer expertise in bio-crystallography, from crystallization of selected targets to resolution of 3D crystal structures by participating as a partner in research projects involving structural studies of single proteins and protein complexes. These projects arise from direct collaboration with research groups at Institut Pasteur and outside organisations. Depending on the expertise of the users, three options can be offered: service provision, instrument allocation, and scientific collaboration. Service provision, which corresponds to the automated crystallization experiments performed in standard conditions, is the option used by the crystallographers. If initial crystallization trials are successful, the platform assists users to reproduce and optimize the crystallization conditions in order to obtain suitable crystals for X-ray data collection. Since 2010, the platform has been involved in more than 24 scientific collaborations in association with 14 research units from 8 scientific departments of the Institut Pasteur and 6 laboratories from other institutions (French or foreign), leading to our co-authorship of 32 peer-reviewed publications. These projects cover many disciplines related to infectious diseases and human health, including defense mechanisms against pathogens, antibiotic resistance, regulation pathways, genetic disorders and drug design. In our poster, we present the instrumentation and robotics available in the platform and a summary of results obtained during the last five years.

Structure-function Analysis of the Chloroplastic Ribulose-phosphate Epimerase Cr-RPE1

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ABSTRACT

Photosynthetic carbon fixation in Eukaryotes relies on the 11 enzymatic catalysis events of the chloroplastic Calvin-Benson cycle. Ribulose-5-phosphate 3-epimerase produces ribulose-5-phosphate from xylulose-5-phosphate as a preliminary to PRK production of the RuBisCO substrate, CO2 acceptor, ribulose-1,5-bisphosphate.

We solved the crystal structure of chloroplastic RPE1 from the unicellular alga *Chlamydomonas reinhardtii*. The polypeptide folds into a barrel of 8 alpha/beta motifs similar to the TIM-barrel type. Substrate is bound via a phosphate-binding motif of strands 7 and 8 while a tetrad of 2 aspartates and 2 histidines chelate a Zinc ion and determine acid/base catalysis. Future work aims at integrating individual structural information at the level of the 11 enzymes system.

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Pressure Dependence of the Infrared Spectra of a Molecular Jahn-Teller Metal

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ABSTRACT

The fulleride salt Cs_3C_{60} occurs in two cubic allotropes, fcc and A15. Both are insulators under ambient conditions, however, at slight pressures they turn into superconductors with a record transition temperature among fullerides. As we have shown before [1], the dynamic Jahn-Teller effect plays a crucial role in the Mott metal-insulator transition, and the Jahn-Teller distortion can be sensitively detected by infrared spectroscopy. By applying chemical pressure through substitution of Cs with Rb, we followed the transition and detected an intermediate state that we termed a Jahn-Teller metal. In the present project, we applied physical pressure to both fcc and A15 Cs_3C_{60} and mapped the temperature-pressure phase diagram by infrared spectroscopy in a diamond anvil cell at the SMIS beamline at Soleil. Our results are in accordance with the chemical pressure data and indicate the presence of the Jahn-Teller metal state.

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Induced Circular Dichroism Signal of Thioflavine T in the Presence of Tau Fibers

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ABSTRACT

Thioflavine T (THT) is a molecular rotor and is commonly used dye to study amyloid-like deposits. Here, we examine the fluorescence properties of Thioflavin T upon binding to amyloid filaments from the microtubule-associated protein Tau. Thioflavin T are more easily obtained as pure chemical compared to others thioflavines and is not a mixture of chemical as Thioflavin S. THT is not optically active chemical in solution. An effective induced fluorescent and induced circular dichroism is observed with THT when bound to Tau fibers compared to THT free in solution or in the presence of not aggregated Tau protein. In the study of amyloid structure formation from intrinsically disordered protein, THT combined the advantage to be able to characterize qualitatively by induce fluorescence and circular dichroism the formation of fibers.

A Case of Polymorphism in a Tetraloop Due to a Crystal Packing Interaction

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ABSTRACT

To generate a single RNA conformer of the Lariat-Capping (LC) ribozyme, we engineered a circular permutation leading to the opening of the scissile bond and to the closure of the natural 5' and 3' extremities using a UUCG tetraloop [1,2]. The loop was supposed to have no effect on the whole structure. When we solved the structure, we noticed that the loop actually opened up in order to weave intimate interactions with a symmetry-related ribozyme molecule.

In order to check whether the conformation of the loop was due to the interaction, or if it opened up due to the design of our construct, we shortened the stem bearing the UUCG loop by one base-pair and solved the structure of this new construct. The crystal structure shows that in this slightly different context, the loop actually adopts the UUCG closed conformation that is observed in general.

We can conclude from these crystal structures that UUCG are indeed polymorphic and dynamic, and can serve interaction purposes, a function usually devoted predominantly to the GNRA tetraloops. This finding changes somehow the status of this kind of loops, which can be thought as a sensor as well as their cousins, the GNRA tetraloops. This finding may also orient future research to better characterize these loops to use them as crystallization modules among other applications.

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3D Laue Micro-diffraction characterization of local microstructure and strain with submicron resolution

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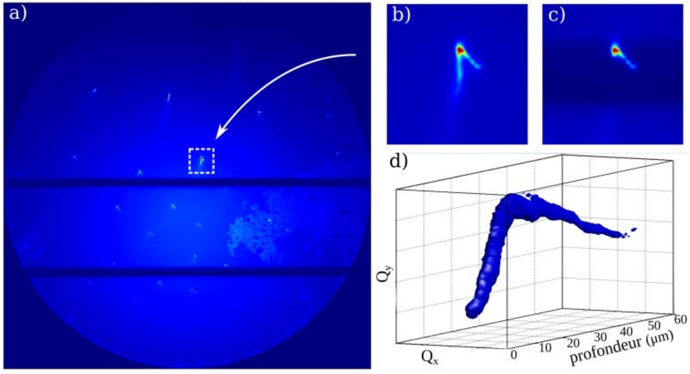
ABSTRACT

Laue microdiffraction is a powerful technique that uses a white micro-focused X-ray beam from a synchrotron source to characterize local microstructural properties and micromechanical behaviours in a wide range of crystalline and polycrystalline materials [1]. Allowing fast two-dimensional mapping of local crystal structure, orientations and deviatoric elastic strains, without sample rotation, the method can reach sub-micron spatial resolution and angular resolution of 10-4, suited for in situ studies [2].

Due to the penetration of X-rays into the sample, from a few microns to millimeters depending on the material, Laue microdiffraction provides in practice depth-integrated diffraction patterns, which superimpose the intensity diffracted by all the grains along the penetration course of the incident beam. The 3D Laue microdiffraction, or « Differential Aperture X-Ray Microscopy » [3], was therefore proposed to extend the capabilities of conventional micro-Laue and resolve the dimension along the incident beam. To this end, a wire (e.g, made of tungsten) is used as an absorption profiler and scanned between the sample surface and the 2D detector (10Hz).

Significant efforts were made to implement 3D Laue microdiffraction on the french CRG beamline IF-BM32 at ESRF [4]. Recent results have demonstrated the capabilities of the currently available setup and analysis tools to characterize microstructural and mechanical features in micro-scale objets [5]. We sought to account for a realistic absorption and proposed therefore a new reconstruction scheme based on an inverse problem formulation that allows for a more accurate and direct data treatment. This was accompanied by the development of a new software package, designed for the beamline users



3D depth-resolved reconstruction of a diffraction spot: a) Laue pattern of a nitrided Ni-Ti alloy, using two tungsten wires of 50 µm diameters, b) initial spot, c) spot partially masked by the wire d) isosurface representation of the reconstructed depth-resolved spot. The intensity spread directions provide information about the modes and heterogeneities of plastic deformation in the surface layer. (Sample: M. Fonovic, A. Leineweber, MPI, Stuttgart)

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Metabolic Fate of the Ferric-complex of the Pyoverdine Synthesized by *Pseudomonas Fluorescens* C7R12 in Strategy I Plant

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ABSTRACT

Despite its abundance, iron is weakly bioavailable for organisms due to its poor solubility in soils under aerobic conditions. Therefore, plants and other organisms have evolved mechanisms to efficiently assimilate iron from the soil. Non-grass plants use a strategy (strategy I) based on soil acidification, reduction of the Fe^{3+} in Fe^{2+} which is incorporated in the roots by iron transporters. We previously showed (Shirley et al., 2011; Vansuyt et al., 2007) that iron nutrition and growth of a strategy I plant could be promoted by the ferric-complex of the pyoverdine, a siderophore produced by microorganisms. If pyoverdine was further localized *in planta* using different immunological technics, mechanisms involved in the uptake of the model ferric-pyoverdine and its fate *in planta* remained still unknown.

To better understand how strategy I plant use pyoverdine for their iron nutrition, X-ray fluorescence (XRF) imaging and Fe K-edge XANES analyses were conducted on LUCIA beamline under cryogenic conditions. Data were collected on two models of plant: *A. thaliana* and pea (*P. sativum*), cultivated with addition of Fe (Fe-pyoverdine complex synthesized by *Pseudomonas Fluorescens* C7R12 or Fe-EDTA complex) or without Fe supply. Collection of XRF maps on stems and roots thin sections of pea allowed direct Fe localization in these organs. XANES spectra obtained on freeze-dried and grounded stems and roots of *A. thaliana* at various culture times were fitted using a set of selected Fe reference compounds to determine the contribution of the different Fe-bearing species. These preliminary results are promising and provide insight into Fe-pyoverdine take-up and into its chemical evolution and translocation from the roots to the shoot.

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Single Molecular Motions using Diffracted X-ray Blinking

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ABSTRACT

In 1998, we proposed a method to observe intramolecular motions by labeling gold nanocrystals with individual single protein molecule and observing the motions of diffracted X-ray spots from labeled individual nanocrystals. This DXT (=Diffracted X-ray Tracking) can trace all rotational motion within single protein molecule using white X-rays[1-4]. When using monochromatic X-rays, it is impossible to track all motions of diffraction spots. However, we detected a clear blinking in diffracted X-ray intensity. In SOLEIL (PROXIMA-1), we conducted first experiment that consisted in the observations of Brownian motions of gold nanocrystals immobilized on polyimide film in aqueous solution using monochromatic X-rays. I collected 200 pictures for each of the 3 sample sets. Exposure time was 40 msec per one image, with the reading time that is set for the Pilatus-6M as being 4 msec. In order to analyze these motions, the autocorrelation ACF of the diffracted x-ray intensity from adsorbed gold nanocrystals is calculated. By monochromatization from the use of white x-rays, DXB (=monochromatic DXT) did in vivo observations of individual single protein molecules with very low x-ray dose. We have recently succeeded in being able to measure single molecular observations with DXB even with a laboratory x-ray source.

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Soft X-ray Spectromicroscopy to Study Electronic Conduction in Hematite Photoanodes

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ABSTRACT

Solar water splitting offers long-term potential for sustainable hydrogen production with low environmental impact, *i.e.* low or no greenhouse gas emissions. During the photoelectrolysis process, electron – hole pairs are generated in insolated semiconductors, which then participate to the water oxido-reduction reactions where O_2 is produced at the photoanode and H_2 at the photocathode [1]. Hematite (α-Fe_2O_3), commonly known as rust, is a semiconductor material with a band gap of 2.1 eV allowing to absorb 40% of the solar spectrum which is optimal for direct solar water splitting applications. The maximum expected photocurrent when hematite is used as photoanode is around 12.6 mA/cm^2 [2].

Hematite continuous films of perpendicularly grown and perfectly defined iron oxide nanorods are deposited on fluorine doped tin oxide (FTO) substrates by aqueous chemical growth (ACG). The hematite photoanodes are characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and photo-electrochemical measurements. X-ray absorption spectroscopy (XAS) is perfectly adapted to study electronic structure in hematite photoanodes [3]. The unoccupied density of states is probed through dipolar electronic transitions from a core to the valence band state relevant to electron conduction in oxide photoanodes [4]. In the case of hematite, electronic transitions between core Fe2p and valence Fe3d levels probe the oxidation state, crystal field induced splitting of the Fe^{3+} by the octahedral symmetry of O neighboring atoms. O K-edge XAS provides information on the O2p unoccupied density-of-states and hybridized with Fe 3d, 4s and 4p levels by excitations of core O1s electrons. The use of a spatially resolved XAS approach with nanometric spatial resolution is necessary to study the electronic structures corresponding to the areas of interest, from the hematite surface along the hematite nanorod toward the photoanode/substrate interface. We present here spectromicroscopic measurements performed with the scanning transmission X-ray microscope (STXM) of the HERMES beamline at SOLEIL. The exploited XAS contrast mechanism gives to STXM approach a very high sensitivity to the detailed electronic structure, needed for physical/chemical mapping (speciation) at a nanoscale level. We present and discuss STXM results obtained on hematite nanorods grown with different parameters.

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Utility of Scanning Transmission X-ray Microscopy for Determining the Dimensions of Core-shell Nanoparticles

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ABSTRACT

A scanning transmission x-ray microscopy (STXM) based methodology[1] is introduced for determining the dimensions (shell thickness, core and total diameter) of core-shell nanoparticles which exhibit a strong x-ray absorption contrast and a sharp interface between core and shell material. A low radiation dosage during data acquisition and, therefore, less x-ray beam induced damage of the sample is achieved by recording STXM images only at two predetermined energies of maximum absorption contrast instead of recording a stack of images across the whole absorption edge. A model core-shell nanoparticle, polytetrafluoroethylene (PTFE) cores with polystyrene (PS) shell, investigated at the HERMES beamline[2] is presented for demonstration. This STXM based methodology yields particle dimensions in good agreement with the scanning electron microscopy (SEM) results (deviation equal or less than 10%). Extension of this methodology to core-shell nanoparticles with inorganic core and organic shell will also be presented and the challenges encountered will be highlighted

REFERENCES

1. A. Hermanns *et al* submitted as proceeding of the ECASIA2017 conference to Surf. Inter. Anal.
2. R. Belkhou *et al Appl. Journal of Synchrotron Radiation.*, ***22****(4): 968-979. (2015)*

LUCIA. A Multidisciplinary Beamline

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N. Trcera[1], D. Vantelon[1]

1. Synchrotron SOLEIL. L'orme des merisiers. Saint Aubin. BP48. F-91192 GIf qur Yvette Cedex
2. CEPIA. INRA

ABSTRACT

The LUCIA beamline (Line for Ultimate Characterization by Imaging and Absorption) is dedicated to micro X-ray absorption (µXAS) and micro X-ray fluorescence (µXRF) spectroscopies in the so-called tender x-rays range (currently 0.6 - 8 keV). This energy domain offers the possibility of determining the speciation (local chemistry, quantitative determination of the local geometric structure around the absorbing atom) of elements performing XAS experiments at the K-edge from sodium to cobalt, the L-edges of manganese to gadolinium, as well as the M-edges of rare earths and actinides.

These two non-destructive techniques can be combined on heterogeneous samples to achieve maps of elements distribution at the scale of the photons spot size (2,5 x 2,5 microns), and describe the local environment around these elements. Micro-XRF and µXAS techniques can be combined with LEED or other micro-spectroscopy such as Raman and Auger, providing simultaneous access to additional structural information, at the same location.

These specificities single out the LUCIA beamline in the international offer and find a large panel of applications in many scientific domains. Applications will be illustrated through a selection of recently published examples.

REFERENCES

Vantelon D., Trcera N., Roy D., Moreno T., Mailly D., Guilet S., Delmotte F., Meltchakov E., Lassalle B., Lagarde P., Flank A.-M. (2016) The LUCIA beamline at SOLEIL. *Journal of Synchrotron radiation,* **23**, (2), pp. 635-640

Flank A.-M., Cauchon G., Lagarde P., Bac S., Janousch M., Wetter R., Dubuisson J.-M., Idir M., Langlois F., Moreno T., Vantelon D. (2006) LUCIA : a microfocus soft XAS beamline. *NIM B*, **246**, 1, 269-274.

TUTORIALS

FOXTROT software:
from detector images to sample curves: first steps after data acquisition at SWING beamline.

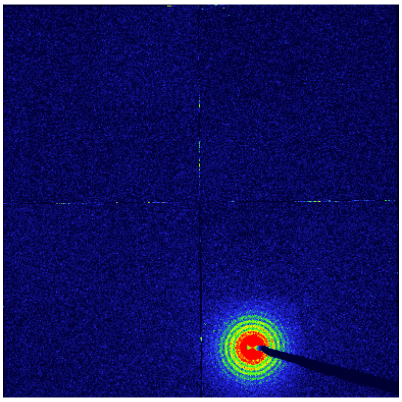
Organizers: Yann Gohon (Orgues). SWING beamline scientists: Thomas BIZIEN, Aurélien THUREAU, Javier PEREZ.

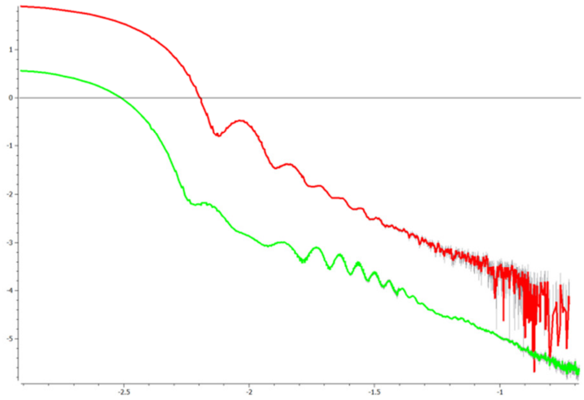
This tutorial aims to help users to acquire more independence in data processing using FOXTROT.
Based on the data reduction of representative samples, this course concerns a broad range of SWING users. Data from particles in solution, liquid crystals, and oriented samples will be considered.

Confirmed participants may install the freely available Foxtrot academic version and the sets of samples used for this demonstration on their own laptop.

Date: 2018/01/19 from 15 h to 18

Location: SOLEIL, room LIBRA – A2.1.32.
The number of participants is limited to 25 people





Processing of multi-modal x-ray imaging datasets at the NANOSCOPIUM beamline

Nanoscopium is a unique innovative hard X-ray beamline, which is dedicated to fast scanning multimodal and multi-length scale X-ray imaging.
It offers simultaneous information in a quantitative manner about the elemental composition (down to trace levels), to chemical speciation and sample morphology and in the same experimental conditions. The fast multi-length scale imaging available at the beamline creates large data-sets with multi-technique data-sets.

The aim of the tutorial is to provide a brief introduction to the analytical techniques available at Nanoscopium and to guide the participants through the basic steps of the related data processing. The elemental distribution maps will be extracted from the scanning X-ray Fluorescence (XRF) dataset with simple quantification. Morphological information will be obtained from the calculated differential phase contrast and scattering maps. The interpretation of the obtained multimodal dataset will be discussed.

A multimodal big data file (>100 Gb) measured at Nanoscopium will be used for the practical training. The tutorial will be done at Soleil with the computers available in the computing room.

The open source softwares Pymca [1], MMX-I [2] and Octave [3] will be presented and used during this tutorial.

The number of participants will be limited to 20 people.

Instructors: K. Medjoubi, A. Somogyi scientists at Nanoscopium

[1] V.A. Solé, E. Papillon, M. Cotte, Ph. Walter, J. Susini, *A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra*, Spectrochim. Acta Part B 62 (2007) 63-68.

[2] Bergamaschi, A., Medjoubi, K., Messaoudi, C., Marco, S., & Somogyi, A. (2016). *MMX-I: data-processing software for multimodal X-ray imaging and tomography*. Journal of synchrotron radiation, 23(3), 783-794.

[3] https://www.gnu.org/software/octave/

LIST OF COMMERCIAL EXHIBITORS

List of Commercial Exhibitors

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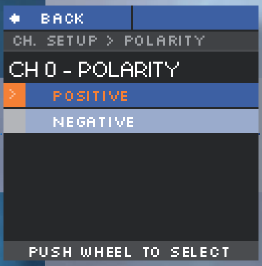

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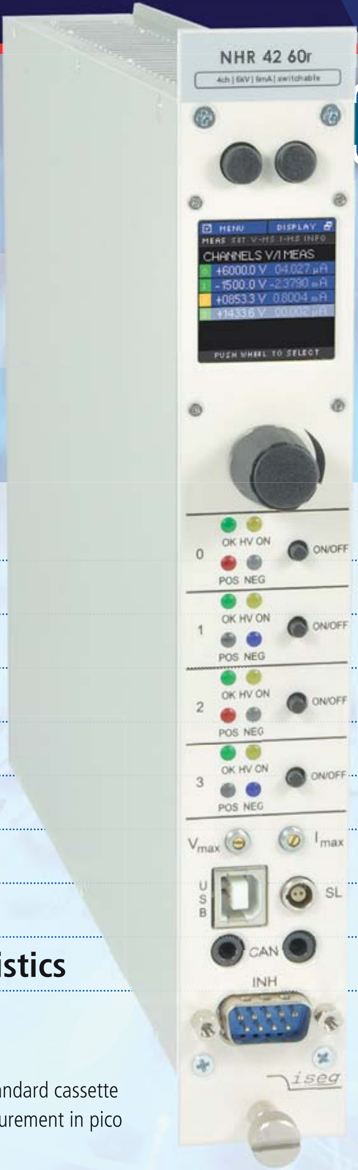

- 4 channels, electronically switchable polarity
- 2 kV / 6 kV versions
- very low ripple and noise
- 6 kV with switchable modes:
  up to 2 kV / 4 mA, 4 kV / 3 mA or 6 kV / 2mA
- Front panel control with 1,44“ TFT display
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- Benchmark setting ripple and noise characteristics

The iseg NHR modules are multi-channel high voltage power supplies in 1/12 NIM standard cassette format. The iseg technology combines ultra precise high voltage generation and measurement in pico amp range.

The NHR series provides up to 4 channels, each with an independent voltage and current control and electronically reversible polarity. The 6kV channel provides a maximum of versatility: with three electronically switchable HV-generation modes it can supply 4 mA up to voltages of 2 kV, 3 mA up to 4 kV or 2 mA up to 6 kV. Alternatively the NHR can be equipped with cost efficient 2 kV / 6 mA channels with one HV output mode.

Several NHR modules can be daisy-chained by CAN and controlled with a single USB connection or by optional iseg iCS system via Ethernet. The module is made of best components such as 24 bit ADC and 20 bit DAC, an excellent front panel control with TFT display plus comprehensive security features.

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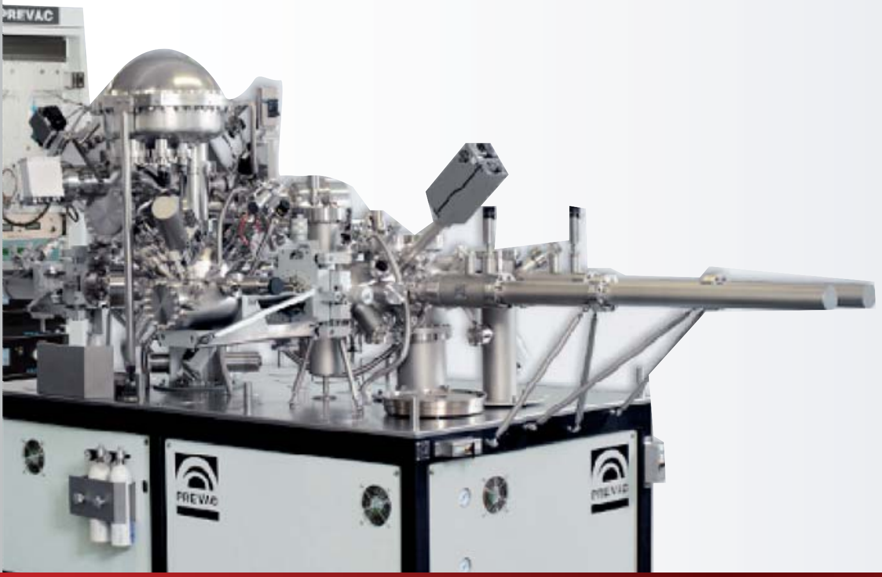

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