

12th | SOLEIL USERS' MEETING

JANUARY 19th & 20th, 2017

Ecole Polytechnique (Palaiseau) & SOLEIL (Saint-Aubin)



SCIENTIFIC COMMITTEE

d'ANGELO Marie (Institut des Nanosciences de Paris)
BOUDON Vincent (Lab. Interdisciplinaire Carnot
de Bourgogne - Dijon)
BROUTIN Isabelle (Lab. de cristallographie
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CARMONA TEJERO Noemi (Lab. de Physique des Matériaux,
Université Complutense - Madrid)
DATCHI Frédéric (IMPMC - Paris)
GIRARDON Jean-Sébastien (Unité de Catalyse et
de Chimie du Solide - Lille)
GOHON Yann (Institut Jean-Pierre Bourgin - Versailles)
GUILLON Emmanuel (Institut de Chimie Moléculaire - Reims)
LYONNARD Sandrine (INAC/SPrAM - CEA - Grenoble)
PENENT Francis (Lab. de Chimie Physique Matière et
Rayonnement - Paris)
PROVOST Karine (Institut de Chimie et des Matériaux
de Paris-Est - Thiais)
TEJEDA Antonio (Lab. de Physique des Solides - Orsay)

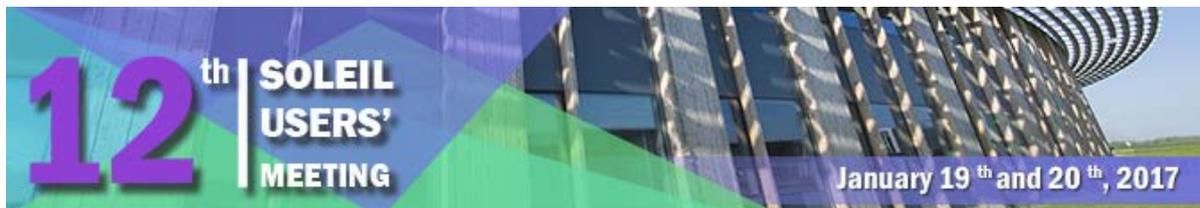
Satellite Workshop

**HiRIS3-2017: High-Resolution
Infrared Spectroscopy with Synchrotron Sources**
January 18th, 2017
SOLEIL (Saint-Aubin)

**XLiq2017: Synchrotron-based X-ray
spectroscopies applied to liquids**
January 17th & 18th, 2017
SOLEIL (Saint-Aubin)

Information and registration:
www.synchrotron-soleil.fr/Workshop/2017/SUM17





Welcome!

The 12th SOLEIL Users' Meeting takes place on January 19th and 20th, 2017 at Polytechnique (Palaiseau) and at SOLEIL.

This invaluable forum for the synchrotron radiation users' community will provide, this year, the opportunity to start thinking about the evolution of the machine and the beamlines.

It will be also the occasion to share scientific, technical and practical issues about the synchrotron radiation use.

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

- *Machine*
- *Upgrade MAX-IV*
- *Coherence*

3 technical workshops will be dedicated to ongoing and future developments on the beamlines for:

- biology
- material science
- reactivity measurements

Scientific communications will be presented during parallel sessions, selected from submitted abstracts.

A social programme with a buffet dinner will be held at SOLEIL on the afternoon of January 19th in conjunction with the posters session, commercial exhibitions and visits of the Facility.

Bienvenue

Le 12ème Colloque des Utilisateurs de SOLEIL se tient les jeudi 19 et vendredi 20 janvier 2017, à l'Ecole Polytechnique et à SOLEIL.

Ce rendez-vous incontournable pour la communauté des utilisateurs du rayonnement synchrotron sera cette année l'occasion d'initier la réflexion sur l'évolution de la machine et des lignes de lumière.

Il sera aussi le lieu pour échanger sur les aspects scientifiques, techniques et pratiques de l'utilisation du rayonnement synchrotron.

Les 3 conférences plénières aborderont différents aspects liés aux évolutions récentes et futures des sources synchrotrons :

- *Machine*
- *Upgrade MAX-IV*
- *Cohérence*

Les ateliers techniques porteront quant à eux sur les développements en cours et à moyen terme sur les lignes de lumière pour :

- la biologie
- les matériaux
- les mesures en réactivité

Les sessions parallèles seront composées d'exposés scientifiques originaux, sélectionnés à partir des résumés soumis.

Un temps de convivialité et de discussion sera organisé à SOLEIL le jeudi 19 janvier après-midi avec la séance posters, les stands d'entreprises, la visite des installations et le buffet dînatoire.

SOLEIL Users' Meeting 2017

January 19th – 20th, 2016

École Polytechnique, Palaiseau – France

&

Synchrotron SOLEIL, Saint-Aubin - France

Summary

- Programme
- Plenary Session
- Parallel Sessions:
 - Biology – Health
 - Chemistry & Physico-Chemistry, In Situ Reactivity, Soft Matter
 - Cultural Heritage, Archaeology, Environment, Geosciences
 - Diluted Matter
 - Electronic & Magnetic Property of Matter, Surfaces and Interfaces
 - Matter & Material Properties: Structure, Organization, Characterization, Elaboration
- Technical Workshops
- Posters Session
 - List of Student Posters
 - List of Other Posters
- List of Commercial Exhibitors
- Companies Advertisements



École Polytechnique, Palaiseau – France
&
Synchrotron SOLEIL, Saint-Aubin - France

Programme

Thursday, January 19

ÉCOLE POLYTECHNIQUE – ARAGO Auditorium

- 09:00 - 10:00 Registration & coffee
- 10:00 - 10:10 Welcome / Introduction
Antonio Tejada - *ORGUES Chairperson*
- 10:10 - 10:20 The word of SOLEIL General Director
Jean Daillant
- 10:20 – 11:05 Towards diffraction limited photon sources on storage rings
Amor Nadji - *Synchrotron SOLEIL, Gif-sur-Yvette, France*
- 11:05 - 11:50 MAX IV: Status and how we got there
Jesper Andersen - *MAX-IV, Lund, Sweden*
- 11:50 – 12:00 **Marc Simon** - *AFURS*
- 12:00 - 12:20 Peer Review Committee 1 Chairman – **Roland Thissen** (5mn)
Peer Review Committee 2 Chairwoman – **Francine Solal** (5mn)
Questions 10mn
- 12:20 - 14:00 *Lunch*
- 14:00 – 14:45 Bragg ptychography: When crystallography meets microscopy
Virginie Chamard - *Institut Fresnel, Marseille, France*

Transfer to SOLEIL (15h00)

Technical Workshops : ongoing and future developments on beamlines dedicated to:

- 15:30 - 17:00
- Biology *BLOCH Auditorium*
 - Material Science *SOLEIL Auditorium*
 - Reactivity measurements *Welcome Building Auditorium*
- 17:00 – 17:30 *Coffee break*



17:30 - 19:30 Posters session / Commercial exhibition / ORGUES and AFURS Booth

18:30 - 19:30 Visit of 3 Beamlines (GALAXIES / TEMPO / SIRIUS)

19:30 - 21:00 *Buffet* / Award of Roger Fourme prize (best student poster)

Friday, January 20

ECOLE POLYTECHNIQUE

9:00 – 10:30 Parallel sessions (see the detailed programme here after)

10:30 - 11:00 *Coffee break*

11:00 - 13:15 Parallel sessions (see the detailed programme here after)

13:15 - 14:30 *Lunch*

Transfer to SOLEIL (14h45)

15:00 – 18:00 **2 tutorials (reserved to registered participants)**

- ***MX Software tutorial*** *Amphitheater, Main Building, SOLEIL*
- ***Chemometric analysis of Quick-XAS data Practical*** *T5 Building, SOLEIL*



Parallel Sessions Schedule

Biology – Health

Chairpersons: Yann GOHON and Isabelle BROUTIN

ECOLE POLYTECHNIQUE –Pierre FAURRE Auditorium

- 09:00 - 09:30
(25'+5') Architecture and assembly of an anti-bacterial weapon: The type VI secretion system
Eric Durand - invited speaker- LISM – IMM, Marseille , France
- 09:30 - 09:50
(15'+5') Microspectrometric insights on the uptake of antibiotics at the single bacterial cell level
Estelle Dumont - UMR MD1, Marseille, France
- 09:50 - 10:10
(15'+5') Tunneling analysis of the efflux pump component OprN using xenon
Gilles Phan - LCRB, UMR 8015 Paris, France
- 10:10 - 10:30
(15'+5') Structural and functional insight in the helicobacter pylori blood group antigen binding adhesin BabA
Kristof Moonens - VIB Structural Biology Research Center, Brussels, Belgium
- 10:30 – 11:00
Coffee break
- 11:00 - 11:30
(25'+5') Synchrotron light contribution to renal pathology
Emmanuel Estève - UMR U1155, Hôpital Tenon, Paris, France
- 11:30 - 11:50
(15'+5') Selection and characterization of artificial proteins targeting tubulin
Valerie Campanacci - I2BC, Gif-sur-Yvette, France
- 11:50 - 12:10
(15'+5') Human tRNA-Dihydrouridine synthase 2: Molecular basis for tRNA recognition by an unusual double stranded RNA-binding domain
Charles Bou Nader LCPB , Collège de France Paris, France
- 12:10 - 12:30
(15'+5') HSP90 regulation by RPAP3-PIH1D1 cochaperones during macromolecular complex assembly
Julien Henri - LBMCE, UMR 8226 IBPC Paris, France
- 12:30 - 12:50
(15'+5') Allosteric regulation of small GTPases by membranes as a pharmacological target
Agata Nawrotek- LBPA, ENS Paris-Saclay, France
- 12:50 - 13:10
(15'+5') Short ragweed pollen allergy in the light of SOLEIL beamlines
Rachel Groeme - Stallergenes Greer, Antony, France



Parallel Sessions Schedule

Chemistry & Physico-Chemistry, In Situ Reactivity, Soft Matter

Chairpersons:

ECOLE POLYTECHNIQUE –MONGE Auditorium

- 09:00 - 09:30
(25'+5')
- A Synchrotron look into the lifecycle of Pt-In catalysts
Hilde Poelman - *Laboratory for Chemical Technology, Ghent, Belgium*
- 09:30 - 09:50
(15'+5')
- A combined in situ XAS/MS/Raman study of Ni-Cu catalysts derived from hydrotalcite-like precursors
Aline. R. Passos - *Synchrotron SOLEIL, Gif-sur-Yvette, France*
- 09:50 - 10:10
(15'+5')
- In situ 1s2p resonant inelastic X-ray scattering (RIXS) applied to cobalt based catalysts
Charlotte Desjacques - *Unité de Catalyse et de Chimie du Solide, Lille, France*
- 10:10 - 10:30
(15'+5')
- Negative thermal expansion in noble metal-based nanoparticles under different gaseous atmosphere
Claudia Zlotea - *Institut de Chimie et des Matériaux de Paris-Est, Thiais, France*
- 10:30 – 11:00
- Coffee break*
- 11:00 - 11:30
(25'+5')
- Competing coexisting phases in 2D water
Jean-Marc Zanotti - *CEA Saclay, Gif-sur-Yvette, France*
- 11:30 - 11:50
(15'+5')
- Infrared spectroscopy study of water confinement in imogolites with internal Si-OH and Si-CH₃ groups
Yuan-Yuan Liao - *CEA Saclay, Gif-sur-Yvette, France*
- 11:50 - 12:10
(15'+5')
- Oxide nanoparticles in water: amorphous to crystal conversion of luminescent yttrium vanadate
Alexis Freitas - *Université Paris-Saclay, Gif-sur-Yvette, France*
- 12:10 - 12:30
(15'+5')
- Organometallic aryl-first row transition metal complexes as key intermediates in C-H functionalization
Vlad Martin-Diaconescu - *Universitat de Girona, Catalonia, Spain*
- 12:30 - 12:50
(15'+5')
- Speciation of ruthenium in TBP/TPH organic phases (structure and reactivity)
Claire Lefebvre - *CEA Marcoule, Bagnols-sur-Cèze, France*



Parallel Sessions Schedule

Cultural heritage, archaeology, environment, geosciences

Chairpersons: Emmanuel Guillon and Noemí Carmona

ECOLE POLYTECHNIQUE – CURIE Auditorium

- 10:30 – 11:00 *Coffee break*
- 11:00 - 11:30
(25'+5') Formation and reactivity of ZnS nanoparticles precipitating in organic wastes
Clément Lévard - CEREGE-UMR7330 - Aix-en-Provence, France
- 11:30 - 11:50
(15'+5') Highlighting the large variability of as speciation in Wetlands: A new insight in as dynamic control
Delphine Vantelon - Synchrotron SOLEIL, Gif-sur-Yvette, France
- 11:50 - 12:10
(15'+5') Investigating Ca speciation and distribution inside cyanobacterial cells forming intracellular carbonates
Karim Benzerara - IMPMC, CNRS, Paris, France
- 12:10 - 12:30
(15'+5') VUV photodynamics of free "tholins" nanoparticles investigated by imaging Angle-Resolved Photoemission
Sarah Tigrine - LATMOS, Université Versailles, Guyancourt, France
- 12:30 - 12:50
(15'+5') 5 years of X-ray imaging of flat fossils at the Diffabs beamline: New sources of data for paleontologists
Pierre Gueriau - Synchrotron SOLEIL et IPANEMA, CNRS, Gif-sur-Yvette, France
- 12:50 - 13:10
(15'+5') Metallurgy of the earliest lost-wax cast
Mathieu Thoury - IPANEMA. CNRS/MCC - Gif sur Yvette (France)



Parallel Sessions Schedule

Diluted Matter

Chairpersons: Vincent BOUDON ad Francis PENENT

ECOLE POLYTECHNIQUE – CARNOT Auditorium

- 09:00 - 09:30
(25'+5')
- Quantum tunnelling of particles within molecules: Synchrotron far-IR spectroscopy of malonaldehyde
Dennis Tokaryk - *University of New Brunswick, Fredericton, New Brunswick, Canada*
- 09:30 - 09:50
(15'+5')
- The far-IR spectrum of formic acid cyclic dimer : A model system for vibrational dynamics
Sabath Bteich - *PhLAM, Lille, France*
- 09:50 - 10:10
(15'+5')
- Photo-ionization and photo-dissociation of PAH cations
Junfeng Zhen - *IRAP, Toulouse, France*
- 10:10 - 10:30
(15'+5')
- A new method for the determination of metal-ligand bonding energy using VUV Synchrotron Radiation
Niloufar Shafizadeh - *ISMO, Orsay, France*
- 10:30 – 11:00
- Coffee break*
- 11:00 - 11:30
(25'+5')
- Many-electron emission in understanding atoms and molecules: Theory and experiment
Kari Jänkäälä - *Oulu University, Finland*
- 11:30 - 11:50
(15'+5')
- Photoionization of the fullerene cation
Suzie Douix - *Synchrotron SOLEIL, Saint-Aubin, France*
- 11:50 - 12:10
(15'+5')
- VUV spectroscopy of free radicals on the DESIRS beamline: Absorption of OH and photoionization of CH and C₂H
Bérenger Gans - *ISMO, Orsay, France*
- 12:10 - 12:30
(15'+5')
- Core-Valence double photoionization $4d^{-1}5p^{-1}$ in xenon studied with multielectron spectroscopy
Mehdi. A. Khalal - *LCPMR, Paris, France*
- 12:30 - 12:50
(15'+5')
- State-selected ion-molecule reactions with CERISES: A very efficient TPEPICO ion source adapted to metastable species produced in a beam
Christian Alcaraz - *LCP et Synchrotron SOLEIL, Orsay, France*
- 12:50 - 13:10
(15'+5')
- Infrared spectroscopy of methoxyphenols involved as atmospheric secondary organic aerosol precursors
Arnaud Cuisset - *LPCA, Dunkerque, France*



Parallel Sessions Schedule

Electronic & Magnetic Property of Matter, Surfaces and Interfaces

Chairpersons: Marie d'ANGELO and Antonio TEJEDA

ECOLE POLYTECHNIQUE – BECQUEREL Auditorium

- 09:00 - 09:30
(25'+5') Spin to charge conversion at room temperature using the α -Sn topological insulator
Nicolas Reyren - UMR CNRS/Thales, Palaiseau, France
- 09:30 - 09:50
(15'+5') Pump-probe diffraction experiment for studying displacive transitions
Isabel González Vallejo - LPS and LOA, Orsay and Palaiseau, France
- 09:50 - 10:10
(15'+5') Ultrafast electronic, spin and lattice separation in LaCoO_3
Manuel Izquierdo - European XFEL, Hamburg, Germany
- 10:10 - 10:30
(15'+5') Mott insulator-metal transition in Sr_2IrO_4
Alex Louat - LPS, Orsay, France
- 10:30 – 11:00 *Coffee break*
- 11:00 - 11:30
(25'+5') Interlayer coupling through a dimensionality-induced magnetic state
Michel Viret - CEA, France
- 11:30 - 11:50
(15'+5') Strong resonances of quasi 1D structures at the Bi/InAs(100) interface
Christine Richter - LPMS, Cergy Pontoise, France
- 11:50 - 12:10
(15'+5') Calculation of XMCD at K-edge under pressure from first principles, application to iron hydride
Nadejda Bouldi - IMPMC et SOLEIL, Paris et Gif sur Yvette, France
- 12:10 - 12:30
(15'+5') Superconductivity, pseudogap, and stripe correlations in high- T_c cuprates
Zailan Zhang - IMPMC, Paris, France
- 12:30 - 12:50
(15'+5') C_{60} thin films on Co(0001) : A structural study to understand magnetic properties
Cynthia Fourmental - SOLEIL et MPQ, Gif sur Yvette et Paris, France
- 12:50 - 13:10
(15'+5') Investigation of organic/metal interface by XPS and STM
YongFeng Tong - SOLEIL and ISMO, Gif sur Yvette and Orsay, France



Parallel Sessions Schedule

Matter and material properties: Structure, Organisation, Characterisation, Elaboration

Chairpersons: F. Datchi and K. Provost

ECOLE POLYTECHNIQUE –ARAGO Auditorium

- 09:00 - 09:30
(25'+5')
- Contribution of Synchrotron Radiation studies to the understanding of the magneto-electric coupling in BaTiO₃ layered artificial multiferroic systems
Antoine Barbier - IRAMIS, CEA, Saclay, France
- 09:30 - 09:50
(15'+5')
- IR imaging of the Paris meteorite with an FPA detector for micro-tomography
Zelia Dionnet - Institut d'Astrophysique Spatiale, Saclay, France
- 09:50 - 10:10
(15'+5')
- Tomographie-X ultra-rapide à haute pression et température
Eglantine Boulard - Synchrotron SOLEIL, Saint-Aubin, France
- 10:10 - 10:30
(15'+5')
- The anomalous behavior of silicate glasses and liquids on densification: A combined microtomography and X-ray diffraction study at high pressure
Alisha Clark - IMPMC, Paris, France
- 10:30 – 11:00
- Coffee break
- 11:00 - 11:20
(15'+5')
- Influence of structural changes on the magnetic properties of Y_{1-x}R_xFe₂(H,D)_{4.2} compounds
V. Paul-Boncourt - ICMPE, Thiais, France
- 11:20 - 11:40
(15'+5')
- Coupling powder diffraction, electron microscopy, solid-state NMR and GIPAW calculations: structure and dynamics of inorganic fluorides
Charlotte Martineau-Corcus - ILV, Versailles, France
- 11:40 - 12:00
(15'+5')
- Relaxation mechanisms in a nanocrystalline gold thin film on a compliant substrate
Pierre Godard - P' Institut, Poitiers, France
- 12:00 - 12:20
(15'+5')
- Time-resolved X-ray diffraction in density-wave systems
Sylvain Ravy - LPS, Orsay, France
- 12:20 - 12:40
(15'+5')
- Structure and growth mechanism of single layer and multi-layer silicene
Alberto Curcella - Institut des Nanosciences de Paris, France
- 12:40 - 13:00
(15'+5')
- Influence of the tetragonal structure on the electronic bands of CH₃NH₃PbI₃ hybrid organic-inorganic perovskites
Min I. Lee - LPS, Orsay, France

PLENARY SESSION

PLENARY SESSION

- PT-01 Towards diffraction limited photon sources on storage rings
Amor Nadji – *Synchrotron SOLEIL, Gif-sur-Yvette, France*
- PT-02 MAX IV: Status and how we got there
Jesper Andersen - *MAX-IV, Lund, Sweden*
- PT-03 Bragg ptychography: When crystallography meets microscopy
Virginie Chamard - *Institut Fresnel, Marseille, France*

Towards Diffraction Limited Photon Sources on Storage Rings

A. Nadji

Synchrotron SOLEIL, Gif-sur-Yvette, France

ABSTRACT

Third-generation low-emittance storage ring synchrotron light sources have been successfully in operation around the world for more than two decades. Today, advances in accelerator technology open new windows of opportunity. On the horizon is a new generation based on multi-bend achromat (MBA) lattice concept promising one or two orders of magnitude higher brilliance and transverse coherence fraction than is available in today's sources, bringing synchrotron light sources closer to their diffraction limit. This new generation will be especially suited to experiments exploiting the coherence properties of the photon beam and to ultra-small focal spot sizes in the regime of several nanometers in the multi-keV photon energy range. MBA lattices have been demonstrated successfully at a light source in Sweden known as MAX IV, and will be put to use in a new project at Campinas-Brazil called Sirius and for several upgrades of existing machines like ESRF (Grenoble-France), APS (Chicago-USA), Spring-8 (Riken, Japan), ALS (Berkeley, USA), SLS (Villigen, Switzerland), Diamond (Oxford, UK), ELETTRA (Trieste, Italy) and SOLEIL (Gif-sur-Yvette, France). In this talk, we survey ongoing work around the world to develop these new sources called Diffraction Limited Storage Ring (DLSR) and the first thoughts for the upgrade of SOLEIL.

MAX IV: Status and how we got there

J. Andersen
MAX-IV, Lund, Sweden

Bragg Ptychography: When Crystallography meets Microscopy

V. Chamard

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ABSTRACT

Imaging complex crystalline materials at the nanoscale is a major challenge of nanoscience, which calls for a microscopy method combining sensitivity to the crystalline properties, 3D imaging capability, in situ compatibility and high spatial resolution. In this context, the recent advents of x-ray lensless imaging methods, based on Bragg coherent diffraction, have opened promising perspectives [1] filling the gap between direct microscopies (AFM, SEM, TEM) and reciprocal-space based x-ray Bragg diffraction analysis.

3D Bragg ptychography microscopy [2] is a coherent diffraction imaging method developed at third generation synchrotron sources, and which merges concepts developed in inverse microscopy and crystallography. This modality is based on the acquisition of far-field Bragg coherent intensity patterns; It exploits the partially redundant information obtained by scanning a finite beam spot size transversally to the sample, while measuring the corresponding 3D far-field intensity diffraction pattern by scanning angularly the sample along the rocking curve. Instead of lenses, numerical tools are employed to retrieve the lost phase [3] and hence the complex-valued sample scattering contrast. Thereby, it ensures access to truly quantitative information, such as the crystalline displacement field, from which the 3D strain component and crystalline plane rotations can be derived, with nanoscale spatial resolution. 3D imaging of extended crystalline samples is then possible [2, 4], opening Bragg coherent diffraction microscopy to a large range of applications.

In this presentation, we will detail the general concepts of Bragg ptychography and further present the developments we have proposed, illustrated by a series of experimental results obtained at synchrotron beamlines on man-made crystalline samples [2-7]. Finally, we will show how Bragg ptychography can be exploited to bring new insights on the crystalline structure of biomineral materials and promotes thereby the understanding of the intriguing mechanisms of biomineralization [8].

REFERENCES

- [1] M. A. Pfeifer, *et al.*, Nature 442, 63 (2006). A. Ulvestad, *et al.*, Science 348, 1344-1347 (2015).
- [2] P. Godard, *et al.*, Nature Communications 2, 568 (2011).
- [3] P. Godard, *et al.*, Optics Express 20, 25914 (2012).
- [4] F. Berenguer, *et al.*, Physical Review B 88, 144101 (2013).
- [5] A. I. Pateras, *et al.*, Physical Review B 92, 205305 (2015).
- [6] V. Chamard, *et al.*, Scientific Reports 5, 9827 (2015).
- [7] S. O. Hruszkewycz, *et al.*, Nature Materials (2016).
- [8] F. Mastropietro, *et al.*, submitted.

PARALLEL SESSIONS

PARALLEL SESSION

Biology - Health

ECOLE POLYTECHNIQUE – Pierre FAURRE Auditorium

Chairpersons: Yann GOHON and Isabelle BROUTIN

- IT-01 Architecture and assembly of an anti-bacterial weapon: The type VI secretion system
E. Durand
- OC-01 Microspectrometric insights on the uptake of antibiotics at the single bacterial cell level
E. Dumont
- OC-02 Tunneling analysis of the efflux pump component OprN using xenon
G. Phan
- OC-03 Structural and functional insight in the *helicobacter pylori* blood group antigen binding adhesin BabA
K. Moonens
- IT-02 Synchrotron light contribution to renal pathology
E. Estève
- OC-04 Selection and characterization of artificial proteins targeting tubulin
V. Campanacci
- OC-05 Human tRNA-Dihydrouridine synthase 2: Molecular basis for tRNA recognition by an unusual double stranded RNA-binding domain
C. Bou Nader
- OC-06 HSP90 regulation by RPAP3-PIH1D1 cochaperones during macromolecular complex assembly
J. Henri
- OC-07 Allosteric regulation of small GTPases by membranes as a pharmacological target
A. Nawrotek
- OC-08 Short ragweed pollen allergy in the light of SOLEIL beamlines
R. Groeme

Architecture and Assembly of an Anti-bacterial Weapon: The Type VI Secretion System

E. Durand

Laboratoire d'Ingénierie des Systèmes Macromoléculaires, Institut de Microbiologie de la Méditerranée, Centre National de la Recherche Scientifique, Aix-Marseille Université, Marseille, France

ABSTRACT

The Type VI secretion system (T6SS) is a multi-protein secretory machine that has been recently shown to be implicated in inter-bacterial competition through the delivery of anti-bacterial toxins with peptidoglycan, lipid or DNA hydrolysis activities directly into the target cell [1]. This machine is composed of 13 different subunits, categorized in two complexes: a cytoplasmic tubular structure related to bacteriophage contractile tails (TTC), built on an assembly platform – or baseplate (BPC), and anchored to the cell envelope by a membrane complex (MC). The tail is composed of puncturing device wrapped by a contractile sheath. In our laboratory, we have demonstrated that the model bacterium, *Enteroaggregative E. coli (EAEC)*, utilizes the T6SS machinery to kill other Gram-negative bacteria [2]. This mechanism involves cell-cell and prolonged contacts between predator and prey bacterial cells. Prey lysis occurs rapidly, in a few tens of seconds after the contraction of the T6SS tail sheath. We recently succeeded to purify the membrane complex (MC), a 1.7 MDa structure that is composed of 10 copies of three proteins: TssJ, -L, and -M. Using negative stain electron microscopy, we collected tens of thousands of images of the complex in different orientation and reconstructed the membrane complex with a resolution of 11.6 Å [3]. We were then able to connect this MC to the rest of the machinery by isolating a complex between TssJLM and the first protein to interact with the MC, namely TssA [4]. This study shed light on the function of TssA and demonstrated for the first time a direct association between the cytoplasmic protein TssA and the membrane embedded TssJLM MC complex. Our research project is dedicated to understand the structure, assembly and functioning of the T6SS in *EAEC*, as a model organism. The project is based on a multi-scale and integrated study of a macromolecular nanomachine, integrating several approaches:

- Cellular scale: fluorescence microscopy, sub-cellular localisation of protein complexes (100-1000 Å), cryo-electron tomography (ECT: 20-60 Å)
- From mid to near-atomic resolution: (Cryo)-electron microscopy and SAXS (3.5-25 Å).
- Atomic resolution: X-ray crystallography (< 3.5 Å).
- “Amino acid” resolution: CX-MS and site-directed mutagenesis.

The presentation will focus on our latest studies that all aim at understanding and deciphering cellular-scale behaviours – namely bacterial competition, pathogenesis/virulence, toxins secretion – at the molecular scale.

REFERENCES

- [1] Durand E, Cambillau C, Cascales E, Journet L. 2014. VgrG, Tae, Tle, and beyond: the versatile arsenal of Type VI secretion effectors. *Trends Microbiol.* Sep;22(9):498-507
- [2] Brunet YR, Espinosa L, Harchouni S, Mignot T, Cascales E. 2013. Imaging type VI secretion-mediated bacterial killing. *Cell Rep.* 3:36-41
- [3] Durand E, Nguyen VS, Zoued A, Logger L, Péhau-Arnaudet G, Aschtgen M-S, Spinelli S, Desmyter A, Bardiaux B, Dujancourt A, Roussel A, Cambillau C, Cascales E and Fronzes R. 2015. Biogenesis and structure of a bacterial Type VI secretion membrane core complex. *Nature.* Jul 30; 523(7562):555-60.
- [4] Zoued A, Durand E, Brunet YR, Spinelli S, Douzi B, Guzzo M, Flaughnatti N, Legrand P, Journet L, Fronzes R, Mignot T, Cambillau C, Cascales E. Priming and polymerization of a bacterial contractile tail structure. *Nature.* 2016 Mar 3;531(7592):59-63.

Microspectrometric Insights on the Uptake of Antibiotics at the Single Bacterial Cell Level

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ABSTRACT

With the continuing emergence of bacterial multidrug resistance, a molecular dissection of the membrane transport associated to cellular imaging analysis is needed to understand the uptake and the activity of antimicrobial agents in bacterial cells. This is particularly acute for Gram-negative bacteria that have two membranes, outer and inner membranes, controlling the transport and the intracellular accumulation of antibiotics.

The permeation process was followed within bacterial population and at single bacteria level to investigate the antibiotic concentration/location in multi-drug resistant isolates and derivative strains. In parallel, antibacterial activities were determined on same bacterial strains in order to correlate the intracellular accumulation of antibiotic to the bacterial susceptibility.

With new original methodologies the uptake/location of fluorescence antimicrobial agents can be followed and studied in bacterial population and individual bacterial cell with DUV microscopy at DISCO beamline. We can analyze the respective involvement of influx and efflux in the internal concentration of various molecules and in the bacterial susceptibility.

Combination of activity determination and image analyses open a new field of research in the molecular understanding of resistance mechanisms and in the rational approach of antibacterial chemotherapy.

Keywords: Antibacterial agents, Enterobacteriaceae, multi-drug resistance, UV fluorescence microspectroscopy, single cell bacterial resolution

Fundings:

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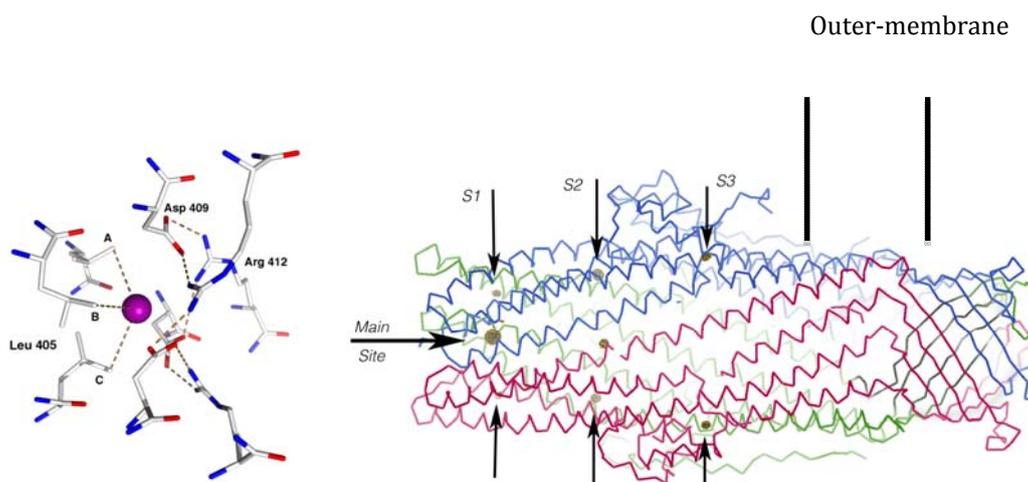
Tunneling Analysis of the Efflux Pump Component OprN using Xenon

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ABSTRACT

In their multidrug resistance fight, Gram-negative bacteria are known to implement a particular three-component assembly of proteins anchored throughout the outer and inner membrane, each of them localized in its particular environment: An inner-membrane transporter, a periplasmic fusion protein and an outer-membrane factor channel, altogether associated to expulse out of the bacteria a large variety of antimicrobial drugs leading to unwanted drug resistance. The present study focuses on OprN, the outer-membrane channel of the efflux pump MexEF from the opportunistic pathogen *P. aeruginosa*. The tunneling mechanism of this drug-resistance mechanism is analyzed with xenon as a probe in order to decipher any aspect able to lead to inhibition of the complex formation or channel opening. Crystals of OprN submitted to a pressure of 20 bar of xenon display several features: 1) A binding site, fully occupied, located in a small cavity along the narrowed channel entrance, on the pseudo three-fold axis of the trimer. This cavity is delimited by the key Leu405 residue, and more interesting, by a polar crown of three salt bridges (Asp409-Arg412) that delimits the cavity on the inner side of the tunnel. A number of secondary sites (S1 → S3) are also distributed within the trimer and able to trace out hydrophobic regions that might be involved in the trimer allosteric gating.



Right: positions of the Xenon sites identified on the OprN structure
Left: details of the main site environment

Structural and Functional Insight in the *Helicobacter Pylori* Blood Group Antigen Binding Adhesin BabA

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ABSTRACT

Helicobacter pylori chronically infects half of the world population; thereby causing chronic gastritis, duodenal ulcers and gastric cancer. On its surface *H. pylori* expresses a family of *Helicobacter* outer membrane proteins (Hops) to mediate attachment to the glycosylated gastric epithelial cell surfaces and overlying mucins, thereby avoiding the harsh environment of the stomach lumen. The best studied Hop member is the blood group antigen binding adhesin (BabA) that mediates attachment to stomach glycoreceptors containing ABO and Lewis b blood group antigens. The presence of BabA is linked to disease-associated strains, presumably because it potentiates delivery of secreted virulence effectors like VacA and CagA. Also *H. pylori* has an extreme genetic diversity, with particularly high rates of adaptive evolution in genes for adherence to host glycan receptors.

We obtained the structures of the adhesin domain of representative BabA isoforms, alone and in complex with ABO/Lewis b glycan receptors to identify the essential components in BabA's carbohydrate binding domain. These structures show that blood group binding involves a highly polymorphic 4-stranded β -sheet domain and critically depends on a disulphide-bound loop in the binding site. Two diversity loops dynamically control blood group and type 1 chain glycan specificity, respectively. We observe *H. pylori* strains can switch blood group preference and co-express BabA isoforms with different binding properties. The ligand-bound structures provide a molecular rationalization of the observed blood group antigen polymorphisms in *H. pylori* clinical isolates.

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Synchrotron Light Contribution to Renal Pathology

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ABSTRACT

Generalization of kidney biopsy in the 1950's was the first step towards modern nephrology. Nowadays, optical microscopy, immunofluorescence and electronic transmission microscopy examinations are highly standardized but some diagnosis are still challenging. Synchrotron mediated Fourier Transform InfraRed spectroscopy allowed us to underline crystalline diversity in kidney biopsies¹. It led us to further explore the potential of Synchrotron Radiation in kidney biopsy deciphering.

PLATIN DETECTION IN CHEMOTHERAPY INDUCED NEPHROTOXICITY

Cisplatin among platin salts based chemotherapies is of major clinical importance in the treatment of many solid cancers. The main toxicity that hampers cisplatin utilisation and therefore patient survival is its nephrotoxicity. Like most tubulointerstitial acute nephritis, cisplatin induced tubulopathy lack specific histological signs.

We used DIFFABS to detect Pt using micro X-Ray Fluorescence in the kidney of mice² and patients³ exposed to either cis or oxali or carboplatin with micrometric resolution. We were able to detect Pt in all samples. Cisplatin was the only drug to induce a redistribution of medullary Zn across the corticomedullary junction where histological lesions develop.

ULTRAVIOLET MICROSCOPY FOR CALCIUM OXALATE DETECTION AND LOCALIZATION IN KIDNEY

Hyperoxaluria is a severe condition that can lead to end stage renal failure. Identification of oxalate calcium (CaOx) deposits in kidney biopsy is a critical step towards diagnostic¹.

Using DISCO UV imaging beamline microscopes we identified that CaOx have an emission peak at 420nm after 275nm excitation. We used this signal to study 20 biopsies of hyperoxaluric patients and 15 diverse controls.

UV fluorescence identified CaOx microcrystals in most hyperoxaluric biopsies: Sensitivity (Se) 80% [56.3-94.3] but it was not very specific (Sp) 58.3% [27.7-84.8]. CaOx Macrocrystals were more evocative of hyperoxaluric nephropathy Se: 80% [56.3-94.3] Sp: 90.9% [58.7-99.7]. CaOx Intratubular accumulation could be evaluated by the ratio of oxalate/aromatic amino acid fluorescence. A ratio under 1 was specific for primary hyperoxaluria in 91.2% of the cases [86.5-94.6] with a Se of 90% [84.5-94.1], it was less interesting in secondary hyperoxaluria: Se 68.9% [61.6-75.6], Sp 91.2% [96.5-94.6]. Combination of these elements in a 3 point histological score gave a Se: 100% [86.1-100] and Sp: 90.9 [58.7-99.8] for 2 elements and Se: 70% [45.7-88.1] with Sp: 100% Sp [71.5-100] for 3.

CONCLUSION

We showed that X-Ray fluorescence was a powerful tool to identify Pt in kidney biopsies. Interestingly Pb, Hg, Cd, Cr, W and Cu have also been associated with renal failure. Therefore, metal screening using μ XRF should deserve serious attention in the future.

UV fluorescence can be used to finely explore CaOx accumulation in kidney. It could be a very interesting tool for diagnostic and fundamental research around oxalate toxicity.

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Selection and Characterization of Artificial Proteins Targeting Tubulin

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ABSTRACT

Microtubules are cytoskeletal filaments critical for multiple cellular processes: they form the mitotic spindle during cell division of eukaryotic cells, they are also the key component of the architecture of cilia and flagella, and they organize the intracellular traffic by forming a filament network on which kinesin and dynein molecular motors move and transport cargos. Pathologies in microtubule structure and regulation are associated with mitotic and neurodegenerative disorders. In cells, microtubules are hollow tubes consisting of 13 laterally associated protofilaments of $\alpha\beta$ -tubulin heterodimers arranged in a head-to-tail fashion. These filaments are highly dynamic, capable of assembling and disassembling, a property related to the ability of tubulin to bind and hydrolyse GTP. Tubulin is a fragile protein, with tendency to form heterogeneous assemblies when not stabilized in a microtubule. This feature is the main issue for tubulin crystallization. To circumvent this problem, several strategies have been reported that use tubulin-interacting proteins as crystallization chaperones. These proteins can be natural cellular proteins, e.g. stathmin (1), or artificial proteins selected from libraries, e.g. DARPin (2, 3).

Here, we report the strategy and results in the selection of artificial proteins, called α Reps, that bind α -tubulin. α Reps form a new family of artificial proteins. They are based on thermostable alpha-helical HEAT-like repeats originally found in thermophilic microorganisms (4). Using phage display, we successfully selected a dozen of α Reps differing both in their number of repeats and in the amino acids sequences of their variable positions. We show that all α Reps interact with tubulin but have different effects on microtubule polymerization. We also determined the structure of 3 different α Rep:tubulin complexes, as a proof of concept of the stabilizing and crystal promoting effects of α Reps on tubulin. Therefore, the α Reps expand the range of tools available to study microtubule. They will be useful in particular for the study of tubulin-interacting proteins that target the β -tubulin subunit.

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Human tRNA-dihydrouridine Synthase 2: Molecular Basis for tRNA Recognition by an Unusual Double Stranded RNA-binding Domain

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ABSTRACT

Human tRNAs contains dihydrouridine at position 20 introduced by the flavin-dependent dihydrouridine synthase 2 (hDus2). Involved in certain cancer cells, this enzyme appears as a promising therapeutic target (1,2).

Recent, computational and crystallographic studies unraveled the structural organization of hDus2 (3,4). The enzyme is formed by three independent domains: (i) an N-terminal catalytic domain containing the FMN redox cofactor, (ii) a central helical-bundle domain and (iii) at the C-terminal extremity, an unusual double stranded RNA-binding domain (dsRBD) that carries most of the RNA binding function. Known as a specific domain of several enzymes involved in mRNA metabolism, the presence of a dsRBD is unique among the tRNA-modifying enzyme family.

Based on NMR, small angle X-ray scattering, protein-RNA X-ray structure and extensive mutagenesis studies, we herein propose a structural model of the tRNA-hDus2 complex that complies with the central role achieved by the dsRBD in RNA recognition. This model also illustrates how functional cooperativity drives tRNA binding and subsequent chemical modification. We will also briefly discuss how this novel type of binding emerged as a specific mechanism of Dus2 enzymes amongst different type of dihydrouridine synthases.

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HSP90 Regulation by RPAP3-PIH1D1 Cochaperones during Macromolecular Complex Assembly

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ABSTRACT

Box C/D small nucleolar ribonucleoparticles, phosphatidylinositol 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.

Allosteric Regulation of Small GTPases by Membranes as a Pharmacological Target

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ABSTRACT

Small GTPases bind guanine nucleotides to regulate diverse cellular and developmental events. Their deregulation underlies multiple pathological conditions including cancer, cardiovascular disease, developmental disorders as well as bacterial and viral infections. There is therefore a considerable need for small molecules able to modulate or inhibit small GTPases in diseases, which is especially challenging because of their structural and dynamics properties. Notably, small GTPase signalling requires their activation by GTP at membrane interfaces, which has remained poorly understood. Here we addressed these issues for small GTPases of the Arf family, which are major regulators of intracellular traffic, and a guanine nucleotide exchange factor (ArfGEF), BRAG2, which activates them in receptor endocytosis, synaptic transmission and muscle formation, and has been associated to tumor invasion and X-linked congenital diseases.

By combining reconstitution of proteins on liposomes, kinetic measurements using fluorescence spectroscopy, X-ray crystallography and molecular dynamics simulations, we show that membranes increase the activity of BRAG2 by more than 1000-fold, and that this considerable effect is achieved by maximization of protein-protein and protein-membrane interactions leading to optimal geometry of the Arf/ArfGEF complex on membranes. These results highlight that the allosteric regulation of ArfGEFs by membranes is a critical component of their cellular functions, and suggests that perturbation of the geometry of the Arf/ArfGEF complex on membrane can lead to inhibition. As a proof of concept, we characterized an allosteric inhibitor, Bragsin, which targets BRAG2 specifically on membranes, and determined the structure of the BRAG2/Bragsin complex. Altogether, our results predict that the allosteric regulation of small GTPase on membranes is a target for pharmacological inhibition with applications in many diseases.

Short Ragweed Pollen Allergy in the Light of SOLEIL Beamlines

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ABSTRACT

Allergy to short ragweed (*Ambrosia artemisiifolia*) pollen is a major health problem. Ten allergens of this invasive plant have been registered by the International Union of Immunological Societies. Among them, two enzymes are the major allergens: the pectate lyase Amb a 1 and the cysteine protease Amb a 11. The latter, recently identified [1], displays high sequence identities with allergens belonging to the C1A family of cysteine proteases. Firstly, the major allergens Der p 1 (24% identity) and Der f 1 (26%) from house dust mites, the most prevalent indoor allergens. Secondly, the plant allergens actinidin from Kiwi fruit (37%) and papain (35%) from Papaya.

To better characterize Amb a 11, a recombinant proform of the molecule (Pro-rAmb a 11) was produced in *Escherichia coli* and refolded. *In vitro* maturation at pH 5.0 induced an autocatalytic processing resulting in the cleavage of both N- and C-terminal propeptides (rAmb a 11), revealing the enzymatic activity. Secondary structures of pro-rAmb a 11, of pro-rAmb a 11 Δ CT lacking the C-term profragment typical of Amb a 11, and of the mature and active rAmb a 11 were assessed by synchrotron radiation circular dichroism (SRCD, DISCO beamline). Spectra of the various forms of Amb a 11 are similar, irrespective of the presence of the N- and C-terminal propeptides, thus indicating that the overall fold of Amb a 11 does not change significantly following maturation.

The purified pro-rAmb a 11 crystallized in orthorhombic P2₁2₁2₁ and trigonal P3₁21 space groups, leading to 2.70 Å and 2.05 Å resolution structures, respectively (PROXIMA 2A beamline). The enzyme is a dimer in the crystals. Indeed, small-angle X-ray scattering coupled to on-site high-performance liquid chromatography (SWING beamline) suggests that the concentrated Amb a 11 solution contains a mixture of monomeric and dimeric forms. Overall, both crystal structures show a typical C1A cysteine protease fold. A specific network of molecular interactions connects the catalytic triad of the enzyme and the N-terminal propeptide. The latter forms a lid that covers the active site, hampering substrate proteolysis.

The allergenicity of Amb a 11 was confirmed in a murine sensitization model. When compared with naive animals, mice sensitized to either pro-rAmb a 11 or rAmb a 11 exhibited airway inflammation, production of serum IgEs as well as induction of Th2 immune responses. Of note, inflammatory responses were higher in mice sensitized with the mature rAmb a 11 form and lower after the use of the irreversible cysteine protease inhibitor E64. It demonstrates that the cysteine protease activity critically contributes to the allergenicity of the molecule [2].

Three Soleil beamlines were used to better characterize the recombinant Amb a 11 protein. This cysteine protease is a key component of the ragweed pollen for allergy diagnosis and immunotherapy purposes. The properly folded and strongly allergenic rAmb a 11 molecule described here represents a valuable tool in this regard.

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PARALLEL SESSION

Chemistry & Physico-Chemistry, In Situ Reactivity, Soft Matter

ECOLE POLYTECHNIQUE – MONGE Auditorium

Chairpersons: Jean-Sébastien GIRARDON and Sandrine LYONNARD

- IT-03 A Synchrotron look into the lifecycle of Pt-In catalysts
H. Poelman
- OC-09 A combined in situ XAS/MS/Raman study of Ni-Cu catalysts derived from hydrotalcite-like precursors
A.R. Passos
- OC-10 In situ 1s2p resonant inelastic X-ray scattering (RIXS) applied to cobalt based catalysts
C. Desjacques
- OC-11 Negative thermal expansion in noble metal-based nanoparticles under different gaseous atmosphere
C. Zlotea
- IT-04 Competing coexisting phases in 2D water
J-M. Zanotti
- OC-12 Infrared spectroscopy study of water confinement in imogolites with internal Si-OH and Si-CH₃ groups
Y.Y. Liao
- OC-13 Oxide nanoparticles in water: amorphous to crystal conversion of luminescent yttrium vanadate
A. Freitas
- OC-14 Organometallic aryl-first row transition metal complexes as key intermediates in C-H functionalization
V. Martin-Diaconescu
- OC-15 Speciation of ruthenium in TBP/TPH organic phases (structure and reactivity)
C. Lefebvre

A Synchrotron Look into the Lifecycle of Pt-In Catalysts

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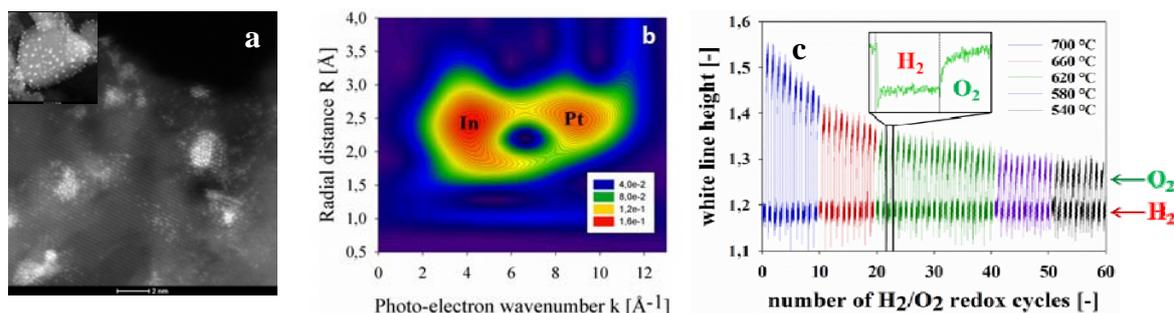
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ABSTRACT

Since their early discovery, bimetallic nanoparticles have become important in various research fields, including heterogeneous catalysis. Catalysts like Pt-In are highly demanded for their properties, e.g. in propane dehydrogenation. The nanoparticle size and composition strongly impact the nanoparticle's performance. The compositional flexibility of layered double hydroxide materials (LDH) can provide a route towards highly performing Pt-based catalysts with tuneable physicochemical properties. Pt(acac)₂ impregnated on a Mg(In)(Al)O_x support, prepared with incorporated In, forms 1.5 nm Pt-In nanoparticles after calcination and subsequent H₂ reduction^[1]. Their catalytic performance and life-time evolution were assessed using fast redox cycles at different temperatures.

As a further step towards controlled production of bimetallic Pt-In catalysts, a one-pot synthesis was explored, based on Mg,Al,Pt,In-containing layered double hydroxides^[2]. Aside from their straightforward synthesis, these Pt-In catalysts exhibit superior propane dehydrogenation activity compared to their multi-step synthesized analogues.

An alternative route to atomically-precise synthesis of bimetallic nanoparticles, containing both noble and non-noble metals like Pt-In, can be achieved by atomic layer deposition (ALD). A bimetal ALD approach was developed for the tailored synthesis of bimetallic nanoparticles, using sequential ALD of Pt on In₂O₃, followed by high-temperature H₂ reduction. The nanoparticles' In content can be accurately controlled over the whole compositional range, and the particle size tuned from microns down to the nanometre scale^[3].



The formation and performance of these bimetallic catalysts can in part be investigated by means of standard laboratory techniques like (in situ) XRD, SEM and STEM-EDX. However, an atom-scale picture of the synthesis process and the functioning in reaction can only be delivered through operando synchrotron-related techniques, such as (Q)XAS (Figure). The latter allow for a true insider's look into the elemental rearrangements that take place.

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A Combined *in situ* XAS/MS/Raman Study of Ni-Cu Catalysts Derived from Hydrotalcite-like Precursors

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ABSTRACT

Hydrotalcite-like or layered double hydroxides (LDHs) compounds are a large family of anionic clay materials which can be represented by the general formula $[M_1-x^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$. Owing to their uniform distribution of cations in the layers, LDHs have been used as precursors of bimetallic catalysts. ¹ Ni catalysts are very active on the production of hydrogen from ethanol steam reforming (ESR). However Ni catalysts suffer deactivation due to coke deposition, adding Cu was found to improve the catalyst stability. ² Ni-Cu LDH-type compounds were produced by the sol-gel method. The catalysts were characterized *in situ* and *operando* under realistic activation and reaction conditions by the combination of Quick-XAS (X-ray Absorption Spectroscopy) for monitoring the metallic phases simultaneously at the Ni and Cu K-edges, the reaction products by mass spectrometry (MS) and coke formation by Raman spectroscopy during ethanol steam reforming reaction on the ROCK beamline at SOLEIL. During the thermal decomposition Ni and Cu oxide nanoparticles supported on alumina were obtained. *In situ* XAS shows that the direct reduction of Ni from the as-dried LDH precursor leads 100% of Ni⁰ at 444°C for the monometallic Ni catalyst, whereas only 93% of Ni⁰ for the calcined catalyst is obtained even after 3h of plateau at 500°C. The addition of Cu to Ni catalysts leads to the enhancement of Ni reducibility since the as-dried Ni-Cu is completely reduced at 393°C (Fig. 1a). All the catalysts are active for ESR, particularly the as-dried Ni-Cu bimetallic catalyst which showed the highest ethanol conversion with high stability (Figure 1b). The deactivation of the catalysts is mainly by carbon deposition observed by *in situ* Raman. As an important conclusion of the work reported herein, we have evidenced that the thermal decomposition of LDHs gave rise to highly dispersed Ni particles. The bimetallic as-dried catalyst becomes 100 % reduced at lower temperature saving energy and hydrogen consumption for the activation. The high performance in the ESR of the catalysts could be related to its higher dispersion.

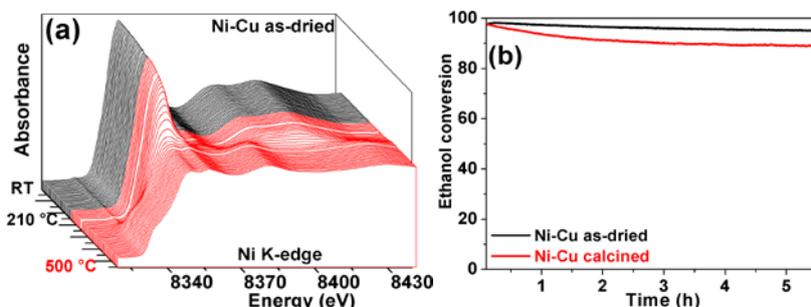


Fig. 1. (a) XANES spectra collected during the activation of the as-dried LDH precursor and (b) ethanol conversion for the as-dried and calcined bimetallic catalysts.

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In situ 1s2p Resonant Inelastic X-ray Scattering (RIXS) Applied to Cobalt Based Catalysts

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ABSTRACT

Cobalt based catalysts supported on alumina are mainly used in the Fischer-Tropsch (FT) process, which consists of production of hydrocarbons from syngas ($\text{CO}+\text{H}_2$) [1]. Cobalt is also used as a promoter in the $\text{CoMo}/\text{Al}_2\text{O}_3$ hydrodesulphurization (HDS) catalysts [2]. In order to improve their catalytic performance, a detailed understanding of their active phase at a molecular scale is mandatory. To get more insights on the electronic structure of the system, we used the resonant inelastic X-ray Scattering (RIXS) at GALAXIES beamline [3]. Indeed, 1s2p RIXS probes $L_{2,3}$ edge of transition metals using hard X-rays allowing *In Situ* experiments. First, we recorded 2D RIXS maps of some cobalt based reference compounds to confirm that 1s2p RIXS technique can separate different spectroscopic signatures in a reference sample (e.g. Co^{2+} and Co^{3+} in Co_3O_4). We also measured 2p XAS spectra on LUCIA beamline [4] of these samples to have pure reference spectra at cobalt $L_{2,3}$ edge to compare with the $L_{2,3}$ spectra obtained through vertical cuts of 2D RIXS maps. The next step was to follow the active phase formation of both FT and HDS catalysts during the activation treatment, using *in situ* 1s2p RIXS [5]. For the active phase formation of HDS catalysts, the *in situ* 2D RIXS maps recorded during the sulfidation process show the transition from an oxide environment to a sulfide one keeping the octahedral geometry. Further evolution of cobalt environment occurs at high temperature (see Figure 1). This conclusions have been complemented by site selective XAS recorded by monitoring the K_β emission line *in situ*.

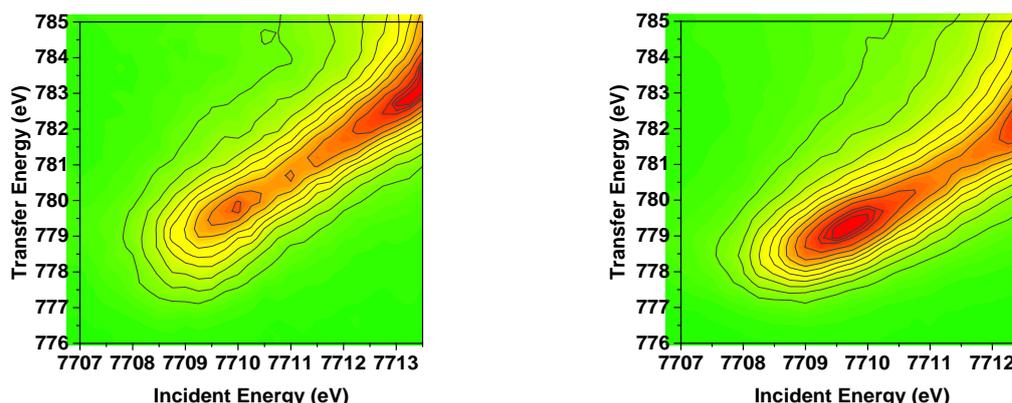


Figure 1 : 2D RIXS maps of $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst (Mo loading $2.7 \text{ at}/\text{nm}^2$, Co/Mo ratio of 0.4) at room temperature (left) and at high temperature (right) under $\text{H}_2/\text{H}_2\text{S}$ flow (90/10, 10 mL per min).

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Negative Thermal Expansion in Noble Metal-based Nanoparticles under Different Gaseous Atmosphere

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ABSTRACT

As compared to the bulk state, supported metal nanoparticles offer larger surface to volume ratios, faster transport properties, altered physical properties and interesting confinement effects that result from the combination of their small dimension and their interaction with the supports. Such nanomaterials are extensively used in heterogeneous catalysis, and are also relevant for energy storage [1,2].

Here, we report *in situ* EXAFS results obtained for three types of supported metal nanoparticles. The experiments were carried out on the ROCK beam line by the help of the Lytle-type cell. [3] The thermal behaviors of Pd (~4.5 nm) and Ir (~1.5 nm) nanoparticles as well as Pd-Ir (~2.2 nm) nanoalloys supported on oxide were studied under 1 bar H₂ and inert gas flow up to 250 °C. Figure 1 shows the thermal evolution of the first-neighbor distance (*R*). While the Debye-Waller factor is increasing with temperature, *R* is decreasing during heating for all nanoparticles, irrespective of the gaseous environment. The differences between nanoparticles can be understood in terms of distinct metal-hydrogen interactions. In the case of Pd nanoparticles, the lattice contracts due to hydrogen desorption from PdH_x hydride below 150 °C [4]. For Ir nanoparticles *R* is larger under H₂ than He due to the formation of Ir-H solid solution [5]. For Pd-Ir nanoalloys the difference between H₂ and He is very small due to very limited hydrogen absorption [5].

The unexpected “negative thermal expansion” is believed to originate from a nanosize effect and a strong interaction with the oxide support. Moreover, this seems to be a more general trend, since a similar behavior was already reported for oxide supported Pt nanoparticles [6].

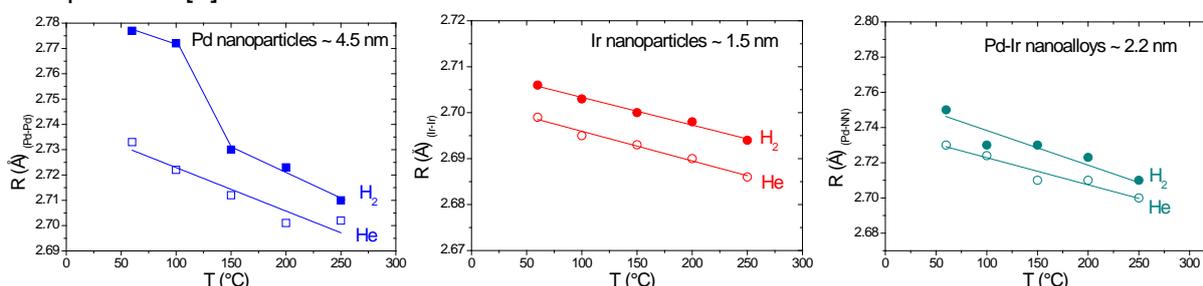


Figure 1. Thermal evolution of the first-neighbor distance for supported Pd (~4.5 nm), Ir (~1.5 nm) and Pd-Ir (~2.2 nm) nanoparticles under hydrogen and inert atmosphere.

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Competing Coexisting Phases in 2D Water

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ABSTRACT

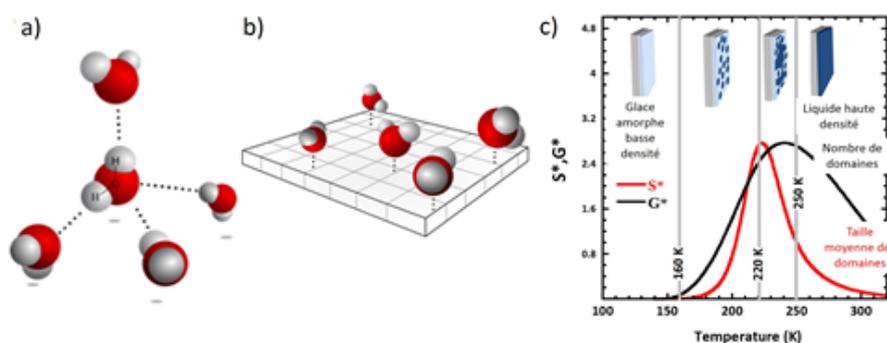


Figure: In two-dimensions, the ideal tetrahedral organization (a) of the network of hydrogen bonds (a) is frustrated (b): a molecule may only engage four hydrogen bonds: one with a Si-OH group of the silica surface and three with neighboring water. c) The two-dimensional water is a heterogeneous system with unexpected physical properties: a glass transition at 165 K, a dynamic transition at 220 K and a liquid-liquid transition at 250 K. Adapted from [1].

The properties of bulk water come from a delicate balance of interactions on length scales encompassing several orders of magnitudes: *i*) the Hydrogen Bond (HBond) at the molecular scale and *ii*) the extension of this HBond network up to the macroscopic level. Here, we address the physics of water when the three dimensional extension of the HBond network is frustrated, so that the water molecules are forced to organize in only two dimensions. We account [1] for the large scale fluctuating HBond network by an analytical mean-field percolation model. This approach provides a coherent interpretation of the different events experimentally (calorimetry, neutron, NMR, near and far infra-red spectroscopies) detected in interfacial water at 160, 220 and 250 K. Starting from an amorphous state of water at low temperature, these transitions are respectively interpreted as the onset of creation of transient low density patches of 4-HBonded molecules at 160 K, the percolation of these domains at 220 K and finally the total invasion of the surface by them at 250 K. The source of this surprising behavior in 2D is the frustration of the natural bulk tetrahedral local geometry and the underlying very significant increase in entropy of the interfacial water molecules.

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Infrared Spectroscopy Study of Water Confinement in Imogolites with Internal Si-OH and Si-CH₃ Groups

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ABSTRACT

Water confined in aluminosilicates nanotubes (imogolites) in the form of self-sustaining thin films was investigated by means of infrared spectroscopy. Two types of imogolites were studied: a hydrophilic imogolite (IMO-OH) with an inner surface fully covered with Si-OH groups and a hybrid imogolite (IMO-CH₃) with a hydrophobic inner surface due to the full coverage with Si-CH₃ groups. The infrared spectra were recorded in the 50 - 4000 cm⁻¹ range as a function of the relative humidity (0 - 100% RH) and temperature (295 K to 50 K). The evolution of the stretching, bending, liberation and connectivity bands were studied. The special features of the H-bond network revealed by both mid- and far- infrared range during adsorption and desorption of water are detected, and provide strong evidence that the water confinement in imogolites can be significantly affected by the geometry of the nanotube, the packing structure, and also by the hydrophobic vs. hydrophilic character. Insights into the relationship between (1) the large specific surface area, (2) restricted geometries, (3) the tunable hydrophilic/hydrophobic character, can serve the scientific community interested in deploying these materials as membranes, catalyst supports, adsorbents and other similar applications.^{1,2}

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Oxide Nanoparticles in Water: Amorphous to Crystal Conversion of Luminescent Yttrium Vanadate

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ABSTRACT

Among families of nanoparticles, oxide nanoparticles synthesised in water are quite peculiar as they tend to form similar morphologies. For instance, titanium oxide, zirconium oxide, zinc oxide, cerium oxide, yttrium vanadate, sized in the 20-150nm range, are made of aggregated crystalline primary grains¹. This two-level structuration is the possible signature of a general non-classical nucleation path, where crystallisation by aggregation² prevails over ion-by-ion growth. Deeper understanding is a key issue when intending to optimise the development of functional materials involving these particles (nanocomposites, thin films, biological labels...). To date, the control and understanding of the nanostructuration is hampered by the lack of direct, in situ, experimental observations of the nucleation process, a subject that we intend to investigate on a model system.

Here, we study the synthesis of YVO₄:Eu nanoparticles by coprecipitation in water, upon mixing two aqueous precursors³. This synthesis is a good model system to study two paradigmatic cases: tuning the pH of the vanadate precursor, we obtain either “classical” polycrystalline particles of 40 nm composed of primary grains of 2 to 5 nm, or monocrystalline-like particles of 40 nm.

To explain this difference in structure, in situ luminescence, pH and SAXS/WAXS studies were conducted simultaneously, from reaction times as short as 5ms. In particular, we demonstrate that the nanostructure is driven by a secondary nucleation from transient disordered intermediate states that we were able to capture in the millisecond range.

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Organometallic Aryl-first Row Transition Metal Complexes as Key Intermediates in C-H Functionalization

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ABSTRACT

First row transition metal complexes offer the promise of green and economically sustainable processes for selective chemical transformations. This is particularly relevant for the selective functionalization of the ubiquitous C-H bond, which currently requires the use of heavy metals, which are scarce, expensive and form toxic byproducts. Recently, several Fe, Co, Ni, and Cu catalyzed C-H functionalization reactions have been reported. Although, high valent metal intermediates are generally invoked in the catalytic process, their mechanisms, unfortunately, are poorly understood.

Therefore we report a series of Co, Ni and Cu model complexes with triazamacrocyclic ligands that are competent catalysts for C-H functionalization.¹⁻³ For these systems, X-ray absorption spectroscopy was applied at the metal K-edge as a direct probe of the electronic and geometric structure of the key intermediates in the reaction pathways. Although distinct C-H activation pathways are observed for different metal centers, such as proton coupled electron transfer (Cu), or concerted metallation deprotonation (Co), all complexes share an analogous high valent aryl-M (M = Ni, Co, Cu) intermediate having a distinct spectroscopic signature that highlights the highly covalent nature of the metal-aryl bond. Follow up correlation of the experimental data with theoretical calculations lead to a better understanding of C-H functionalization and reaction mechanisms were derived for each of the model systems for both the C-H activation step and the ensuing coupling step.

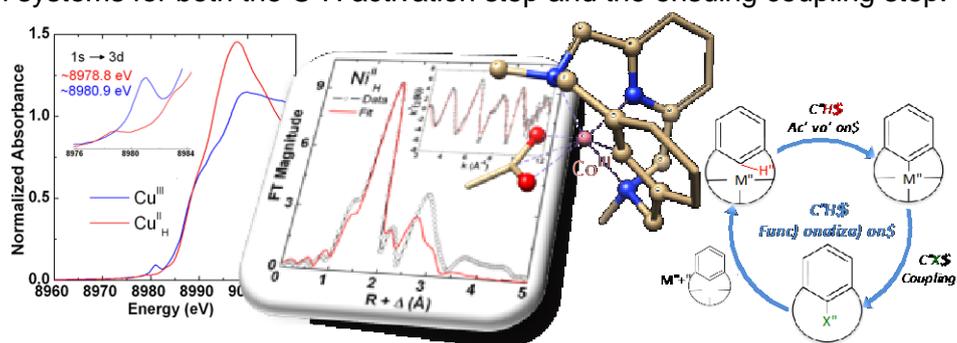


Fig. 1: X-ray absorption spectroscopy coupled with theoretical calculations as probes of geometric and electronic structure for a series of Co, Ni, Cu triazamacrocyclic based C-H functionalization catalysts.

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Speciation of Ruthenium in TBP/TPH Organic Phases (Structure and Reactivity)

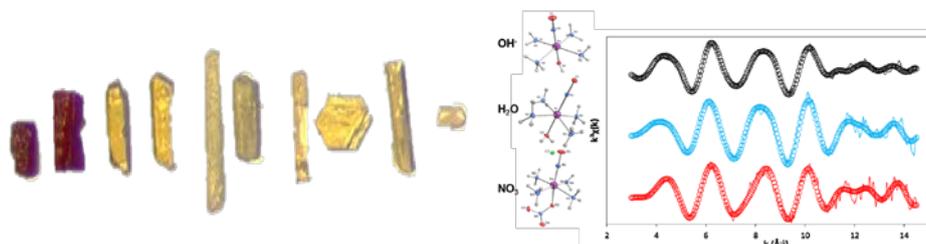
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ABSTRACT



Ruthenium is one of the major fission products and is slightly extracted by the tributylphosphate (TBP) with uranium and plutonium during the reprocessing of the spent nuclear fuels within the PUREX process [1].

During dissolution of used nuclear fuel in nitric acid, ruthenium forms trivalent nitrosyl complexes with nitrate, nitrite, hydroxo and aquo ligands. Its speciation is not very well described in nitric acid media, but a general formula was proposed: $[\text{RuNO}(\text{NO}_3)_x(\text{NO}_2)_y(\text{OH})_z(\text{H}_2\text{O})_{5-x-y-z}]^{3-(x+y+z)}$ where x , y , z depend on the chemical conditions. It is assumed that only the most nitrated complexes are extracted to the organic phase with a quantitative yield [2, 3].

The study of Ru complexes is made much more difficult by the co-existence of several species with low ligand exchange kinetics [4]. There must be several extracted species and polydispersity in both aqueous and organic phase.

In this study, different complementary spectroscopic techniques were used to have a better understanding of the ruthenium local environment in simulated reprocessing solutions. It includes vibrational spectroscopy and X-ray absorption spectroscopy (EXAFS).

The Ru nitrosyl form was firstly confirmed in both phases, and then the coordination sphere of this core was probed. The ruthenium extraction mode by TBP (direct complexation with Ru and/or second sphere coordination) was investigated as a function of initial conditions. Hydrolysis effect was highlighted as well as the ruthenium speciation in the organic phases, depending on acidity of the initial solution. At the end, the aging process of ruthenium in the TBP phase was qualitatively characterized.

This study was supported by synthesis of reference compounds under monocrystalline form and then structurally characterized by XRD. Their EXAFS spectra were recorded and used as a database to fit EXAFS spectra of experimental solutions. Some DFT calculations were also made to calculate Debye-Waller factors and compare them to the factors determined by fitting model compounds data. This will permit to restrict Debye-Waller factor for solvent extraction samples to obtain accurate stoichiometry.

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PARALLEL SESSION

Cultural Heritage, Archaeology, Environment, Geosciences

ECOLE POLYTECHNIQUE – CURIE Auditorium

Chairpersons: Emmanuel GUILLON and Noemi CARMONA-TEJERO

- IT-05 Formation and reactivity of ZnS nanoparticles precipitating in organic wastes
C. Lévard
- OC-16 Highlighting the large variability of as speciation in Wetlands: A new insight in as dynamic control
D. Vantelon
- OC- 17 Investigating Ca speciation and distribution inside cyanobacterial cells forming intracellular carbonates
K. Benzerara
- OC-18 VUV photodynamics of free “tholins” nanoparticles investigated by imaging angle-resolved photoemission
S. Tigrine
- OC-19 5 years of X-ray imaging of flat fossils at the Diffabs beamline: New sources of data for paleontologists
P. Gueriau
- OC-20 Metallurgy of the earliest lost-wax cast
M. Thoury

Formation and Reactivity of ZnS Nanoparticles Formed in Organic Wastes

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ABSTRACT

Incidental NPs are produced and dispersed in the environment in much larger amounts than manufactured NPs and with much less consideration of their environmental impact. This is potentially the case for ZnS NPs that form in a variety of anaerobic environments such as municipal and agricultural organic wastes. As an example, ZnS NPs with sizes ranging from 2.5 to 7.5 nm in diameter were observed in final sewage sludge products potentially accounting for about 80% of the Zn present in the sludge.¹ In most countries, these organic wastes are spread on cultivated soils as fertilizer, which may represent an important source of nanomaterial into the environment. Zinc can be phytotoxic for crops at doses commonly found in organic wastes.² Although ZnS is poorly soluble from a thermodynamic point of view ($K_{sp}=10^{-24.7}$), ZnS NPs are known to transform to oxidized products in oxic environments quicker than bulk ZnS. As an example, the oxidation rate of bulk sphalerite was shown to be relatively slow when incubated in soils under oxic conditions: 0.6% per year in a sub-tropical soil and 1.2 % per year in a temperate soil.³ In contrast, we have recently shown that ZnS NPs formed in pig slurry were quickly oxidized after spreading on crop fields.⁴

The parameters controlling the oxidation of ZnS NPs are currently unknown. Available data is insufficient to elucidate whether the reported differences in oxidation rate are related to medium properties or to size effects. Given the likely dominance of ZnS NPs in municipal and agricultural wastes and the widespread use of these wastes in agricultural practices, a more fundamental understanding on the factors controlling the formation, chemical reactivity, mobility, bioavailability and toxicity of ZnS NPs under different environmental conditions is needed.

Here, we will present some results regarding the characterization of ZnS NPs in different organic wastes (e.g. pig slurry, sewage sludge) as well as preliminary results on the size-dependent properties of these NPs.

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Highlighting the Large Variability of as Speciation in Wetlands: A New Insight in as Dynamic Control

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ABSTRACT

Due to the importance of arsenic (As) speciation for its mobility from the groundwater to the aquifer, we investigated the behavior of As during the oxidation of an iron (Fe) and organic-rich wetland soil solution. A soil from the Naizin Kervidy wetland (France) was incubated in the laboratory to obtain a reduced solution which was then oxidized and filtered through a progressively decreasing pore size (5 μm , 3 μm , 0.2 μm , 30 kDa and 5 kDa). The fractional distribution of As among the particulate, colloidal and truly dissolved phases was investigated and coupled to speciation study using XAS at the As K-edge on the DiffAbs beamline and at the Fe K-edge on the LUCIA beamline, HPLC and SEC-ICP-MS and organic matter characterization using GC-MS and fluorescence spectroscopy. The results showed that a majority of As was present as As(V) but a small amount of As(III) remained, despite the advanced oxidized conditions. The chemical and XAS analyses showed that As was associated with Fe-OM-rich colloids in the 0.2 μm -30 kDa size range and associated with OM-rich colloids below 30 kDa. The 0.2 μm -30kDa fraction corresponded also to a transitional phase in terms of OM composition and degradation which had an influence on OM complexation affinity for Fe. A fraction of Fe thus formed ternary complexes with OM and were observed in the smallest fractions. A non-negligible amount of the As(V) was found as organic methylated species in all the fractions. These biological produced compounds could be bound to Fe(III) phases, colloidal OM or integrated in organism structures. Even if the As was more concentrated in the 0.2-30kDa fraction, by comparing the total dry masses of all fractions, we determined that about 90% of the As was contained in the particulate fractions and thus immobilized. However the bioavailability of these As compounds and their potential remobilization during the reduced period need to be assessed.

Investigating Ca Speciation and Distribution inside Cyanobacterial Cells Forming Intracellular Carbonates

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ABSTRACT

Cyanobacteria are a phylogenetically and ecologically diverse phylum of bacteria, which have impacted the global cycle of carbon for billions of years and induced the oxygenation of the atmosphere. Despite the geological importance of carbonate biomineralization by cyanobacteria, involved mechanisms are yet poorly understood. Recently, several cyanobacterial species forming amorphous Ca-containing carbonates intracellularly were discovered [Couradeau et al., 2012; Benzerara et al., 2014]. They are phylogenetically diverse and present in various environments in various geographical sites worldwide [Ragon et al., 2014]. Not all cyanobacterial species can form intracellular carbonates and we have not determined yet what physiological differences between these species explain intracellular vs extracellular calcification. Recently, we suggested that this may be due to a difference in homeostasis of calcium: cyanobacteria forming intracellular carbonates may sequester Ca to a higher extent [Cam et al., 2015; Li et al., 2016]. However, we need further quantification of Ca at the nm-scale in cells to support this hypothesis. STXM appears as a particularly appropriate tools for this purpose [Cosmidis et al., 2014]

Several strains of cyanobacteria forming intracellular carbonates were cultured in BG-11 with 50 or 350 μM of Ca under constant illumination at 30°C. We studied cells at the C K-edge and the Ca L_{2,3} edges by STXM on the HERMES beamline. We obtained images with a spatial resolution better than 40 nm and XANES spectra which allowed to locate and quantify the different Ca species present in the cells. Here, I will show the first results obtained.

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VUV Photodynamics of Free “Tholins” Nanoparticles Investigated by Imaging Angle-resolved Photoemission

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ABSTRACT

Titan, the largest moon of Saturn, has a dense atmosphere whose upper layers are mainly composed of methane (CH₄) and molecular nitrogen (N₂). Their photochemistry leads to the formation of aerosols at very high altitudes (>800 km)¹. Once these aerosols are formed and through their descent towards the surface, they will still interact with persistent UV/VUV radiations, at different energies, that can reach lower atmospheric layers. This interaction has some impact, for example on the radiative transfer or on the ionization yield of the atmospheric compounds.

Models are a good way to study those processes, but the lack of data on the refractive index or the absolute absorption/ionization cross sections of the aerosols can be an obstacle.

In order to shed some light and quantify those processes, we ionize analogs of aerosols (tholins) produced with the PAMPRE experiment (LATMOS) on the SAPHIRS platform of the DESIRS VUV beamline (synchrotron SOLEIL), equipped with an aerodynamic lens. The aerosols are injected directly under vacuum as isolated free nanoparticles². The generated photoelectrons are then collected with a Velocity Map Imaging detector and their energetic and angular signatures are analyzed by ARPES (Angle-Resolved PhotoElectron Spectroscopy).

Both the nanoparticles size distribution and the incident wavelength determine the parameters governing the photoemission process (intra-particles electron mean free path, photon penetration depth) as revealed by the angular distribution of the photoelectron showing in some cases a marked forward/backward asymmetry with respect to the photon axis^{3,4}. Those parameters may provide us with information on the optical behavior of the aerosols, and how they contribute to the global albedo (ie reflectivity) of Titan atmosphere. In addition we can extract the ionization threshold energy together with the absolute absorption cross sections of the aerosols, from which altitude dependent photodynamics can be unraveled. Such information is important since the corresponding formed slow electrons may be involved in the formation of anions via dissociative electron attachment for instance.

We will present here the experiments performed, at different VUV energies, on Titan's aerosol analogs with the ARPES method and show how the first results can have implications regarding Titan's atmosphere overall optical characteristics.

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5 Years of X-ray Imaging of Flat Fossils at the Diffabs Beamline: New Sources of Data for Paleontologists

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ABSTRACT

Paleontology relies on the accurate description of the anatomical characters preserved in fossils for deciphering the evolutionary history of life. However, many fossil forms remain difficult or impossible to describe using conventional imaging methods such as optical photography and microscopy. The last ten years have witnessed the development of a series of X-ray-based imaging techniques that proved to be fantastic sources of new anatomical, but also chemical, information with no, or only limited, sample preparation (e.g. [1]). X-ray tomography is now commonly used to access the internal morphology of three-dimensionally preserved fossils with an unprecedented level of detail (e.g. [2]). Yet, it suffers from a physical limit for the study of flattened fossils due to the extremely high difference in X-ray absorbance in different directions. Imaging of flat fossils, however, strongly benefitted from critical improvement towards rapid scanning X-ray fluorescence, which produces 2D distributions of major-to-trace elements over decimeter-scale objects, including entire fossil birds [3]. Besides revealing hidden anatomy [4], such approach also get insight into the fossils chemistry, offering unexpectedly detailed paleobiological, paleoenvironmental and taphonomic information through the characterization of their organic, elemental and mineralogical compositions [1,3]. Some developments performed at the Diffabs beamline during the last 5 years appear particularly promising. Here, we will present the main results that arose from our successive experiments, and will discuss the new possibilities offered by the multi-technique data acquisition 'flyscan' platform.

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Metallurgy of the Earliest Lost-wax Cast

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ABSTRACT

Among the variety of the meta-families of materials gathered under the term *ancient materials*, their heterogeneity at multiple spatial scale is a common specificity that generate strong implication for their analyses¹. Thus, on the one hand such complexity can be considered as a strong constraint that limits the amount of information that can be extracted from them, and on the other hand, it can be seen as an inspiration to develop novel imaging-based analytical strategies allowing to decipher hidden recorded information.

To characterize crystal defects in semiconductor science, photoluminescence spectroscopy is a well-established technique². However, in the field of ancient materials, if the pioneering work in the early 20th century established UV photoluminescence photography as an important tool to visualize contrast of materials on works of arts of museum artefacts, very scarce works have been undertaken to impart luminescence-based technique capabilities to retrieve quantitative information on the composition or structural specificities of materials at the microscale. Since few years, synchrotron photoluminescence imaging has emerged as a promising method to study heterogeneous materials, composed of inorganic and organic compounds as those in ancient material sciences^{3,4}. In the frame of a PhD work conducted at IPANEMA, the full-field photoluminescence imaging set up of the DISCO beamline of SOLEIL has been fully optimized to characterize semiconductor phases of archaeological and cultural heritage samples. Those instrumental developments have conducted to enhance critical parameters to tackle the multi-scalar heterogeneity of ancient materials: Particular effort have been undertaken to increase the spatial dynamics and the spectral dynamics in emission and excitation to collect low-signal emission at the sub-microscale from heterogeneous systems and in particular on archaeological artefacts, in order to respond at best to archaeological and cultural heritage-related questions with a topological, chemical, electronic and crystalline analysis.

In particular, within the study of a 6,000-year-old amulet from Mehrgarh (Baluchistan, Pakistan) identified as the oldest known artefact made by lost-wax casting, we demonstrate that our novel approach allows accessing the spatial distribution of crystal defect fluctuations at the crystallite level across centimeter-wide fields of view. Such capabilities allow revealing the coexistence of two hitherto indistinguishable non-stoichiometric cuprous oxide phases. Such results were the missing brick to access key information on the early step of this fundamental invention, still in use nowadays for precision casting⁵. We therefore demonstrate the exceptional potential of high spatial dynamics-photoluminescence imaging to study nano- and poly-crystalline materials for applications within a variety of fields, ranging from quality control in semiconductor solid-state physics to geophysics, archaeology, cultural heritage and environmental sciences.

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PARALLEL SESSION

Diluted Matter

ECOLE POLYTECHNIQUE – CARNOT Auditorium

Chairpersons: Vincent BOUDON and Francis PENENT

- IT-06 Quantum tunnelling of particles within molecules: Synchrotron far-IR spectroscopy of malonaldehyde
D. Tokaryk
- OC-21 The far-IR spectrum of formic acid cyclic dimer : A model system for vibrational dynamics
S. Bteich
- OC-22 Photo-ionization and photo-dissociation of PAH cations
J. Zhen
- OC-23 A new method for the determination of metal-ligand bonding energy using VUV Synchrotron Radiation
N. Shafizadeh
- IT-07 Many-electron emission in understanding atoms and molecules: Theory and experiment
K. Jänkälä
- OC-24 Photoionization of the fullerene cation
S. Douix
- OC-25 VUV spectroscopy of free radicals on the DESIRS beamline: Absorption of OH and photoionization of CH and C₂H
B. Gans
- OC-26 Core-Valence double photoionization $4d^{15}p^{-1}$ in xenon studied with multielectron spectroscopy
M.A. Khalal
- OC-27 State-selected ion-molecule reactions with CERISES: A very efficient TPEPICO ion source adapted to metastable species produced in a beam
C. Alcaraz
- OC-28 Infrared spectroscopy of methoxyphenols involved as atmospheric secondary organic aerosol precursors
A. Cuisset

Quantum Tunnelling of Particles within Molecules: Synchrotron Far-IR Spectroscopy of Malonaldehyde

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ABSTRACT

In the molecule malonaldehyde ($C_3O_2H_4$), the two oxygen atoms lie at the two ends of an open ring formed by the three carbon atoms. There is a potential energy minimum near each of these oxygens, with an energetic barrier between them. One of the hydrogen atoms of malonaldehyde is located in this region. In the molecule's ground vibrational state, the proton from this hydrogen atom has insufficient energy to surmount the barrier. Classically this means that this proton should remain in the energy well near one or the other of the oxygen atoms. However, quantum-mechanical tunnelling allows it to penetrate through the barrier and thus to exist simultaneously in the two energy wells. This proton thus becomes a quantum blur that is smeared out between the two oxygen atoms. Malonaldehyde is one of the smallest systems to exhibit this phenomenon, and is thus a prototype of intramolecular quantum tunnelling.

The effects of tunnelling on the energy structure of the molecule are pronounced: instead of particular levels existing in degenerate pairs, corresponding to the proton existing in one energy well or the other, the pairs of levels separate slightly. When spectra of the molecule are taken, the separation results in an apparent doubling of the spectral features, and thus the degree of tunnelling-induced splitting of energy levels can be deduced. I will describe our experiments at the Canadian Light Source synchrotron, where we have successfully taken far-IR spectra of malonaldehyde at high resolution. These spectra have allowed us to refine the description of the tunnelling-splitting of the ground vibrational state, and to measure it for several excited vibrational states. The data have also allowed us to interpret and refine the analysis of microwave spectra of this molecule taken over 40 years ago. Taken together, the far-IR and microwave data allow us to build a rather complete picture of the ground and low-lying vibrationally excited states of this fascinating species.

The Far-IR Spectrum of Formic Acid Cyclic Dimer: A Model System for Vibrational Dynamics

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ABSTRACT

Carboxylic acids are one of the most abundant classes of organic compounds. They are widely used in the production of polymers, for drug design, in the synthesis of food additives or as solvents. As the simplest carboxylic acid, formic acid (FA) may act as an excellent model to study the general physical and dynamical properties of acids. In addition, it is a molecule of significant importance in both atmospheric and astrophysical chemistry.

It is well known that the dimeric form is predominant in the gas phase at temperatures below 423 K.¹ The cyclic conformation of the dimer (FACD) is an elementary system to be understood for the concerted hydrogen transfer through equivalent hydrogen bonds, which is an important process within biomolecules. In this context, the far-IR range is a crucial spectral region firstly because it gives a direct access to the intermolecular vibrational modes involved in this process rather than an indirect access via intramolecular modes which are perturbed upon dimerization. Secondly, due to its centrosymmetric conformation, the FACD exhibits no pure rotation spectrum, so that ground state (GS) information can only be derived from the IR rovibrational bands. However, due to congestion and broadening effects (Doppler), IR bands are not rotationally resolved at room temperature.² So far, only small parts of the mid-IR ν_5 -GS band have been observed in jet-cooled conditions using laser techniques.^{3,4} Unfortunately, such techniques do not give access to the far-IR region at present time.

We present here the first observation of a far-IR band (ν_{24} -GS) of FACD, rotationally resolved, recorded using the Jet-AILES apparatus coupled to a high resolution FTIR spectrometer (Bruker IFS125HR) using far-IR synchrotron radiation.⁵ Splittings due to vibration-rotation-tunneling are clearly observed as in the case of ν_5 -GS band. Analysis is in progress starting from the GS constants obtained by Goroya *et al.* and with the support of electronic structure calculations.⁶

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Photo-ionization and Photo-dissociation of PAH Cations

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ABSTRACT

Interstellar polycyclic aromatic hydrocarbons (PAHs) are strongly affected by the absorption of vacuum ultraviolet (VUV) photons in the interstellar medium (ISM), yet the branching ratio between ionization and fragmentation is poorly studied. This is crucial for the stability and charge state of PAHs in the ISM in different environments, affecting in turn the chemistry, the energy balance, and the contribution of PAHs to the extinction and emission curves. We studied the interaction of PAH cations with VUV photons in the 7–20 eV range from the synchrotron SOLEIL beamline, DESIRS. We recorded by action spectroscopy the relative intensities of photo-fragmentation and photo-ionization for a set of eight PAH cations ranging in size from 14 to 24 carbon atoms, with different structures. At photon energies below ~ 13.6 eV fragmentation dominates for the smaller species, while for larger species ionization is immediately competitive after the second ionization potential (IP). At higher photon energies all species behave similarly; the ionization yield gradually increases, leveling off between 0.8 and 0.9 at ~ 18 eV. Among isomers, PAH structure appears to mainly affect the fragmentation cross section but not the ionization cross section. We also measured the second IP for all species and the third IP for two of them; all are in good agreement with theoretical ones, confirming that PAH cations can be further ionized in the diffuse ISM. Determining actual PAH dication abundances in the ISM will require detailed modeling. Our measured photo-ionization yields for several PAH cations provide a necessary ingredient for such models.

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A New Method for the Determination of Metal-ligand Bonding Energy using VUV Synchrotron Radiation

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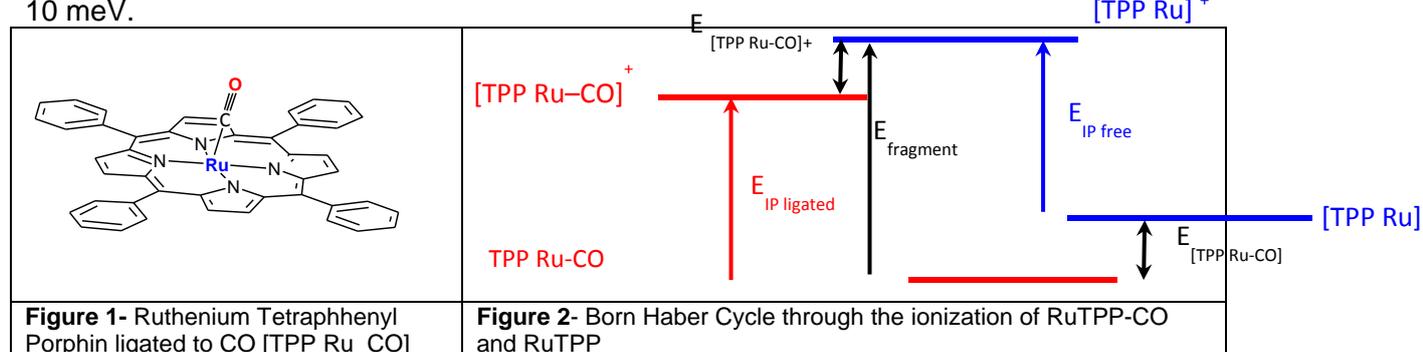
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ABSTRACT

Today scientists are able to model biological processes at the molecular level. However to build an accurate model, the bonding energy of the different partners of the chemical reaction as well as their ionisation potentials are critical data that need to be precisely measured.

Here, we present a new method for the determination of the energy of Ruthenium-Carbonyl bond energy in the complex Ruthenium-CO tetraphenyl porphyrin complex [TPP Ru CO] (**Fig 1**), using the SAPHIRS experimental setup equipped with the DELICIOUS III spectrometer installed on the DESIRS VUV beamline of SOLEIL. We have chosen to study [TPP Ru CO] because this complex is a model compound for studying the mechanism of association and dissociation of a ligand with a hemoprotein. Ruthenium lies in the same column of Mendeleiev table as Iron. Iron II porphyrin is difficult to manipulate even in solution, due to its high affinity for molecular oxygen. Besides, [TPP Ru CO] is a robust and commercial compound and is very stable with respect to heating.

We have investigated the unimolecular decomposition of ligated compounds [TPP Ru CO] in the gas phase via VUV synchrotron-based experiments. We have measured precisely the ionisation potential of [Ru TPP CO]- $E_{IP \text{ ligated}}$, RuTPP - $E_{IP \text{ Free}}$ - and the dissociation threshold of CO from [TPP Ru CO]⁺ - E_{frag} . Combining these values following the Born cycle schematized in **Fig 2**, we have determined the binding energy of Ru-CO in the neutral species and in the cation. The determined binding energies are in very good agreement with the theoretical values obtained via quantum chemistry calculations (DFT) by A. de La Lande and S.Chen. To our knowledge, this is the first time that a Born Haber cycle is coupled to a synchrotron radiation study allowing the determination of a bond energy with the precision of 10 meV.



Many-electron Emission in Understanding Atoms and Molecules – Theory and Experiment

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ABSTRACT

Many-electron emission by a single photon pulse is often considered as a nonlinear effect present at high field conditions in experiments carried out at conventional or free-electron lasers. However, in contrast to such assumption, experiments that study phenomena leading to emission of multiple electrons at synchrotron radiation sources is also a very active and field of science (see e.g., recent review [1]). Since photoemission at weak field is primarily a one-electron process described by the dipole approximation, understanding the emission of several electrons from such event requires accounting electron-electron interactions. The many-electron ionization at weak fields thus inherently probes the internal interactions of the system, whereas high field ionization directs to strong photon-matter coupling.

Traditionally the most intensively studied many-electron emission process in atomic scale systems is photoionization followed by Auger electron emission. In addition, recent advances in experimental techniques in coincidence detection methods of multiple electrons and ions have enabled studies of direct many-electron photoionization and many-electron Auger process.

In this presentation the experimental techniques currently practiced at SOLEIL for many-electron coincidence detection of gas phase atoms and molecules, namely magnetic-bottle time-of-flight spectrometer [2], and core-level electron spectroscopy will be described [3]. The presentation will give also an overview to the theoretical framework based on scattering theory formalism used for understanding the experimental results [4]. As examples of our recent work in many electron emission, core-shell photoionization of atomic rubidium [5] and double photoionization of aromatic molecules [6] will be described. In addition, processes following tender X-ray deep core photoionization of xenon [7] and hydrogen chloride [8] will be discussed.

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Photoionization of the Fullerene Cation

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ABSTRACT

Since its discovery, buckminsterfullerene (C_{60}) and its ions have attracted much interest especially for their spectroscopic applications¹. However, determination of spectroscopic properties of ions is difficult experimentally and most of the experimental data on ion photoionization have been obtained using the so-called merged beam technique^{2,3}.

The photoionization cross section of C_{60}^+ investigated by the merged-beam method agreed qualitatively well with theoretical calculations but appeared to be smaller than predicted theoretically. In addition, these cross sections were also found 4 to 5 times smaller for the radical cation than for neutral C_{60} .

We have therefore investigated photoionization of the C_{60}^+ cation with two different methods in order to obtain absolute photoionization cross-sections. First, the merged beam method (MAIA setup @ PLEIADES)⁴ based on the spatial overlap of high-energy ion beam with a beam of probe particles was used in the 25-45 eV range using filters to remove any high order radiation. Secondly, data were obtained using the ion trap method⁵ in the 8-25 eV range, also using the DESIRS gas filter to ensure spectral purity.

Experimental results have been compared to real time TDDFT calculations, using the Octopus code⁶. Although the merged-beam cross-sections agreed with previous measurements, ion trap results appeared in excellent agreement with theory and with neutral cross sections. This discrepancy between both methods is ascribed to the different ion sources used. The ECR ion source used by the merged beam setup provides an important amount of energy to the precursor ions (C_{60}^+). This energy leads to strong fragmentation channels and production of electronic excited species, which consequently affects the optical properties of the ion⁷.

The ion trap method can now be used to determine accurate absolute photoionization cross-section of large molecules. Besides, this method could be used in future work to measure absolute data on other phenomena, such as photodissociation or photodetachment for molecular targets and clusters that can be produced by modern ionization sources.

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VUV Spectroscopy of Free Radicals on the DESIRS Beamline: Absorption of OH and Photoionization of CH and C₂H

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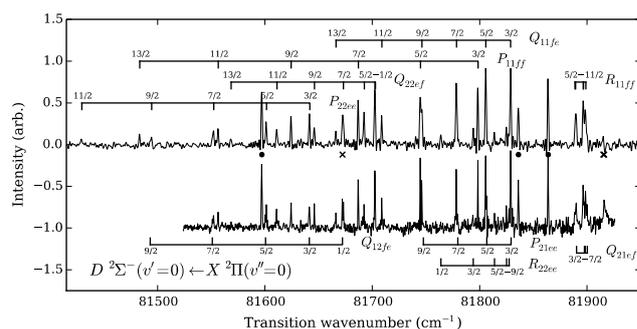
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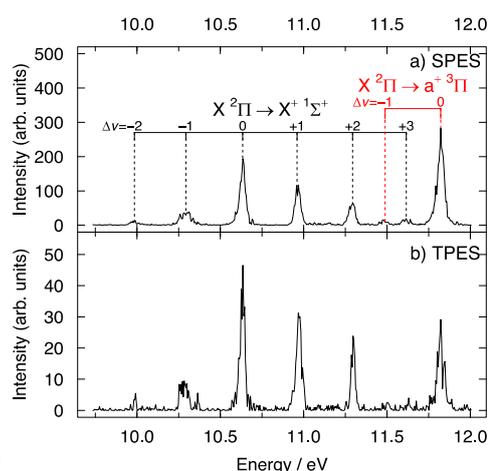
ABSTRACT

VUV spectroscopy of free radicals requires “*tour de force*” experimental methods for both the radical production and the excitation in the VUV range. Thanks to different optimized radical sources (radiofrequency discharge, flow tube reactor,...) and to the DESIRS beamline at the SOLEIL synchrotron facility which delivers VUV photons with a high resolution and a high flux, we have demonstrated the potential of the SAPHIRS and VUV-FTS endstations of DESIRS in this important field. This kind of spectroscopy is highly demanded, especially by the astrophysics and combustion communities, for which free radicals play important roles in the photochemistry of their relevant media.

In this talk, the results obtained for the absorption spectroscopy of the OH radical (see left figure) [1], and the photoelectron spectroscopy of the CH (see right figure) and C₂H radicals [2,3] will be presented.



Figures: Absorption spectrum of the OH radical recorded with the VUV FTS setup (left figure) and photoelectron spectra (SPES: slow photoelectron spectrum and TPES: threshold photoelectron spectrum) of the CH radical recorded with the SAPHIRS setup (right figure).



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Core-Valence Double Photoionization $4d^{-1}5p^{-1}$ in Xenon Studied with Multielectron Spectroscopy

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ABSTRACT

Direct measurement of photoelectrons or Auger electrons resulting from inner-shell ionization of positive ions is extremely difficult [1] though such information is of primary interest for plasmas characterization and modeling. Another way to obtain the Auger spectra from ions is given by core-valence double ionization of the neutral atom [2].

The experiments were carried out at the SEXTANTS beamline of the SOLEIL French synchrotron facility. It uses the HERMES magnetic bottle time of flight spectrometer [3] which allows the detection of all the electrons in coincidence.

We have studied Xe $4d^{-1}5p^{-1}$ core-valence double photoionization at 120eV photon energy. In a first step, two photoelectrons are emitted and followed by an Auger electron:

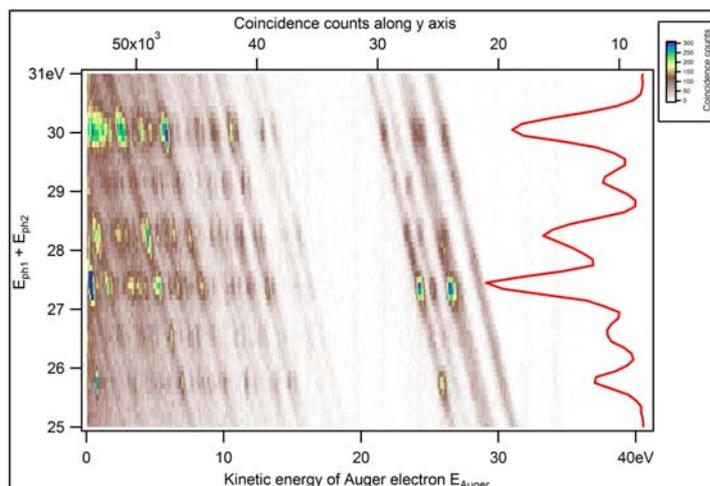
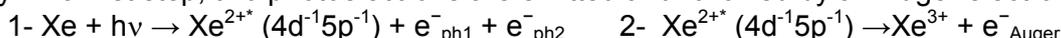


Figure 1: Two-dimensional coincidences map between two photoelectrons and the Auger electron. The sum of the two photoelectron energy is plotted in red.

The spectroscopy of the intermediate $\text{Xe}^{2+} 4d^{-1}5p^{-1}$ states is performed by detecting in coincidence two photoelectrons with the Auger electron (Fig. 1) and can be compared with results from MAIA experiment [1]. The Auger decay of each selected core-valence state is also obtained and are in good agreement with Multiconfiguration

Dirac–Fock calculations.

Other processes lead also to Xe^{3+} ions, as double Auger decay following 4d inner-shell ionization [4], but the coincidence measurements allow to filter those different channels.

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State-selected Ion-molecule Reactions with CERISES: The New TPEPICO Spectrometer Adapted to Species Produced in a Beam

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ABSTRACT

Probing the reactivity of $R^+ = CH_3^+, C_2H_5^+, C_2H^+, \dots$ ions is of great importance for the modeling of complex media such as planetary ionospheres (Titan, ...) or plasmas. The method of choice to investigate the effect of the parent ion excitation on its reactivity is the photoionisation of the neutral molecule with VUV photons and, for a pure state selection, the use of the TPEPICO technique.

However, as the radicals ($R^\bullet = CH_3^\bullet, C_2H_5^\bullet, C_2H^\bullet, \dots$) are not stable species, they have to be produced in situ. This has been done on the CERISES setup by adding a new molecular beam chamber enabling the production of the radicals and, subsequently, of their cations by photoionisation. These last two years, by varying the photon energy (without further state selection), we have been able to probe the reactivity of the methyl cation (CH_3^+) with the methane (CH_4) and other C_1 - C_4 hydrocarbons as a function of its excitation and collision energy.

To go further in the state-selection of these special ions, we have developed in 2016 a new threshold photoelectron detector adapted to the molecular beam configuration of CERISES. It has been successfully tested on the DESIRS beamline, during the last week programmed with the 8-bunch mode of operation of SOLEIL in October 2016. Its characterization with standard gases will be described as well as the production of methyl cations in the TPEPICO mode. We have reached the targeted energy resolution and have increased by a factor 3 the efficiency of photoelectron detection and by more than an order of magnitude the rejection of false coincidences compared to the standard source (without molecular beam).

This open to all users of CERISES, which is an experiment associated to SOLEIL, very new possibilities to study the reactivity of state-selected ions such as R^{+*} and also ionic clusters $(M)_n^{+*}$.

Acknowledgments: For technical help from H. Bauduin and Gilles Perilhous on the mechanical development of the new TPEPICO spectrometer and from J.-F. Gil (DESIRS) for the installation of CERISES at SOLEIL, and for financial support from the RTRA "Triangle de la Physique" (RADICAUX and NOSTADYNE projects), SOLEIL, the French Planetology Program (PNP) and the COST actions CM1401 ("Our Astrochemical History"), TD1308 ("ORIGINS") and CM1204 ("XLIC").

Infrared Spectroscopy of Methoxyphenols Involved as Atmospheric Secondary Organic Aerosol Precursors

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ABSTRACT

Methoxyphenols are emitted in the atmosphere from biomass burning and recent works have shown the potential role of these oxygenated aromatic species in the formation of secondary organic aerosols (SOA).¹ IR spectroscopic data that would enable their remote measurement in the atmosphere remain scarce in the literature.

The first part of the presentation will be dedicated to gas phase measurements of the fundamental vibrational bands of these semi-volatile compounds. Far-IR cross-sections of 4 methoxyphenols have been determined using the THz synchrotron radiation available at SOLEIL. Mid- and near-IR regions have also been investigated with a conventional Fourier transform IR setup and allowed to provide a set of vibrational cross-sections at room temperature. In addition, gas-phase cross sections of two nitroguaiacol isomers, two intermediate products involved in the formation of SOA have been measured in the mid- and near-IR with a heated multi-pass cell. Harmonic and anharmonic DFT calculations were carried out for all the studied compounds and allowed a full assignment of the recorded rovibrational bands.²

The second part of the presentation deals with ATR-FTIR measurements of pure methoxyphenols in condensed phase and IR absorption measurements on SOA produced in the LPCA atmospheric simulation chamber by OH oxidation of guaiacol and syringol, two methoxyphenol compounds contributing significantly to the production of SOA in the atmosphere.^{3,4} Vibrational fingerprints of nitromethoxyphenols are unambiguously observed and the influence of relative humidity on SOA has been tested using a specific hydration cell in the AILES beamline of SOLEIL.

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PARALLEL SESSION

Electronic & Magnetic Property of Matter, Surfaces and Interfaces

ECOLE POLYTECHNIQUE – BECQUEREL Auditorium

Chairpersons: Marie d'ANGELO and Antonio TEJEDA

- IT-08 Spin to charge conversion at room temperature using the α -Sn topological insulator
N. Reyren
- OC-29 Pump-probe diffraction experiment for studying displacive transitions
I. González Vallejo
- OC-30 Ultrafast electronic, spin and lattice separation in LaCoO_3
M. Izquierdo
- OC-31 Mott insulator-metal transition in Sr_2IrO_4
A. Louat
- IT-09 Interlayer coupling through a dimensionality-induced magnetic state
M. Viret
- OC-32 Strong resonances of quasi 1D structures at the Bi/InAs(100) interface
C. Richter
- OC-33 Calculation of XMCD at K-edge under pressure from first principles, application to iron hydride
N. Bouldi
- OC-34 Superconductivity, pseudogap, and stripe correlations in high-Tc cuprates
Z. Zhang
- OC-35 C_{60} thin films on Co(0001) : A structural study to understand magnetic properties
C. Fourmental
- OC-36 Investigation of organic/metal interface by X-ray photoelectron spectroscopy and scanning tunneling microscopy
Y. Tong

Spin to Charge Conversion at the α -Sn Topological Insulator Surface

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ABSTRACT

In recent years, “new phases of matter” have emerged from the interplay between SOC and low dimensionality, such as chiral spin textures and spin-polarized surface and interface states. These states can be exploited in spintronics devices where they open new possibilities [1]. Thin layers of tin in its alpha phase, α -Sn, display surface states typical of topological insulator with spin and momentum locking. This has been predicted in 2007 [2] and observed [3,4] five years later by ARPES, in particular at the SOLEIL Cassiopee beamline, where it was demonstrated not only a characteristic linear dispersion, but also the expected spin polarization (using SARPES) [4]. Such dispersion suggests the ability of these surface states to “convert” spin currents into charge currents and reciprocally through the so-called (inverse) Edelstein effect [1].

Using spin-pumping, we demonstrated the largest spin (J_s) to charge (J_c) current density conversion at the time, using samples grown and ARPES-characterized at the Cassiopee beamline, reaching $\lambda = J_c/J_s = 2.1$ nm [5]. (This quantity has a dimension, because the charge current propagates at a 2D surface while the spin current is 3D.) Despite these very encouraging results, the exploration of our α -Sn films was impinged by the large conductance of the InSb substrate used to stabilize the α phase through epitaxial strain. Moreover, the estimated spin-lifetime in these experiments is much lower than the one of free α -Sn surfaces, proportionally reducing the conversion efficiency. We hence try to solve both these issues by using an “artificial” substrate and to “encapsulate” the surface states below an insulating layer of MgO or Al_2O_3 . These recent efforts will be presented.

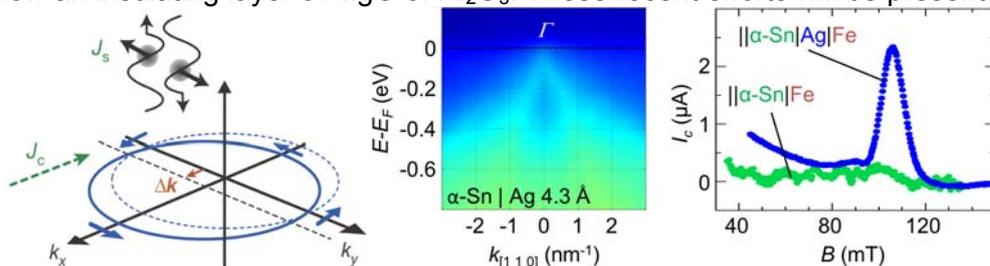


Fig. 1: At the surface of a topological insulator, the coupling between the spin and the momentum of the electrons allows spin-to-charge conversion as illustrated (left). With ARPES, we verify that the linear dispersion is preserved when a layer of Ag is deposited on top of α -Sn (center), unlike when we deposit Fe. As a consequence, we could observe spin-to-charge conversion in the first case and not in the latter one (right).

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Pump-probe Diffraction Experiment for Studying Displacive Transitions

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ABSTRACT

A15 structures have been intensively studied in the sixties because of their large superconducting transition temperature T_c . For example Nb_3Sn has had the highest T_c for a long time. However, Nb_3Sn is also known for displaying a displacive transition above the superconducting transition temperature. At $T=38K$ indeed, Nb_3Sn undergoes a cubic to tetragonal phase transition. This martensitic transition corresponds to a weak distortion of the cubic phase as well as to a dimerization of the Nb atoms along the Nb chains. This typical displacive transition is accompanied by a large and incomplete softening of acoustic phonons[1,2]. In the Labbé-Friedel model[3], the origin of the structural phase transition is based on the singularity of the density of states close to the Fermi energy.

In this context, we have performed a pump-probe experiment at the Cristal beamline by using x-ray diffraction at 8keV with a 70ps x-ray pulse width. After 35fs laser excitation in the low temperature phase, the Nb_3Sn sample reaches the high temperature phase too rapidly to be observed with our time resolution and then slowly relax toward the low temperature phase. This out-of-equilibrium behavior seems to display a continuous response as respect with the laser fluence. However, the very low relaxation rate measured during this experiment is still not understood. We will present the different results obtained at Cristal and propose different theoretical approaches taking into account the peculiar features of our compound.

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Ultrafast Electronic, Spin and Lattice Separation in LaCoO₃

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ABSTRACT

Understanding the origin of the spin transition in LaCoO₃ (LCO) is one of the longstanding aims in condensed matter physics. Besides its fundamental interest, a detailed description of this crossover will have a direct impact on the interpretation of the semiconductor-to-metal transition (SMT) and the properties of the high temperature metallic phase in this compound, which has shown to have important applications in environmental friendly energy production domains. So far, most of the understanding of the system has been achieved from static experiments as a function of the temperature and theoretical studies [1,2]. DFT++ calculations have allowed us to understand the important role of correlation-driven charge and spin fluctuations in the explanation of both the spin and the STM transition in LaCoO₃[3].

In this contribution, we report all-optical and optical-soft x-ray pump-probe experiments performed across the SMT of LCO with different time resolution. Picosecond studies have demonstrated the formation of a laser induced transient metallic state[4]. All-optical studies with femtosecond resolution have shown an ultrafast excitation of the system within 140 fs. Finally, spectroscopic studies with soft x-ray femtoslicing pulses have unraveled the properties of the transient metallic state, in which the electronic, spin and lattice degrees of freedom are excited on different time scales demonstrating the relevance of soft x-ray femtosecond sources to investigate correlated systems[5].

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Mott Insulator-metal Transition in Sr_2IrO_4

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ABSTRACT

Decreasing correlations are expected from 3d to 5d elements, because 5d orbitals are more extended than 3d orbitals. On the other hand, the spin-orbit coupling is strong for 5d elements and this could change this picture. Indeed, the compound Sr_2IrO_4 , with 5 electrons in the 5d shell, is insulating and it is considered as the archetype of Mott insulators induced by strong spin-orbit coupling¹. This layered compound is an ideal system where to explore metal-insulator transition induced by doping.

We have investigated with angle resolved photoemission at the CASSIOPEE beamline how this transition takes place in the case of Rh substitutions. The evolution of the resistivity towards the metallic state is presented in Fig. 1. Although Rh is isovalent to Ir, it is believed it induces an effective hole doping^{2,3}. With photoemission, we observe a shift of the Fermi level towards the highest occupied band with Rh doping, the appearance of hole pockets at X point (see Fermi Surface in Fig. 2 for 15% Rh doping), but the persistence of a residual “pseudogap” and absence of quasiparticles peaks. We will discuss the role of Rh in the transition and the nature of the induced metallic state.

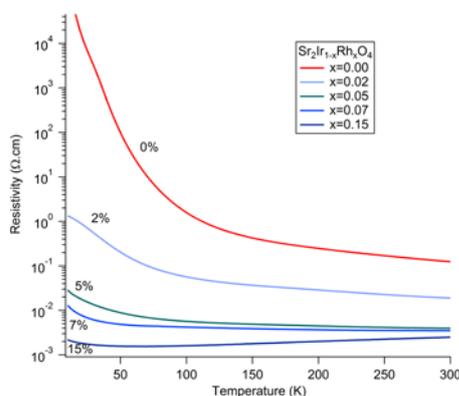


Fig. 1: Resistivity of $\text{Sr}_2(\text{Ir}_{1-x}\text{Rh}_x)\text{O}_4$ for $x=0.02$ to 0.15. Insulator-metal transition is visible at about 7% of Rh.

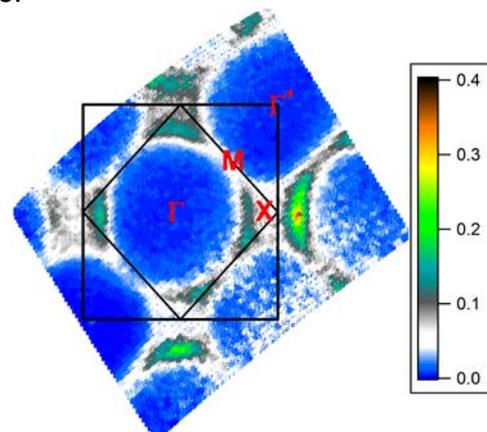


Fig. 2: Fermi surface of $\text{Sr}_2(\text{Ir}_{0.85}\text{Rh}_{0.15})\text{O}_4$. Square hole pockets are present around X points

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Interlayer Coupling through a Dimensionality-induced Magnetic State

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ABSTRACT

The recent discoveries of a number of fascinating unexpected phenomena at interfaces between different perovskite oxides have been received with tremendous enthusiasm, leading to the emergence of the field of oxide interface engineering [1]. One such phenomenon is the observation of exchange bias in superlattices composed of nominally paramagnetic metallic LaNiO₃ and semiconducting ferromagnetic LaMnO₃ ultrathin layers [2]. A shift of the magnetization loop is observed when samples are field-cooled below 20K. The effect is strongest for superlattices grown along the [111] pseudocubic direction, which maximizes the interactions between the Mn and Ni atoms at the interface. The presence of exchange bias reveals the existence of a strong interfacial coupling and implies the emergence of magnetism in the nominally paramagnetic LaNiO₃ layers. Moreover, as temperature is increased, the sign of the exchange bias is found to change to 'positive'. At even higher temperature, exchange bias disappears and is replaced by a state where inter-layer coupling interactions dominate. A precise resonant soft X-ray reflectivity study indicates that the (LNO)₇/(LMO)₇ multilayers are antiferromagnetically arranged, as clearly demonstrated by the presence of the first and second half-order Bragg using polarised X-rays. Hence, the magnetic interaction through 7 monolayers of LaNiO₃ is antiferromagnetic. The induced magnetism in LaNiO₃ and its interfaces will be discussed in the light of these measurements. We will show that the entire temperature behaviour can be explained considering that the (1/4,1/4,1/4) antiferromagnetic state present in insulating bulk nickelates is recovered in ultrathin LaNiO₃.

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Strong Resonances of Quasi 1D Structures at the Bi/InAs(100) Interface

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ABSTRACT

The InAs(100)(4x2)-c(8x2) reconstructed surface exhibits low dimensional self-organized structures. It was shown [1] that this reconstruction is formed by one-dimensional In-chains running along the [011] direction. These In-chains are separated by about 1.7 nm from each other and are regularly distributed over the whole surface. The region between the chains is occupied by two dimer rows, which are parallel to the In-chains. ARPES measurements reveal two-resonance surface states at normal emission appearing at 31 and 61 eV photon energy.

After deposition of bismuth on the InAs(100) surface Bi-atoms self-assemble into an ordered pattern of Bi nano-lines separated by 4.3 nm. One can distinguish the enhanced valence-band emission at 0.34 eV below the Fermi level (Fig a)) reported recently on the well-ordered Bi-nanoline surface, which arises from the (2x1)-Bi areas between the nanolines [2].

This surface resonance depends strongly on the direction of the electric field of the 31 eV photons and is visible for linear polarised light parallel to the indium lines i.e. perpendicular to the bismuth lines (Fig a)).

In Fig b) we observe the signature of a pseudo one-dimensional structure: the dispersion of the surface states is clearly limited to the direction parallel to the Bi-lines.

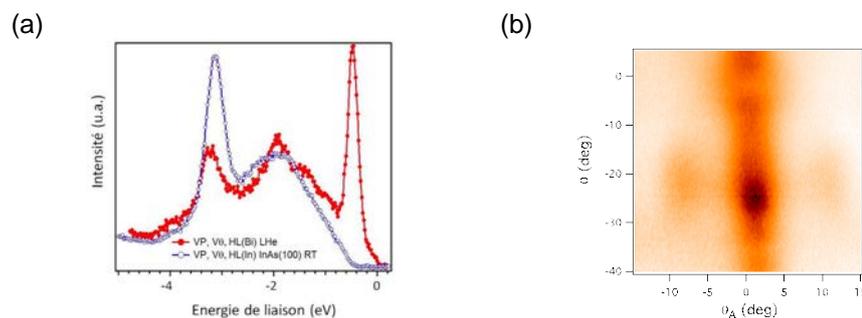


Fig : (a) Normal emission spectra ($h\nu=31$ eV) of a clean InAs(100)4x2 surface (blue) with In nanolines and in the presence of Bi nanolines (red); (b) Constant energy surface (binding energy 300 meV) showing the quasi-1D-States

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Calculation of XMCD at *K*-edge under Pressure from First Principles, Application to Iron Hydride

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ABSTRACT

In addition to their geophysical interest (iron and hydrogen are the main constituents of the Earth's core), the understanding of iron hydrides is essential for studying the behavior of hydrogen in transition metals. The absorption of hydrogen by metals or alloys is indeed a promising solution to address the crucial problem of storage of hydrogen, which will allow its use as fuel.¹

The iron hydride FeH can be synthesized by application of a 3.5 GPa pressure on Fe in a H₂ environment.² Hydrogen induces a structural change in iron and also a drastic change in its magnetic properties. The combination of X-ray Absorption Spectroscopy (XAS) with X-ray Magnetic Circular Dichroism (XMCD) is a very powerful technique to investigate this kind of change under pressure. XAS provides information on the local structure. XMCD, which is the difference for a magnetic material between the absorption of left and right circularly polarized X-rays, is a combined effect of magnetic ordering and spin-orbit coupling. It gives element-specific information on the magnetic properties of the sample. As XAS and XMCD are recorded simultaneously, it allows obtaining the structural and magnetic properties in the same condition, in particular at the exact same pressure which is valuable given the difficulties to know precisely and reproduce pressure conditions.

We will present the XAS and XMCD spectra at Fe *K*-edge of an iron foil under pressure in a H₂ environment that have been recorded on ODE beamline and which confirmed the existence of a transition around 3 GPa.

In order to help interpreting the experiment, the spectra have been calculated *ab initio* with a monoelectronic plane-waves code based on Density Functional Theory: the X Spectra package of Quantum Espresso. The idea is to compute the charge density in the presence of a core-hole and then compute the absorption cross section using Lanczos algorithm. The calculated XAS and XMCD spectra will be compared with experimental ones. We will also discuss in detail the way of introducing pressure in the calculation. Each term (most important multipole and relativistic contributions³) of the cross section will then be discussed in link with the density of states. This study will give a unique insight into the effect of hydrogen on the electronic and magnetic structure of iron.

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Superconductivity, Pseudogap, and Stripe Correlations in High- T_c Cuprates

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ABSTRACT

Underdoped La-214 cuprate, are known to shows charge-modulations in the "stripes" [1], form rather than in Charge-Density-Wave one. These stripes modulation are (quasi)-static close to hole doping of 1/8, where they suppress superconductivity. In contrast to this, the pseudo-gap phase of the other cuprate compounds recently revealed rather Charge-Density-Wave [2-4] type of charge modulation, that possibly also competes with superconductivity. In this context, to better understand how the stripe phase competes with superconductivity, we use Angle Resolved Photoemission Spectroscopy on CASSIOPEE beamline, to study the electronic band structure and gap in La-214 cuprates at 1/8 doping ($\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ ($x=0.12; y=0,0.4$)) and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x=0.12$)). A well-defined nodal quasi-particle peak is found to exist in the stripe-order state, and we study it as a function of temperature and doping, together with the gap and pseudo-gap.

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C₆₀ Thin Films on Co(0001): A Structural Study to Understand Magnetic Properties

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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 C₆₀ based spin-valve presenting a magneto-resistance at room temperature [Gobbi2011]. Moreover, it is crucial to understand how the interface structure affects magnetic properties of the device in order to improve them.

Surprisingly, the magnetic properties of thin Cobalt films can be drastically modified by the deposition of C₆₀ molecules. To determine the structure of the interface and its link with magnetism, we are studying the structure of a model sample of C₆₀ thin films on a Co(0001) single crystal by surface x-ray scattering at the SIXS beamline at SOLEIL synchrotron, and scanning tunneling microscopy at MPQ, two complementary techniques giving respectively reciprocal and real space information. Ab-initio calculations complete the panel of tools used for the investigations.

Firstly, we will see how the C₆₀ affects the magnetization of Cobalt thin films by modifying hysteresis cycles. Then, we will focus on C₆₀/Co(0001) monolayer structure, before and after annealing (Fig. 1), and show that we were able to evidence an irreversible structural transition in temperature while annealing. Finally, we will see that we are capable of growing a highly crystalline C₆₀ fcc crystal on Co(0001).

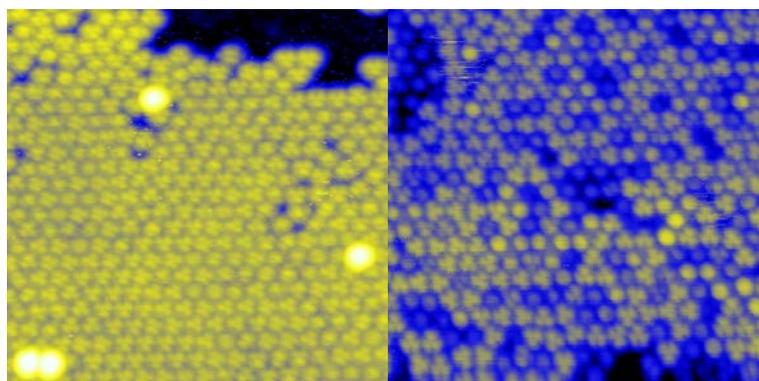


Figure 1: (20x20) nm² STM images at 2V of a C₆₀ ML on Co(0001) before (left image) and after annealing up to 300°C (right image). One can see that after annealing C₆₀ is organized in two levels. Thanks to GIXD measurements, we can conclude that it is due to the creation of Cobalt vacancies under some C₆₀ molecules.

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Investigation of Organic/Metal Interface by X-ray Photoelectron Spectroscopy and Scanning Tunneling Microscopy

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ABSTRACT

Molecules architecture on metal surfaces has been an important issue in exploration of nanodevices. Thereby, organic molecular films with large highly ordered configuration have attracted considerable interest as it provides a better insight into the intrinsic properties of the films themselves. In particular, the organic/metal interface properties have proven to be of vital importance in determining the chemical and physical properties of the up-growing films, and in defining the performance of the thin film device. Here, we discuss electronic and structural properties of NTCDA (1,4,5,8- naphthalence-tetracarboxylic dianhydrid) molecular films grown on Ag(110) single crystal surface. Using various techniques, we aimed to analyse the characteristics of the organic/metal interface. High-resolution and low temperature scanning tunneling microscopy (LT-STM) was utilized to obtain the detail of the two molecular domains predicted by low energy electron diffraction (LEED) experiment. In addition, we were able to visualize with high precision the molecular orbitals within the single molecule at the level of the naphthalene core. Photoemission including core level, UPS and NEXAFS spectra was used to understand the chemical properties at the interface. By combining UPS spectra and scanning tunneling spectroscopy (STS) data, we could determine the binding energies of both the HOMO feature and the LUMO partially-filled through a charge transfer process at the interface. On the other hand, the C K-edge near edge X-ray fine structure (NEXAFS) spectra confirm the strong interaction at the interface and by using angular dependence approach of the NEXAFS intensity we determined the exact orientation of the NTCDA molecules over the surface.

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PARALLEL SESSION

Matter & Material Properties: Structure, Organization, Characterization, Elaboration

ECOLE POLYTECHNIQUE – ARAGO Auditorium

Chairpersons: Frédéric DATCHI and Karine PROVOST

- IT-10 Contribution of Synchrotron Radiation studies to the understanding of the magneto-electric coupling in BaTiO₃ layered artificial multiferroic systems
A. Barbier
- OC-37 IR imaging of the Paris meteorite with an FPA detector for micro-tomography
Z. Dionnet
- OC-38 Tomographie-X ultra-rapide à haute pression et température
E. Boulard
- OC-39 The anomalous behavior of silicate glasses and liquids on densification: A combined microtomography and X-ray diffraction study at high pressure
A. Clark
- OC-40 Influence of structural changes on the magnetic properties of Y_{1-x}RxFe₂(H,D)_{4.2} compounds
V. Paul-Boncourt
- OC-41 Coupling powder diffraction, electron microscopy, solid-state NMR and GIPAW calculations: Structure and dynamics of inorganic fluorides
C. Martineau-Corcus
- OC-42 Relaxation mechanisms in a nanocrystalline gold thin film on a compliant substrate
P. Godard
- OC-43 Time-resolved X-ray diffraction in density-wave systems
S. Ravy
- OC-44 Structure and growth mechanism of single layer and multi-layer silicene
A. Curcella
- OC-45 Influence of the tetragonal structure on the electronic bands of CH₃NH₃PbI₃ hybrid organic-inorganic perovskites
M.I. Lee

Contribution of Synchrotron Radiation Studies to the Understanding of the Magneto-electric Coupling in BaTiO₃ Layered Artificial Multiferroic Systems

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ABSTRACT

Multiferroic materials are of high technological interest because they may become key components of genuine devices in fields as important as spintronics, sensors, memory cells etc. Magnetolectric coupling attracts especially considerable research efforts. Unfortunately intrinsic single phase multiferroic materials are very seldom. Associating, at the nanoscale, ferromagnetic and ferroelectric materials is a seductive route. To tackle this issue combined structural, ferroelectric and magnetic measurements are necessary.

In the present work we chose to explore several possibilities resulting from the combination of single crystalline atomic oxygen assisted molecular beam epitaxy grown thin films of the prototypical ferroelectric BaTiO₃ (that exhibits reasonable electric polarization while being cheap and environment friendly) with ferromagnets. In a first approach we considered doping obtained by co-deposition with Fe and Ni. However within these structures the magnetic ions couple mostly within antiferromagnetic long range orders [1].

In a second approach we considered full oxide structures built with additional ferrimagnetic CoFe₂O₄ spinel layers, [2,3] which are highly magnetostrictive. Both ferroelectric and ferromagnetic ordering temperatures are well above room temperature and the stack is fully oxidized promising superior chemical stability. We elaborated samples on conducting substrates allowing electrical polarization of the fully single crystalline and epitaxial stack. For local measurements we choose to electrically polarize the ferroelectric bottom layer of the layered sample using Piezo-Force Microscopy (PFM).

We combined laboratory tools with state of the art synchrotron radiation based techniques including X-ray diffraction (DiffAbs and SIXS beamlines), magnetic dichroism (DEIMOS), and spectromicroscopy (HERMES and I06-DIAMOND) to describe the artificial multiferroic structures for structural, chemical, magnetic and ferroelectric behaviors. We could evidence a complex interplay between the structure, polarization or magnetic state, strain relaxation and the long range orderings.

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IR Imaging of the Paris Meteorite with an FPA Detector for Micro-tomography

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ABSTRACT

Heterogeneity of the astrophysics material at high resolution

Primitive extraterrestrial materials (meteorites, IDPs) are characterized by a large mineralogical and compositional heterogeneity at different scales (from nm to mm) [1], which witnesses the complexity of the pre-accretional (solar nebula) and post-accretional (parent bodies) processes [2]. This heterogeneity has been observed by different techniques such as micro infrared (IR) spectroscopy mapping but with a limited resolution ($> 5 \mu\text{m}$). IR spectroscopy is a powerful tool as it is (a) totally non-destructive (b) comparable to astronomical observations of primitive Solar System small bodies (asteroids, comets, TNOs) [3] and ISM dust [5]. With the development of a new detector (Focal Plan Array (FPA)), IR mapping with high spatial resolution and IR tomography is now possible. Here, we report the results of high-resolution Fourier Transform IR spectral imaging experiments at micron scale using FPA and synchrotron radiation of the Paris meteorite (CM chondrite [4]). The FTIR microanalyses were performed in the SMIS beamline with a FPA detector and a globar source. The first preparation was obtained by crushing the meteorite sample between diamond windows. We measure the spatial distribution of chemical/mineralogical components (organic materials, anhydrous silicates, hydrated silicates, carbonates) of the Paris meteorite and the correlation between the organic and silicate phases down to a scale of $\sim 1 \mu\text{m}$. Mapping using FPA detectors is powerful as it allows a high spatial resolution in a very limited acquisition time (less than 20 min for a grain of $50 \times 40 \mu\text{m}$ vs more than 200 min with a "classical" mapping).

IR Micro-tomography

A second grain (size $\sim 20 \mu\text{m}$) of the Paris meteorite was prepared using a new method by welding it on a needle using a Focused Ion Beam (FIB) microscope. The main advantage of this preparation is to keep the 3D structure of the sample, and to make the grain available for FTIR micro-tomography [6, 7]. We have performed IR micro-tomography on our sample and reconstructed the 3D distribution of the components. These data have been coupled with X-rays micro-tomography performed at the PSYCHE beamline on the same sample, providing qualitative information about porosity and structure of the grain. We compare our results with IR micro-tomography of the Murchison meteorite [8].

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Tomographie-X Ultra-rapide à Haute Pression et Température

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ABSTRACT

L'imagerie par rayon-X a trouvée de nombreuses applications pour l'étude des propriétés physiques des matériaux sous haute pression et température et suscite de nombreux développements. La radiographie (imagerie 2D) à haute résolution et haute vitesse, par exemple, permet désormais de pouvoir mesurer des viscosités de l'ordre de 10^{-2} Pas de matériaux fondus à haute pression [e.g. 1]. La tomographie X basée sur rayonnement synchrotron a permis d'étendre l'imagerie à la 3D afin de visualiser la texture complète de l'échantillon. Plus récemment, de nombreuses méthodes de tomographie X ont été développée afin d'étudier des échantillons sous haute pression et température, c'est le cas par exemple de la micro-tomographie au travers de la RoToPEC [2] ou de la nano-tomographie au travers de cellules à enclumes de diamant (CED) [e.g. 3]. Nous présenterons ici une nouvelle méthode de tomographie X ultra-rapide au sein d'une cellule Paris - Edimbourg 4 colonnes ainsi que les premiers résultats sur la fusion de silicate dans une matrice solide de silicates obtenus pour des vitesses d'acquisition de 10 secondes à haute pression et température. En utilisant un plateau tournant doté d'une grande précision de mouvement ainsi que d'une grande vitesse de rotation, le temps d'acquisition d'un scan nécessaire pour une reconstruction 3D a pu être réduit à seulement quelques secondes (contre ~ 20 min en RoToPEC et 2h en CED). Cette méthode de tomographie ultra-rapide, complémentaire aux méthodes pré-existantes, offre de nouvelles possibilités dans les domaines des sciences des matériaux et sciences de la Terre notamment lorsque le temps d'acquisition est critique.

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The Anomalous Behavior of Silicate Glasses and Liquids on Densification: A Combined Microtomography and X-ray Diffraction Study at High Pressure

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ABSTRACT

Properties of liquid silicates are important for many geophysical phenomenon, from the formation of a magma ocean early in Earth's history to liquids trapped in the mantle today. The glassy state is commonly used as an analog for the high-pressure extrapolation of liquid properties. However, a universal densification mechanism for silicate glasses and liquids remains unclear. In this project, we study silicate liquids and glasses along the MgO-SiO₂ binary at high pressures and temperatures using a combination of 3D *in situ* tomography with *in situ* X-ray diffraction on the Psiché beamline at Soleil Synchrotron to obtain density and structural properties, respectively, of the liquid and glassy states. We use these results to investigate the role of network flexibility and polyamorphism in the high-pressure behavior of silicate glasses and liquids. These data are fundamentally important in developing an accurate equation of state for amorphous silicates at modest pressure (<15 GPa).

Correlations between Structural and Magnetic Properties of $Y_{1-x}Gd_xFe_2(H,D)_{4.2}$ Compounds

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ABSTRACT

Original structural and magnetic properties have been found for $YFe_2(H,D)_{4.2}$ compounds showing a giant (H,D) isotope effect. $YFe_2(H,D)_{4.2}$ compounds are cubic above 360K. Upon cooling they undergo a transition from cubic (Fd-3m) to rhombohedral (R-3m) and then monoclinic (Pc) structures due to H(D) ordering in preferential interstitial tetrahedral sites [1]. The monoclinic distortion favors a ferromagnetic to antiferromagnetic transition with an itinerant metamagnetic behavior at T_{F-AF} . T_{F-AF} is higher for the hydride (131 K) than for the deuteride (84 K) due to its larger cell volume (+0.8 %) [2]. Partial substitution of Y by Gd influences both the order-disorder and magnetic transitions, with a significantly large isotope effect [3, 4]. $Y_{0.9}Gd_{0.1}Fe_2D_{4.2}$ shows only one sharp magnetic transition at $T_{F-AF} = 102$ K whereas $Y_{0.9}Gd_{0.1}Fe_2H_{4.2}$ displays three magnetic transitions at 155, 182 and 270 K.

Powder diffraction experiments have been performed on $Y_{0.9}Gd_{0.1}Fe_2(H,D)_{4.2}$ compounds, using the CRISTAL beam line of SOLEIL, to solve the structural changes observed versus temperature and understand the origin of these different magnetic properties.

$Y_{0.9}Gd_{0.1}Fe_2D_{4.2}$ patterns were refined with one single monoclinic structure upon cooling below 300 K. This structural behavior is similar to that observed for $YFe_2D_{4.2}$ and can explain the existence of the magnetic transition at 102 K. The higher transition temperature ($T_{F-AF} = 102$ K versus 84 K) can be related to the larger cell volume induced by Gd for Y substitution.

The SR-XRD patterns of $Y_{0.9}Gd_{0.1}Fe_2H_{4.2}$ have been measured upon cooling from 300 K down to 120 K and heating from 250 K to 310 K. Between 310 and 290 K, the powder diffraction patterns were refined with a mixture of two monoclinic phases with slightly different cell parameters. Between 290 and 270 K, a cubic phase appears and one of the monoclinic phase grows at the expense of the other. These structural transitions correspond to the sharp magnetic transition observed at 270 K. From 270 to 120 K, the weight percentage of the cubic phase remains constant, while those of the monoclinic phases vary. Below 200 K a cell volume increase is observed corresponding to the magnetic transitions observed around 155 and 182 K. In addition, upon cooling a contraction of a , c and β monoclinic cell parameters and an expansion of the monoclinic b parameters were observed for both monoclinic phases, corresponding to an increase of the monoclinic distortion. Further studies will be performed to observe the influence of Gd content and (H, D) concentration on such strong correlation between structural and magnetic properties.

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Coupling Powder Diffraction, Electron Microscopy, Solid-state NMR and GIPAW Calculations: Structure and Dynamics of Inorganic Fluorides

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ABSTRACT

The combination of complementary physical measurements such as powder diffraction, electron microscopy or solid-state nuclear magnetic resonance (NMR) spectroscopy with computation modelling of structure or NMR parameters is a strategy that is receiving growing interest, since it allows solving the structure of compounds for which diffraction only fails or leads to incomplete solution. This is particularly useful for powdered samples in which several nuclei can be observed by NMR.

Here we illustrate the whole process step-by-step with a case study example of a barium-aluminum fluoride. Powder synchrotron X-ray and electron diffraction data are first used to find an initial structural model. However, the localization of the fluoride atoms is impeded by the large electron density of the surrounding barium atoms, and the confrontation of the GIPAW calculated ¹⁹F and ²⁷Al NMR parameters with the experimental NMR data indicate some imperfections in the structural model. Additional contrast is therefore searched from neutron diffraction data. Refined model is obtained, for which the GIPAW calculated NMR parameters are in better agreement with the experimental data. Finally, the dynamics of the fluorine sub-lattice is described at the atomic level by variable temperature measurements and dipolar-based NMR experiments, used as filter for the rigid framework. This combined strategy, generalizable to numerous materials, offers a description of the structure with a much higher degree of details than what would have been achieved using these techniques individually.

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Relaxation Mechanisms in a Nanocrystalline Gold Thin Film on a Compliant Substrate

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ABSTRACT

This presentation will be focused on some of our last results obtained thanks to the unique testing machine available at the DiffAbs beamline. Thin films are deposited on compliant substrates (Kapton® in our case) which are biaxially loaded with a controlled force ratio. The elastic deformation is monitored in-situ. Several Bragg reflections are observed simultaneously with a two-dimensional detector. Moreover, the macroscopic strain ϵ is precisely measured thanks to an optical camera and a digital image correlation analysis. Knowing the macroscopic strain and the elastic strain allows to deduce the plastic deformation occurring in the metallic film.

We work in particular on metallic thin films deposited on compliant substrates. These composites find useful applications in flexible electronic circuits, biocaptors, artificial muscles or skin, etc.

We will concentrate on relaxation experiments. A 500 nm thick nanocrystalline gold thin film was equibiaxially stretched. Rather than doing a monotonous tensile test, we applied strain jumps and let the sample relax for 500 seconds. We observed that after a strain jump, the macroscopic strain in the polymeric substrate-metallic thin films remains constant. More surprisingly, the elastic strain in the film decreases. That is, a part of the elastic strain is reduced through plastic events. Models exist that characterize so called activation volumes thanks to the relaxation amplitude and rate. These activation volumes are interesting in that they are signatures of the plastic mechanisms: atomic diffusion, dislocation nucleation, dislocation interactions etc. We correlate for the first time the evolution of the activation volumes to the change of Bragg peaks shape. It is observed that the evolution of the coherent domain size is greatly dependent on the crystalline orientation: the isotropic texture component (mainly small grains at the substrate-film interface) shows a continuously increasing strain heterogeneities whereas the main texture component (columnar grains, 50 to 100 nm in diameter, with their (111) planes parallel to the specimen surface) present a change in plastic mechanism. The data gathered lead to the following scenario: there is a stress-assisted annealing at the very beginning of the test, then from $\epsilon \sim 0.3\%$ dislocations are continuously emitted and the density of point defects decreases, and starting from $\epsilon \sim 1.2\%$ the density of mobile dislocations decreases.

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Time-resolved X-ray Diffraction in Density-wave Systems

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S.O. Mariager^e, J.A. Johnson^e, S. Grübel^e, A. Lübcke^e, L. Huber^e,
M. Kubli^e, M. Savoini^e, V. Esposito^e, G. Ingold^e, P. Beaud^e,
S.L. Johnson^c and S. Ravy^b

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ABSTRACT

Spin- (SDW) and Charge-density waves (CDW) systems are ubiquitous states in solid state physics. They both correspond to a modulation of the spin- or the charge-density, with twice the Fermi wave vector of the electron gas. Both states are gapped, which make them sensitive to impulsive absorption of laser infrared pulses. Interestingly enough, CDW are generally coupled to the lattice, which make them easy to observe by X-ray diffraction.

In this work, we compare the dynamical behavior of CDW after an infrared laser pulse in three different DW systems: Chromium¹, $K_{0.3}MoO_3$ (so-called blue bronze)², and 1T-TaS₂^{3,4}. In all three cases, the CDW is strongly depressed after the pulse in an ultrafast way, which could lead to a melting of the state, and it recovers with different mechanisms which depend on the compounds.

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Structure and Growth Mechanism of Single Layer and Multi-layer Silicene

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ABSTRACT

The last years have seen a growing interest in the research and characterization of 2D materials, due to their interesting and exotic properties. In particular, for free-standing silicene, the 2D allotrope of silicon, DFT simulations predicts the existence of Dirac cones in the electronic structure. This makes silicene an appealing candidate for microelectronic devices. Experimentally, 2D Si arrangements have been reported on several substrates, among which Ag(111) is by far the most thoroughly studied.

Silver was thought to weakly interact with the Si sheet; however joint experimental studies and DFT simulations have shown a non-negligible interaction [1]. The various structures observed are predicted to be buckled honeycomb lattices. The electronic band structures computed are however far from the one of free-standing silicene and depend on the precise atomic positions. In order to decouple the Si layer from the Ag substrate, researchers have tried to synthesize multi-layer silicene. The structure of the films obtained is however highly controversial. Whereas some claim that it corresponds to silicite, a graphite analogue for Si, others affirm that it corresponds to diamond-like Si covered with Ag.

Combining grazing incidence X-ray diffraction (GIXD) and density functional theory (DFT) simulations we managed to give an accurate structure model of the (4x4) reconstruction of silicene on Ag(111), putting in evidence the role of the substrate relaxation[3]. The silicene layer shows a buckling of 0.76 Å and the relaxation of the substrate results in a vertical displacement of the Ag atoms at the interface layer of about 0.25 Å. The relaxation decreases exponentially in the layers deeper beneath the surface.

Regarding the synthesis of multi-layer silicene, we performed real-time GIXD during Si evaporation. We clearly evidence the formation of diamond-like silicon, with a large density of stacking faults. Comparing the experimental structure factors with the theoretical ones obtained from models known in the literature, we conclude that the surface is terminated with the $(\sqrt{3}\times\sqrt{3})$ Ag/Si(111) reconstruction, which shows the surfactant behavior of Ag atoms in the growth of Si/Ag(111). At once, our data rules out also the others Ag-free models previously proposed.

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Influence of the Tetragonal Structure on the Electronic Bands of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Hybrid Organic-inorganic Perovskite

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ABSTRACT

Hybrid organic-inorganic halide perovskites have become a promising material for photovoltaics due to their high performance of energy conversion efficiencies and their low-temperature and low-cost fabrication in solution^{1,2,3}. The most outstanding performance, which has exceeded to 22%⁴, is contributed by methylammonium lead halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$, MAPbI_3 , or MAPI). A requirement to further improve the performances is the better understanding of the electronic band structure, which has remained experimentally elusive until now. Also, the impact of the structural phase transitions on the band structure in the operation temperature range of solar cells must be elucidated. We have studied the structural transitions in MAPI as a function of the temperature on CRISTAL beam line. Our experimental results allowed us to retrieve the atomic structure of both tetragonal and orthorhombic phases of MAPI . This atomic structure was then contrasted with the first experimental determination of the band structure of MAPI with k resolution measured at CASSIOPEE beam line. Our results of ARPES show that the electronic periodicity in the tetragonal phase of MAPI (below 50°C) corresponds to that of the high temperature cubic phase. This will lead to the explicitness of the insensitivity of solar cells in the usual range of operating temperatures from -20°C to 45°C despite the cubic tetragonal structural transition.

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TECHNICAL WORKSHOPS

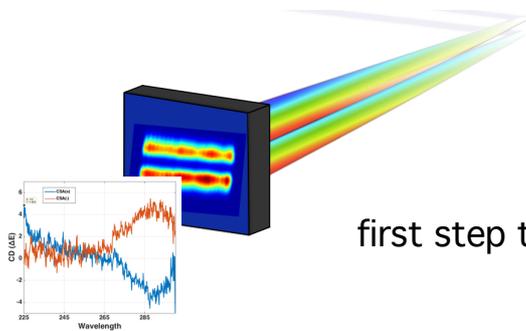
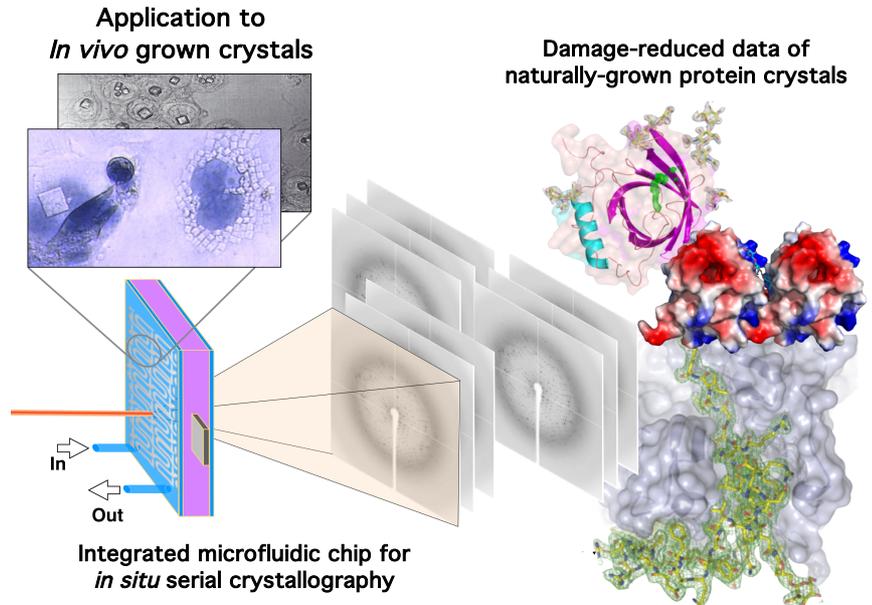
Actual and future developments at SOLEIL on beam lines dedicated to ...

biology

Four short presentations will be given by SOLEIL scientists,
followed by a discussion on long term perspectives and users' expectations

- Leo Chavas (PX1):
Serial crystallography at SOLEIL

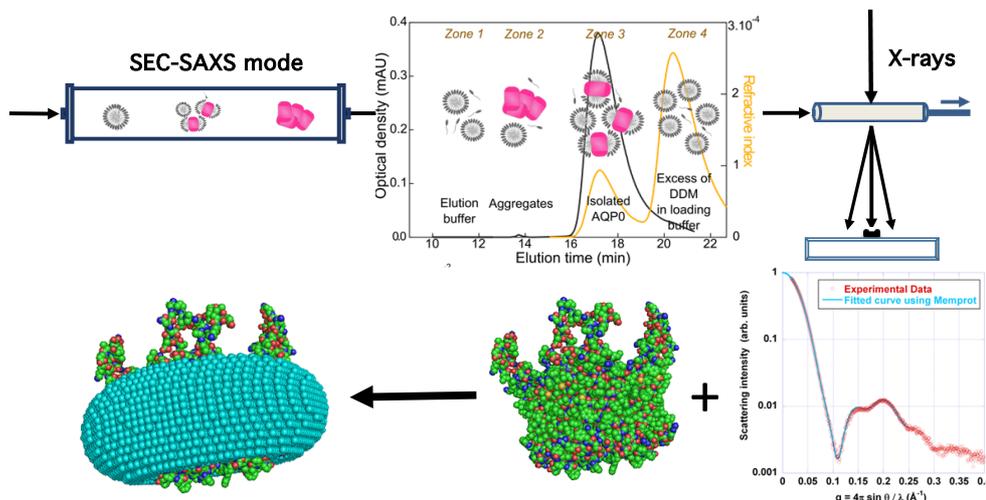
- Benedikt Lassalle (LUCIA):
Microfluidics at SOLEIL:
a few achievements and many
projects to come



- François Auvray (DISCO):
Dispersive SRCD,
first step to temporal and spectral combination

- Javier Perez (SWING): SAXS for Biology at SWING beamline:
from current developments to long-term perspectives

Detergent corona modeling for further analysis of MPs interactions with related partners



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Beamlines and reactivity measurements: on-going and future measurements

Three talks will precede a round table :

« *Probing in situ the reactivity of advanced nanomaterials:
from solid formation mechanisms to catalysis* »

David Portehault (GALAXIES)

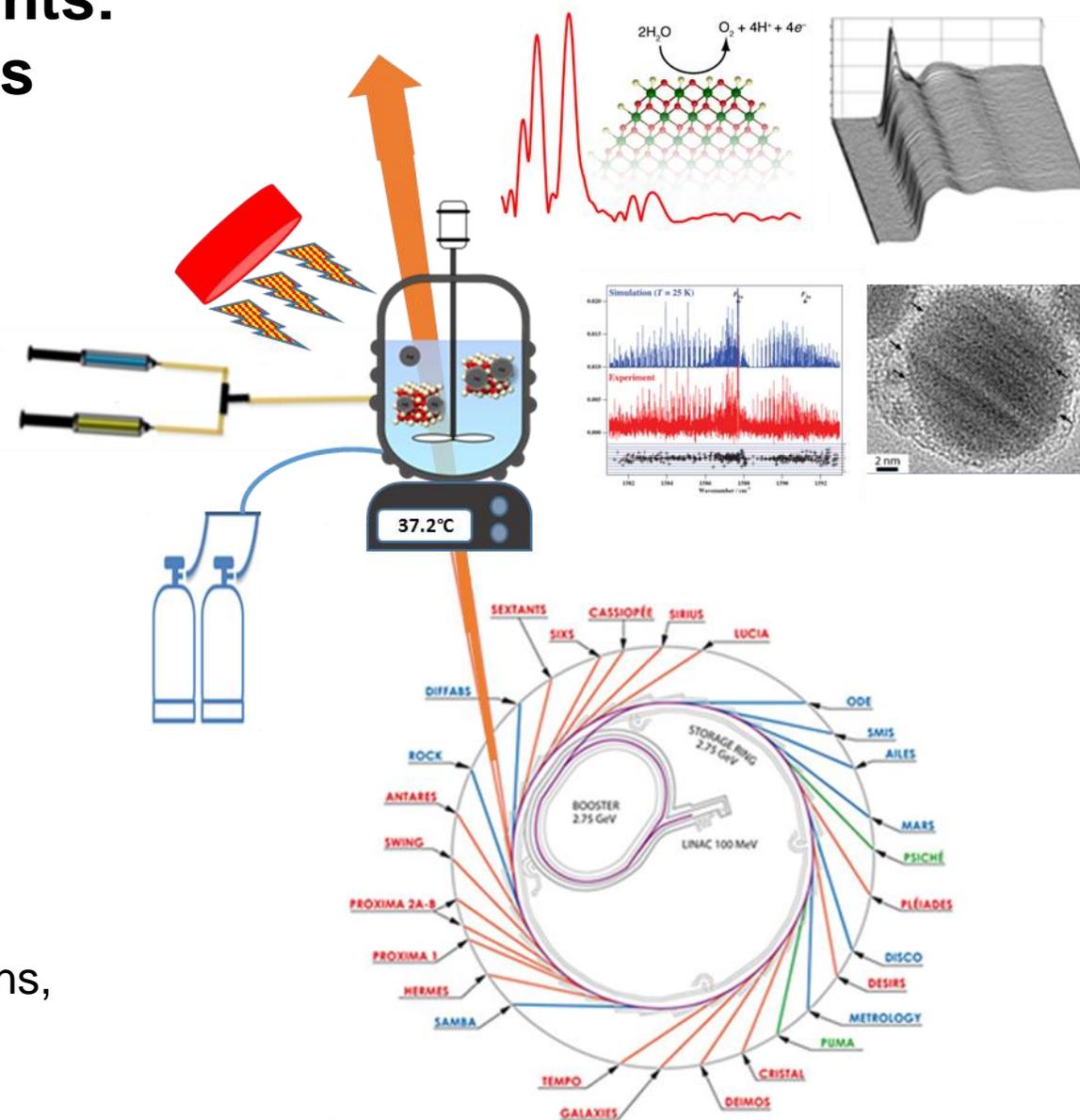
« *Near Ambient Pressure Core Level Photoemission* »

François Rochet (UPMC/TEMPO)

« *Operando catalysis studies
by surface sensitive x-ray scattering techniques* »

Alina Vlad (SIXS)

Please come to this workshop and ask your questions,
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Probing *in situ* the Reactivity of Advanced Nanomaterials: From Solid Formation Mechanisms to Catalysis

D. Portehault

Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris (CMCP), 11 place Marcelin Berthelot, F-75005, Paris, France

ABSTRACT

“Nanomaterials design” is a wide domain that encompasses synthesis, processing, and use of nanomaterials to address various application fields. In the specific case of nanoparticles, if the formation mechanisms in syntheses and the particles evolution in batteries or in catalysis are well known for relatively simple compositions, such as single metal oxides, they are mostly unreported for nanoparticles of more complex compositions and crystal structures. Acquiring this knowledge is nonetheless mandatory for further understanding and development of new materials and exploration of new application fields.

In this presentation, we will show how synchrotron radiation-based spectroscopies enable to address the different facets of nanoparticles design, from the formation mechanisms, to the evolution of the materials under operation.

First, synthesis processes will be addressed by taking the example of the precipitation of vanadium oxyhydroxide nanoparticles in water by “Chimie douce”. X-ray absorption performed on the SAMBA beamline of SOLEIL enables to decipher reaction mechanisms at the origin of polymorphism control.¹

Second, the focus will shift to metal-boron alloys²⁻⁴ catalytically active for the transformation of carbon dioxide into methane, an important industrial reaction, also relevant for environment preservation. Near-Ambient Pressure X-ray photoelectron spectroscopy performed on the TEMPO beamline has been coupled with state-of-the-art environmental transmission electron microscopy to unravel the true nature of the catalytically active species, thus leading to a shift in paradigm in the field.⁵

Finally, we will present preliminary data recorded on the GALAXIES beamline demonstrating the suitability of X-ray absorption to address the fate of metal-heteroelement alloys in electrocatalytic processes related to energy harnessing.

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POSTERS SESSION

List of Student Posters

- PO-BH-01** Analysis of Dystrophin Fragments 3D Structure in the Presence of Isotropic Bicelles
R. Dos Santos Morais
- PO-BH-02** Suppressor of Fused, a Hedgehog Signalling Protein, Presents a Zn Binding Property and Different Oligomerization States
S. Makamé
- PO-BH-03** Application of Chemical Multimodal and Multiscale Imaging to the Gd-based MRI Contrast Agents Localization in Deep Cerebellar Nuclei using X-ray Fluorescence in the Nanoscopium Beamline
M. Rasschaert
- PO-CP-04** Study of Keto-enol Tautomerism in Acetylacetone, in Gas Phase and in Solvent
B. Casier
- PO-CP-05** Study of Amorphous - Crystalline Phase Transition in Phase Change Materials
M. Gallard
- PO-DM-06** On the Use of Difference Bands for Modelling SF₆ Absorption in the 10µm Atmospheric Window
M. Faye
- PO-DM-07** Analysis of the ($\sqrt{3}/\sqrt{7}/\sqrt{9}$) bending triad of the quasi-spherical top molecule SO₂F₂
F. Hmida
- PO-DM-08** Evolutionary Algorithm-based Analysis of the Rovibrational SCl₂ Stretching Bands of Thionyle Chloride
A. Roucou
- PO-EM-09** Resonant inelastic X-ray Scattering Study of Magnetic Excitations in the High Temperature Superconducting Parent Compound Ca₂CuO₂Cl₂
B.W. Lebert
- PO-MM-10** Incorporation of Plasmonic Gold Nanoparticles Organized in Ordered Copolymer Films
F. Aubrit
- PO-MM-11** Investigation of Neutral Excitations in the Topological Magnon Insulator Lu₂V₂O₇
J.T. Feng
- PO-MM-12** Electrochemistry of Resistivity Changes in TaN/TiTe/Al₂O₃/Ta Conducting Bridge Random Access Memories
M. Kazar Mendes
- PO-MM-13** Dynamics of Magneto-structural Phase Transitions in MnAs/GaAs(001) Probed by Time-resolved X-ray Diffraction
L. Lounis
- PO-MM-14** Increasing the Magnetic Anisotropy through Onion-like Magnetic Nanoparticles
K. Sartori
- PO-MM-15** Application of X-ray Standing Waves for the Characterization of Chemical Processes and Interfacial Diffusion in Pd/Y based Multilayers using HAXPES
M-Y. Wu

Analysis of Dystrophin Fragments 3D Structure in the Presence of Isotropic Bicelles

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ABSTRACT

The protection of cell membrane against shearing stresses is ensured by cytoskeletal proteins. Among them, dystrophin¹ (Fig. 1) plays a key-role in muscle and its absence leads to the severe Duchenne Muscular Dystrophy (DMD), whereas its deficiency causes heterogeneous Becker Muscular Dystrophy (BMD). Exhaustive knowledge of dystrophin membrane interaction is needed to help for gene therapy strategies devoted to DMD and BMD. Dystrophin is a large (427 kDa), monomeric, amphipathic, and fibrous protein, whose structural analysis is not accessible by NMR and X-ray crystallography due to its size and its flexibility. Nevertheless, its three-dimensional structure is being elucidated through the combined use of SAXS and molecular modeling². Previous work of J.F. Hubert's team highlighted that the interfacial properties of dystrophin are modulated according to the region of the protein involved, the nature of lipids, as well as the membrane curvature, that play key-roles in the physiology of the muscle cell^{3, 4, 5}. To understand what might be the role of these interactions in vivo, we aim to determine the structure and the interaction mode of dystrophin fragments in the presence of the bicelle membrane mimic. To carry out this project, SAXS and SANS data are coupled to molecular modeling (Fig. 2), in order to propose suitable all-atom models of dystrophin fragments bound to membrane lipids.

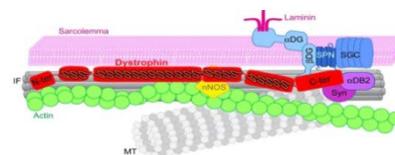


Fig 1: Schematic illustration of dystrophin (in red) interactions with its identified partners.

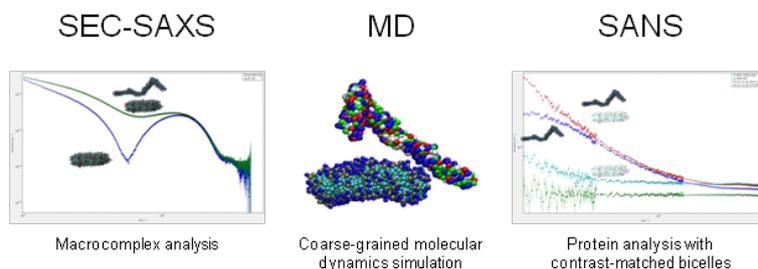


Fig 2: Graphical overview of the strategy employed. *Left:* SEC-SAXS intensity measured (SWING, SOLEIL) for bicelles with (green) or without (blue) R11-15 dystrophin fragment. *Middle:* R11-15/bicelle coarse-grained molecular dynamics simulation. *Right:* SANS intensity measured (D22, ILL) for buffer (green), contrast-matched deuterated bicelles (cyan), R11-15 dystrophin fragment with (red) or without contrast-matched

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Suppressor of Fused, a Hedgehog Signalling Protein, Presents a Zn Binding Property and Different Oligomerization States

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ABSTRACT

The Hedgehog (HH) signalling pathway was discovered during the 1980's. Since then, this pathway has been described to be involved in the development of many metazoans. The HH pathway is very conserved and its disruption causes many human diseases as holopresencephaly and some mutations of proteins in this pathway cause cancers. The HH pathway activation leads to the expression of some genes *via* the activation of its transcription factor, Cubitus interruptus (CI). On the other hand, when the pathway is switched off, CI is phosphorylated, partly degraded into a shorter, repressing form and inhibited by another protein, Suppressor of fused (SUFU). Recently, the structure of human and drosophila SUFU has been published in the PDB data bank. We performed solution studies to further characterise SUFU.

In fact, after expressing and purifying dSUFU, hSUFU and zSUFU, I have conducted ICP-AES, SAXS, CD and SEC-MALS experiments. The data obtained reveal that SUFU has a Zn binding property. The analysis of its amino acid sequence reveals a conserved sequence H₇₁WH₇₃Y that may be associated with cation chelation. Indeed the mutation of the histidine 71 in dSUFU reveals a decrease in Zn binding. Furthermore, SAXS data obtained on all three proteins show that hSUFU and zSUFU present different oligomerization states than dSUFU in solution. This information was validated by SEC-MALS. In addition, CD data confirm that these proteins belong to the same family as they present similar secondary structure component after BeStSel estimation.

As the mutation of some residues in the Nterm of hSUFU is involved in some cancers and the mutation of the two histidines limits the stabilization of dSUFU, the analysis of the experiment data obtain at SOLEIL may leads to new insights regarding the structure of SUFU proteins.

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Application of Chemical Multimodal and Multiscale Imaging to the Gd-based MRI Contrast Agents Localization in Deep Cerebellar Nuclei using X-ray Fluorescence in the Nanoscopium Beamline

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ABSTRACT

Gd³⁺ is widely used for MRI examinations because of its paramagnetic properties. Nevertheless, since this ion is toxic its utilization as contrast agent in clinic requires its chelation by a ligand. Two major types of ligands are on the market to build Gadolinium Contrast Agents (GdCAs): linear (L-GdCAs) and macrocyclic (M-GdCAs). Marketed for more than 30 years, they were assumed to have a very good tolerance, and to be completely eliminated in a few hours after administration by the urinary tract. However, a recent clinical study (Kanda et al, 2015) found a T1 enhancement in some brain structures, increasing with the number of GdCA injections. Numerous studies followed on this topic, proofing that this phenomenon occurs only with L-GdCAs, and that some gadolinium is indeed trapped in the central neural system, inducing the T1 enhancement. This is in coherence with the fact that M-GdCAs are thermodynamically more stable, and is therefore less likely to dechelate *in vivo*.

Several key-questions are therefore pending on this Gd brain uptake topic: how does it cross the healthy blood brain barrier? What are the neuro-toxicological consequences? In which specific structures is Gd stored, and why? In what form is Gd stored (chelated or free)? To answer these last two questions, we performed X-Ray Fluorescence (XRF) studies on the Nanoscopium beamline (at 9 keV) of the Synchrotron SOLEIL in correlation with analytical TEM studies. This aims to, in define areas of interests, to characterize the cellular and subcellular elements at a (sub-)micrometer scale. Rats received 20 intravenous injections of an L-GdCA, gadodiamide (Omniscan), over 5 weeks. An MRI examination (4.7 T) confirmed a T1 enhancement in a cerebellar structure namely the deep cerebellar nuclei (DCN), caused by a local Gd uptake. This area was dissected, embedded in epon and prepared to perform both analytical transmission electron microscopy by EELS (energy electron loss spectroscopy) and X Ray Fluorescence (XRF) examinations. The EELS-TEM analysis of a 50nm thick sample did not allow detecting the presence of electron dense spots containing Gd. This is probably because of the low local concentration of Gd. Therefore, the study by XRF was required to detect low Gd concentrations. The high sensitivity of this approach revealed the presence of Gd in all the scanned area of a 500µm thick DCN sample, and demonstrated its concentration in some specific regions denoted as regions of interest (ROIs). In addition, XRF allowed us to study the potential co-localization or exclusion of Gd with others elements, such as Fe, Cu and P, at about 500nm spatial resolution. This resolution is enough to perform further characterization of the ROIs and allows performing correlative multimodal imaging using focused ion beam scanning electron microscopy (FIB-SEM) which provides high ultrastructural information. In conclusion, combination of MRI, analytical TEM, and FIB-SEM whit XRF performed at the Nanoscopium beamline is a powerful tool to investigate, by multi-modal imaging, the Gd trapped in the DCN. Indeed, we hypothesize that Gd³⁺ may dechelate from its ligand, and then either precipitate with anions (e.g. PO₄⁻) or transmetallate with Fe or Cu ions, by a competition between these metals (highly concentrated in the DCNs) for the ligand for which they have a high affinity.

Study of Keto-enol Tautomerism in Acetylacetone, in Gas Phase and in Solvent

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ABSTRACT

The proton-transfer processes are very important in chemistry. One of these processes is the keto-enol tautomerism. β -diketones are a special candidate relative to this mechanism due to the strong intramolecular hydrogen bond, that makes the enolone form more stable than the diketo form. We therefore investigated through density functional theory^{1,2} all the possible conformers for both forms. Then we searched for minimum energy paths³ between the most stable forms of diketo and enolone, to get an idea of activation energy barrier. In a first step, we studied the acetylacetone molecule in gas phase⁴. Secondly, we added some explicit water molecule(s) to take into account the solvent, and its influence on the proton-transfer mechanism.

All these recent results were studied through the VASP code (Vienna Ab-initio Simulation Package) employing the CI-NEB method⁵ (Climbing-Image NEB). In gas phase, the reaction barrier is high. The addition of some water molecule in the reaction path induces a strong diminution of the transition energy. To understand the significant diminution of the activation energy, we studied by QTAIM (Quantum Theory of Atoms In Molecules) the evolution of the atomic energies along the path. Therefore, we have shown an important role played by the oxygen atom(s) of the water molecule(s). We present here the results of these analyses.

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Study of Amorphous - Crystalline Phase Transition in Phase Change Materials

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ABSTRACT

Phase-change materials (PCMs) are promising materials for data-storage applications. They are already used in rewriteable optical data storage (DVD, Blue ray) and offer a great potential for non-volatile Phase-Change Random Access Memories (PCRAM) [1-3]. In this technology, the storage mechanism is based on a rapid and reversible transition between the amorphous and crystalline states. Upon crystallization, PCMs exhibit changes in the crystal structure and in the electronic properties : the mass density, the optical reflectivity and the electrical resistivity reveal a steep variation. The large optical contrast between the amorphous and crystalline phases is generally accompanied by a large change in mass density [4] that may lead to void formation with a subsequent degradation of PCRAM cells reliability [5]. The average change in mass density upon crystallization is well known for usual PCM such as Ge₂Sb₂Te₅ (GST) or GeTe, but little is known about the influence of size on the density change and on the crystallographic texture, which may change drastically the stress in the PCM.

The aim of this work is to address the physical phenomena involved during the crystallization of thin and ultrathin films of chalcogenides. The possibility of down-scaling PCM requires an understanding of the phase transition mechanism i.e. the relation between strain, surface energy, atomic structure and size as a function of the temperature. Analysis techniques like X-ray Diffraction (XRD), X-ray Reflectivity (XRR) and Pair Distribution Function (PDF) allow *in-situ* characterization prior to and during the phase transition. GeTe thin films (thickness from 100 nm down to 5 nm) have been studied on DiffAbs beamline (Synchrotron SOLEIL). The results will be shown and discussed.

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On the Use of Difference Bands for Modelling SF₆ Absorption in the 10μm Atmospheric Window

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ABSTRACT

To model correctly the SF₆ atmospheric absorption requires the knowledge of the spectroscopic parameters of all states involved in the many hot bands in the 10μm atmospheric. Nevertheless, due to their overlapping, a direct analysis of the hot bands near the 10,5 μm absorption of SF₆ in the atmospheric window is not possible. It is necessary to use another strategy, gathering information in the far and mid infrared regions on initial and final states to compute the relevant total absorption.

In this talk, we present new results of an analysis of spectra recorded at the AILES beamline at the SOLEIL Synchrotron facility. For these measurements, we used a IFS125HR interferometer in the 100 – 3200 cm⁻¹ range, coupled to a cryogenic multiple pass cell [1]. The optical path length was varied from 45 to 141 m with temperatures between 223 and 153 K. New information has also been obtained on $\nu_2 + \nu_4 - \nu_5$, $2\nu_5 - \nu_6$ and $\nu_3 + \nu_6 - \nu_4$, which allow to derive improved parameters for ν_5 , $2\nu_5$ and $\nu_3 + \nu_6$. This is used to model the more important $\nu_3 + \nu_5 - \nu_5$ and $\nu_3 + \nu_6 - \nu_6$ hot band contributions. Including these new parameters in the XTDS model [2], we substantially improved the previous SF₆ parameters.

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Analysis of the ($\nu_3/\nu_7/\nu_9$) Bending Triad of the Quasi-spherical Top Molecule SO_2F_2

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ABSTRACT

Sulfuryl fluoride SO_2F_2 has a very interesting property: it is not only an atmospheric pollutant¹ but also an asymmetric top molecule with C_{2v} symmetry close to an accidentally spherical rotor².

A new high-resolution infrared spectrum of the (ν_3, ν_7, ν_9) bending triad of SO_2F_2 in the 550 cm^{-1} region has been recorded at 165 K using a multi-pass cell³ coupled to a high-resolution Bruker IFS 125 interferometer with a spectral resolution of 0.00102 cm^{-1} located at the AILES beamline of the SOLEIL Synchrotron.

Analysis of the triad has been performed in the $O_3 \supset \mathcal{T}_d \supset C_{2v}$ group chain with C_{2v} Top Data System based on tensorial formalism and vibrational extrapolation method⁴. Hamiltonian operator has been developed respectively to the fourth and sixth order for the ground state and the bending triad.

We were able to get a satisfying fit of 79 parameters. A total of 4474 IR lines up to $J_{\max} = 84$ have been assigned and fitted in frequency with a global root mean square deviation (RMS) of $0.422 \times 10^{-3} \text{ cm}^{-1}$.

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Evolutionary Algorithm-based Analysis of the Rovibrational SOCl_2 Stretching Bands of Thionyl Chloride

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ABSTRACT

Thionyl chloride (SOCl_2) is a volatile inorganic compound extensively used in the industry and whose monitoring in the gas phase is critical both from environmental and military concerns.

Pure rotational and rovibrational spectra of SOCl_2 and several of its isotopologues, were characterized recently in the microwave, submillimeter, and far-infrared spectral regions^{1,2}. The rotationally resolved vibrational spectra of the SOCl_2 asymmetric ν_5 (459 cm^{-1}) and symmetric ν_2 (500 cm^{-1}) SOCl_2 stretching fundamental bands have been measured by means of high resolution ($R = 0.001\text{ cm}^{-1}$) FT-FIR spectroscopy on the AILES beamline of the SOLEIL synchrotron facility. These two bands overlap with a strong SO_2 band (520 cm^{-1}) arising from the very efficient hydrolysis of SOCl_2 with residual traces of water³.

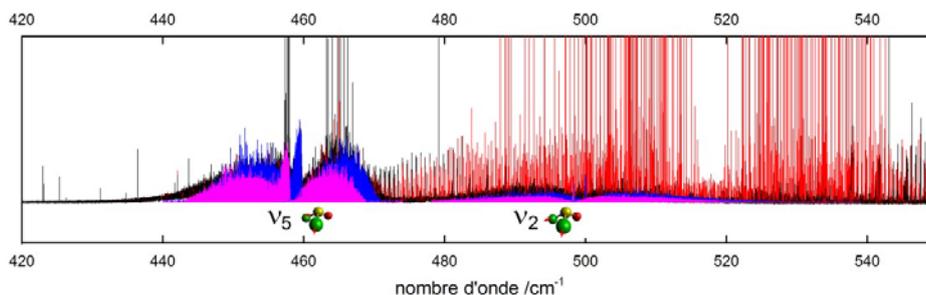


Fig. 1: Synchrotron-Based FT-FIR spectrum of ν_5 and ν_2 bands of SOCl_2 mixed with a strong SO_2 band (in red)

Evolutionary algorithms implemented in the automated fit programs *ga* and *ga-mr*, developed by the Nijmegen and Düsseldorf groups⁴, have enabled the analysis of the ν_5 and ν_2 bands of two isotopologues ($^{32}\text{S}^{16}\text{O}^{35}\text{Cl}_2$ and $^{32}\text{S}^{16}\text{O}^{35}\text{Cl}^{37}\text{Cl}$), despite the presence of the SO_2 band and thus demonstrating the power and efficiency of evolutionary algorithms applied to the spectroscopic analysis of congested spectra. A global fit containing these new data and all available experimental measurements enabled the determination of very accurate molecular parameters of which the structure of SOCl_2 is obtained.

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Resonant inelastic X-ray Scattering Study of Magnetic Excitations in the High Temperature Superconducting Parent Compound $\text{Ca}_2\text{CuO}_2\text{Cl}_2$

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ABSTRACT

Magnetic excitations have been studied intensely for their possible role in the Cooper pair formation which leads to high temperature superconductivity (HTS) in the cuprates [1]. Here we use resonant inelastic x-ray scattering (RIXS) to study $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ [2], a HTS cuprate parent compound for which the inelastic neutron scattering studies are infeasible due to crystal size limitations. The specific advantage of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ with respect to the already well-studied, and isostructural, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound is that it is the only HTS cuprate composed of only low Z ions, which makes it far more suitable for advanced theoretical calculations [3].

We will look at $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ using RIXS at the Cu L3, O K, and Cu K edges. Results from the Cu L3 edge [4], probing primarily the single magnon contribution, will be compared to recent measurements at the O K edge on the SEXTANTS beamline, which probe the bimagnon contribution. As well, RIXS measurements taking place February 2017 on the GALAXIES beamline at the Cu K edge will be discussed.

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Incorporation of Plasmonic Gold Nanoparticles Organized in Ordered Copolymer Films

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ABSTRACT

In order to obtain optical composite materials, we study the formation of gold nanoparticles (AuNPs) inside a self-assembled diblock copolymer polystyrene-*block*-poly(vinylpyridine) (PS-*b*-PVP).

We report here the formation of AuNPs by sonication and their introduction in ordered films of PS-*b*-PVP. The spin-coating of a PS-*b*-PVP solution in an appropriate solvent on a substrate casts a film of perpendicularly oriented cylinders. The orientation of the cylinders normal to the substrate was confirmed by GISAXS experiments.

The addition of gold salt -gold (III) chloride (AuCl₃)- and a following ultra-sound treatment before casting the film provide small, spherical AuNPs (2-3 nm in size) located, after deposition, inside the PVP cylinders. Larger AuNPs (3-4 nm) were also obtained by either increasing the initial gold amount in solution or proceeding to a seeded-growth by adding gold salt and operating sonication over an already AuNP-containing solution. These AuNPs locate also inside the cylinders after casting the film and exhibit a plasmon resonance.

The impact of the presence of the AuNPs inside the cylinders was investigated by GISAXS and AFM. The cylinders orientation is not disturbed by the AuNPs, despite a swelling of the cylinder diameter.

This method of insertion of AuNPs in patterned films provides new plasmonic nanocomposites.

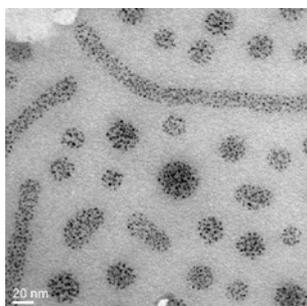


Figure. TEM picture of the AuNPs confined inside the cylindrical PVP domains of the PS-*b*-PVP film. The average diameter is around 2 nm. The amount of initial gold per pyridine for this sample was 5 equivalents.

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Investigation of Neutral Excitations in the Topological Magnon Insulator $\text{Lu}_2\text{V}_2\text{O}_7$

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ABSTRACT

Certain materials with pyrochlore structure display an anomalous Hall Effect (AHE)¹. In the case of ferromagnetic $\text{Lu}_2\text{V}_2\text{O}_7$ the AHE was explained by the presence of the Dzyaloshinskii-Moriya interaction². We used the AERHA spectrometer³ installed on the SEXTANTS beamline⁴ to perform resonant inelastic soft X-ray scattering (RIXS) studies⁵ on single crystal $\text{Lu}_2\text{V}_2\text{O}_7$ at V L_3 (2p-3d) and O K (1s-2p) edges, with high overall energy resolution (140 meV). Measured orbital excitations show similar peak positions in both V L_3 and O K data. The measured spectra were compared to crystal-field multiplet calculations⁶ performed for vanadium ions considering single formal valence states (V^{3+} , V^{4+} , and V^{5+}). The calculations indicate that vanadium has a mixed valence state in $\text{Lu}_2\text{V}_2\text{O}_7$ which could support an itinerant electron dynamic mechanism⁷ in this compound.

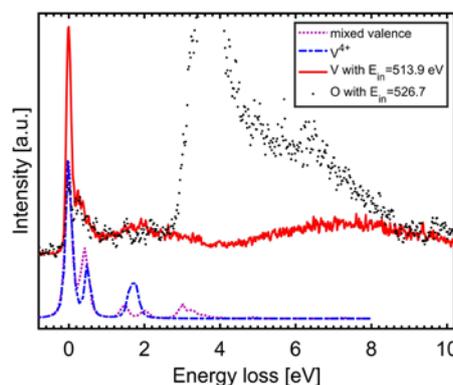


Fig. 1: Experimental V L_3 edge (red line) and O K edge (black points) RIXS spectra taken at 25 K compared with the crystal-field multiplet calculations for V^{4+} and mixed valence.

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Electrochemistry of Resistivity Changes in TaN/TiTe/Al₂O₃/Ta Conducting Bridge Random Access Memories

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ABSTRACT

Resistive Random Access Memories are interesting candidates for the next generation of non-volatile memories. Data storage principle is based on switching the resistivity between two high and low resistance states by applying voltage or current pulses. In conducting bridge random access memories (CBRAMs) under electrical bias, a conductive path is assumed to be created by ions diffusion from the active electrode into the solid electrolyte^[1]. In this work, we use hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. The HAXPES experiments were performed at the Galaxies beamline, Soleil. We investigate Al₂O₃ based CBRAMs with TiTe alloy for the active electrode (see Figure 1. (a))^[2]. Measurements are performed on as-deposited samples, after ex-situ forming and after RESET operation. Changes in chemical bonding states, observed after forming, show some reduction of Ti (Figure 1 (b)) together with Ta oxidation. This result suggests oxygen migration, probably in the O²⁻ form, pushed by the upper negative bias towards the interface between the solid electrolyte (Al₂O₃) and the Ta bottom electrode. On reversing the polarity of the applied voltage (RESET operation), we observe Ti oxidation and Ta reduction, thus characterizing an oxygen migration towards the active top TiTe electrode.

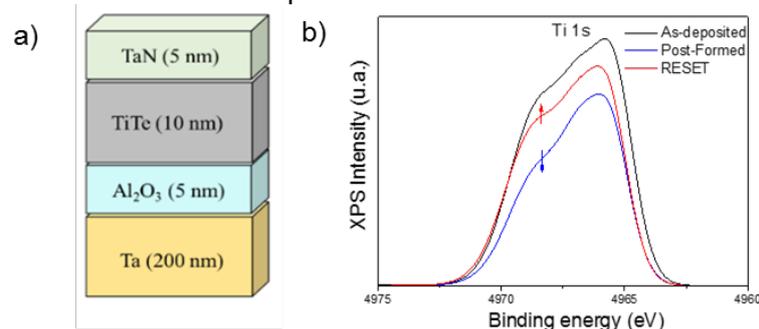


Fig. 1: (a) Schematic of the TaN/TiTe/Al₂O₃/Ta CBRAM (b) Ti 1s core level peaks obtained by HAXPES

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Dynamics of Magneto-structural Phase Transitions in MnAs/GaAs(001) Probed by Time-resolved X-ray Diffraction

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ABSTRACT

Spintronic devices are most often controlled by applied magnetic fields or by the injection of spin-polarized currents. Using temperature as the control parameter widens the field of application of such devices. We study bilayers that couple, via surface dipolar fields, a material exhibiting a magneto-structural phase transition (MnAs) to a soft ferromagnetic layer (Fe). When MnAs is grown on GaAs(001), epitaxial constraints lead to α/β phase coexistence in the form of regular stripes over the 10-40°C range. A direct correlation exists between MnAs microstructure and Fe magnetization reversal [1]. Recently, it was shown that the Fe magnetization switching could be achieved by a femtosecond laser excitation [2].

Previous results indicate that the Fe reversal by a single fs pulse has a rather slow dynamic, with characteristic time above several hundreds of ps and that the process has a fluence threshold. In order to gain insight into the phenomena at play in the Fe magnetization reversal following an ultrashort laser excitation, time resolved diffraction studies were carried out using an optical pump/x-ray probe scheme at the CRISTAL beamline.

Our measurements (Fig. 1) show that the α/β phase coexistence is reached during the return to equilibrium, on the ~10 ns timescale, above a fluence threshold that matches well the values required for Fe magnetization reversal. Also, formation of α/β stripes-like structure during the transient α/β coexistence is consistent with our measurements.

Together, these results provide a coherent picture of the laser induced Fe magnetization reversal process in Fe/MnAs, correlating it with the transient α/β pattern formation during the return to equilibrium driven by thermal diffusion.

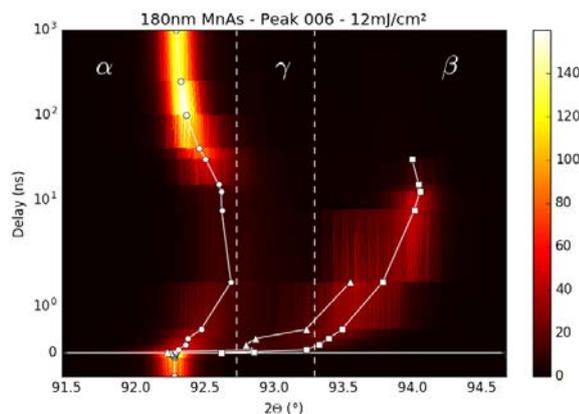


Fig. 1: Intensity diffracted at 8keV by a 180nm thick MnAs layer epitaxially grown on GaAs(001) following a 800nm ultrafast laser excitation. The α/β phase coexistence appears during the cooling step, after ~10 ns.

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Increasing the Magnetic Anisotropy through Onion-like Magnetic Nanoparticles

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ABSTRACT

Bulk iron oxide (Fe_3O_4) is ferrimagnetic at room temperature, while for size smaller than 30 nm, the Fe_3O_4 nanoparticles become superparamagnetic¹. 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 interface³. 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 (Fe_3O_4) 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 parameters⁴. Despite a high crystallinity interfacial phase Fe_3O_4 @ CoO nanoparticles remain superparamagnetic at room temperature, because of the Néel temperature ($T_N = 290$ K) of CoO . Within this framework, our effort deal 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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Application of X-ray Standing Waves for the Characterization of Chemical Processes and Interfacial Diffusion in Pd/Y based Multilayers using HAXPES

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ABSTRACT

We characterize Pd/Y multilayer and several derivative systems [1] designed to work in $\lambda=7.5$ - 11nm range using hard x-ray photoemission spectroscopy (HAXPES) combined with x-ray standing waves [2]. Experiments were performed in September at the GALAXIES beamline. Investigation of the physical structure of the samples (interface roughness and diffusion, compound formation) and the relation to the experimental performance will help optimize the deposition process and improve its optical properties. The Pd L3 and M5, Y L3 and M5, B K, and C K HAXPES spectra of five samples with and without the B₄C barrier layer of different thicknesses were measured. The chemical processes taking place in the Pd/Y multilayers without diffusion barrier, or with B₄C layers of different thickness acting as diffusion barriers will be identified once the data treatment is finished. Structural information of the multilayers will be revealed by comparing the experimental data with simulations. We expect to obtain a clear in-depth description of the stack from its chemical structure point of view. The effect of oxidation of the very first of the stack will be observed and the different chemical states of the various elements located, either at the interfaces or in the center of the layers. The positioning of x-ray standing waves enhancement for the emission is realized by rotating the grazing incident angle around Bragg angle.

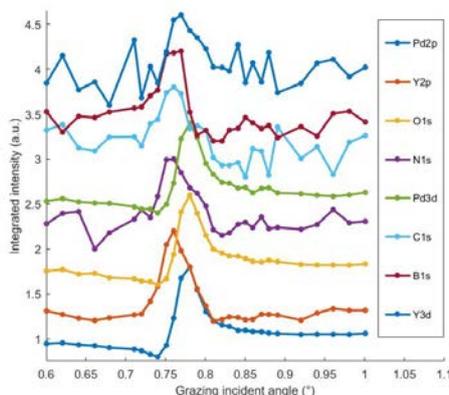


Figure 1: XSW curve, *i.e.* angular distribution of the intensity, of the photo-emission of sample [B₄C/Pd/Y]₄₀+B₄C cap as the grazing incident angle moves through its Bragg angle. (Incident beam energy 10keV, multilayer period being 4.7nm.)

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List of Other Posters

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J-M. Bizau
- PO-02** Stories about the Friendship between Prussian Blue Analogs and XAS/XMCD in the Hard X-ray Range
A. Bordage
- PO-03** Infrared imaging and spectroscopy with six decades of spatial dynamic range
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- PO-04** The Vibronic Structure of HC5N Cation Revealed by VUV Photoelectron-spectroscopy and ab initio Calculations
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Y. Ménesguen
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A. Somogyi
- PO-16** Projet Dichro50 : Une Révolution des Outils de Mesure du Dichroïsme Magnétique
M. Stora
- PO-17** Role of Local Structure Modification on Phase Transition Behavior of Functional Materials
A. Tayal

K-shell Photoionization of O^{4+} and O^{5+} : Experiment and Theory

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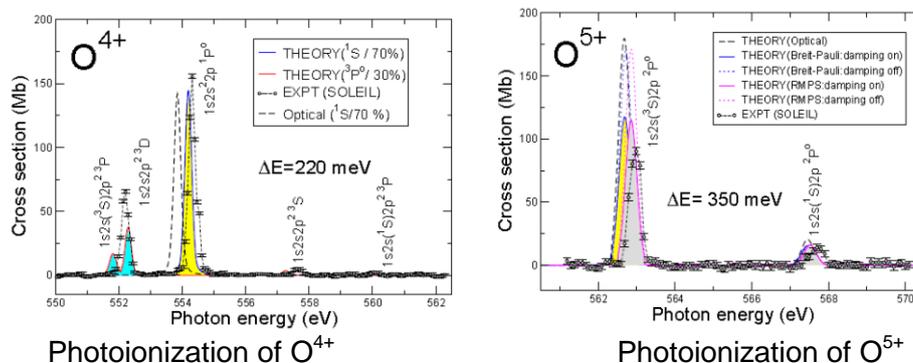
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ABSTRACT

Absolute cross sections for the K-shell photoionization of Be-like (O^{4+}) and Li-like (O^{5+}) atomic oxygen ions were measured for the first time (in their respective K-shell regions) by employing the ion-photon merged-beam technique at the PLEIADES beam line of SOLEIL synchrotron-radiation facility[1]. High-resolution spectroscopy with a resolution of 3200 (~70 meV, FWHM) was achieved with photon energy from 550 eV up to 670 eV. The measurements are compared with theoretical results from the R-matrix with pseudo-states (RMPS) method [2], the screening constant by unit nuclear charge (SCUNC) approach [3] and with available satellite observations. Various discrepancies between our present ground based measurements, made at SOLEIL, and the Chandra and XMM-Newton satellite observations are observed. We note that for both atomic ions, the R-matrix with pseudostates results favour those from the SOLEIL radiation facility.



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Stories about the Friendship between Prussian Blue Analogs and XAS/XMCD in the Hard X-ray Range

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ABSTRACT

Prussian Blue Analogs (PBA; $A_xM_4[M'(CN)_6]_{(8+x)/3}$, A= alkali cation and M,M'= transition metals) are intensively investigated as they can be used as functional materials, precursors of oxides and alloys, and model-compounds for methodological developments. In the first two cases, X-ray Absorption Spectroscopy (XAS) at the M and M' K edges is crucial to characterize the crystallographic and electronic structures at the atomic scale. It often brings the key information to completely understand the different behavior of two similar PBAs or to fully characterize a transformation mechanism. In the case of the methodological developments, PBAs form a very rich family of compounds with the same FCC structure, but whose stoichiometry can be varied at will (nature of the two transition metals and of the alkali cation, number of alkali cations per unit cell,...). They are thus ideal candidates for a deep investigation of the transition metal K-edge X-ray Magnetic Circular Dichroism (XMCD), whose fundamental processes must still be elucidated.

We will present three examples (Figure 1) on the contribution of XAS and its derivative techniques to the investigation of PBAs for their different applications: (i) the photomagnetic properties of the $Rb_2Co_4[Fe(CN)_6]_{3.3}$ PBA as nanoparticles by an in situ Co and Fe K-edge XAS study [1,2], (ii) the calcination of a $Co_4[Co(CN)_6]_{2.7}$ PBA in the Co_3O_4 oxide by Co K-edge site-selective XAS [3] and (iii) the development of a methodology to quantify small structural distortions from transition metal K-edge X-ray Magnetic Circular Dichroism [4].

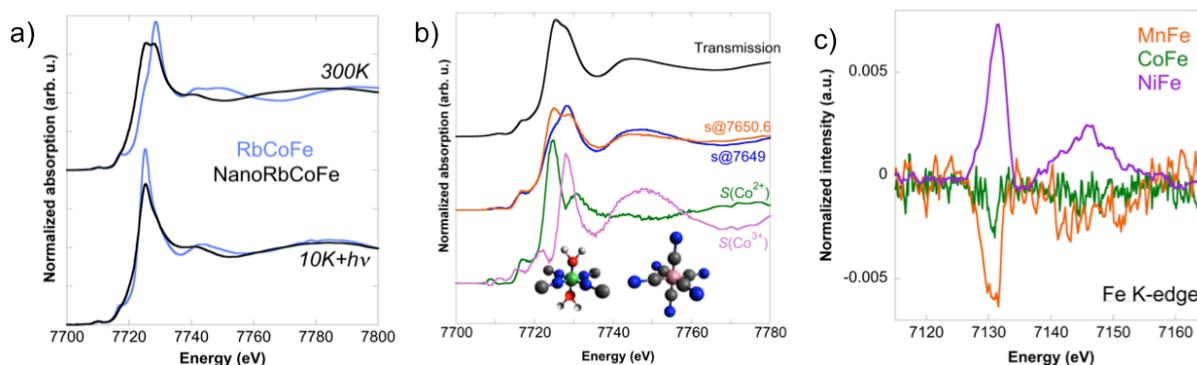


Fig. 1: (a) In situ Co K-edge XAS on the $Rb_2Co_4[Fe(CN)_6]_{3.3}$ PBA and its corresponding nanoconfined compound [1,2]. (b) Co K-edge site-selective XAS of the monometallic $Co_4[Co(CN)_6]_{2.7}$ PBA [3]. (c) Fe K-edge XMCD on a series of $M_4^I[Fe^{III}(CN)_6]_{2.7}$ PBAs (M = Mn, Co, Ni) [4].

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Infrared Imaging and Spectroscopy with Six Decades of Spatial Dynamic Range

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ABSTRACT

FTIR spectroscopy and microscopy are well-established methods in the synchrotron world and beamlines exist at more than thirty facilities around the planet. Although the intensity of IR radiation lags behind that of thermal sources, the size of the electron beam and small extraction angles of synchrotron (SR) beamlines provide 100-1000 times higher brightness when focused. In practice this allows diffraction limited raster mapping and spectromicroscopy. Experiments exploiting diffraction limited capabilities at the SMIS beamline range from biology to high-pressure physics. Some of the recent results will be highlighted from a selection of fields demonstrating this capability.

FTIR imaging is routinely provided by the platforms of all major FTIR microscope manufacturers. The synchrotron advantage can also be realized in the field of imaging by exploiting the beam characteristics of the source. By accumulating spatially oversampled datasets it is possible to break the far-field diffraction limit via the application of point spread function deconvolution. After the construction of the first synchrotron endstations for full-field imaging the next step was to exploit the high brightness of the synchrotron source in realizing tomography measurements. In this section of the presentation the current developments and preliminary results in the field of 2D and 3D spectroscopic imaging at SMIS will be also highlighted.

Scanning probe microscopy combined with infrared light exploiting near field physics had been demonstrated as a new paradigm in infrared spectromicroscopy and implemented at several synchrotron beamlines. The two currently existing methods, light scattering based scanning probe near-field optical microscopy (sSNOM) and photothermal spectroscopy and imaging using AFM detection (AFM-IR) are available through several commercial instruments. Currently, we are in the process of adapting a combined sSNOM and AFM-IR microscope to the synchrotron beam. At the time of submitting this abstract we have already demonstrated the full sSNOM capability, which will be included in the presentation. Technical details about the challenges of the implementation will be also discussed.

The Vibronic Structure of HC₅N Cation Revealed by VUV Photoelectron-spectroscopy and *ab initio* Calculations

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ABSTRACT

Cyanobutadiyne H-C≡C-C≡C-N, a molecule of astrophysical interest, is a member of the cyanopolyne 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 HC₅N 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 HC₅N⁺ 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 HC₅N that we have recorded in 2014 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.

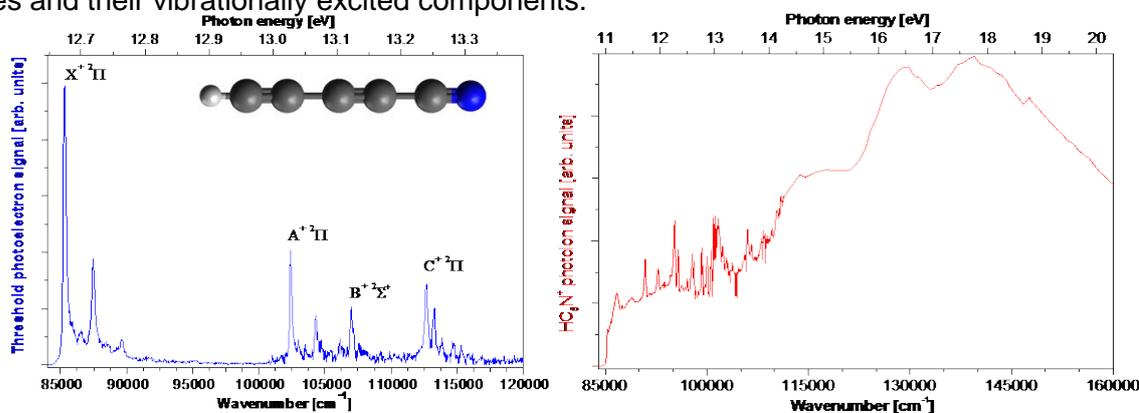


Fig. 1: Overview of the HC₅N TPEPICO spectrum and photoionization yield recorded on the DESIRS beamline

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Deformation of Harmonic Ti-6Al-4V Studied In-situ through Synchrotron X-ray Diffraction

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ABSTRACT

The compromise between ductility and mechanical resistance is a long-standing dilemma in materials science. The titanium alloy Ti-6Al-4V studied in this work combined these contradictory characteristics thanks to a new process of powder metallurgy which leads to what is called a **harmonic microstructure**. This microstructure is characterized by a bimodal size distribution consisting of fine grains, named "shell", and coarse grains, named "core" (Fig. 1), evenly distributed, interconnected and forming a 3D network. It is heterogeneous on a microscopic scale but homogeneous on a macroscopic scale [1-2]. Moreover the alloy is composed by two main crystallographic phases (hexagonal close-packed Ti- α and body-centered cubic Ti- β). This elaboration allows achieving mechanical properties combining ductility and high mechanical strength.

The main objective of this work, carried out as part of the ANR HighS-Ti project (ANR-14-CE07-0003), is to understand and explain the mechanical behavior of this unusual microstructure. In this presentation, the first results of a uniaxial tensile test under in situ synchrotron radiation (X-Ray Diffraction) will be presented. Quantitative analysis of the displacement of the Bragg peaks leads to the fact that the various grains families require different value of stress to initiate plastic deformation. The intrinsic phase selectivity of X-ray diffraction allowed monitoring the elastic strain of the α - and β -phases independently during the macroscopic deformation. Finally, qualitative analysis of the evolution of the diffraction patterns suggests a destruction of the harmonic structure from a value of strain of about 4%, probably induced by twinning deformation.

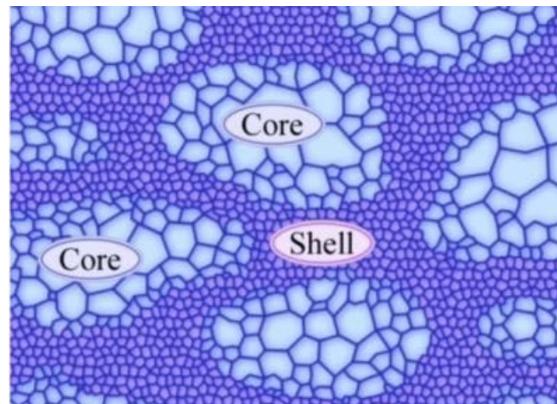


Fig. 1: Representation of the harmonic Ti-6Al-4V microstructure consisting of a 3D "Core-Shell" network.

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Fermi Surface Anisotropy of the Metallic Boron Doped Diamond

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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 has evidenced a small Fermi surface centered at the center of the Brillouin zone, and the polarization of the SR light oriented in several directions has allowed to separate the three different hole sheets of the Fermi surface. The experimental data are compared with the theoretical Fermi surface obtained using the k.p model.

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Large Area 7-channel Silicon Drift Detector Array

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ABSTRACT

Energy-dispersive X-ray analysis and X-ray fluorescence analysis are often carried out with Silicon Drift Detectors (SDDs) due to their superior spectroscopic performance and high count rate capability.

For applications where very large sensor areas are needed, KETEK developed the VA560 7-channel SDD Array with a total collimated area of 560 mm², mounted in an evacuated detector head, with an outer diameter of only 45 mm. The unique array configuration offers a high fill factor of about 35% with one central detector element, which is unprecedented in the competitive environment. The SDDs are read out with an ultra-low-capacitive ASIC (CUBE) to ensure a high count rate capability, even at high ambient temperatures. To achieve a Peak-to-Background ratio of greater than 10,000 and to suppress stray lines, each of the SDDs is equipped with an on-chip collimator, either made of Zirconium or a multilayer stack, avoiding any fluorescence lines other than Aluminium. The SDD chip thickness is 450 µm, optimized for an X-ray detection energy range of 1.5 keV to 30 keV. Each detector is cooled individually with a two-stage thermoelectric cooler to an operating temperature of -50°C. The VA560 entrance window is made of an aluminized polyimide foil with a thickness of 7.5 µm, offering a photon absorption comparable to 25 µm Beryllium.

First measurement results revealed an energy resolution (FWHM) of the Mn-K_α line better than 139 eV per channel for peaking times between 0.5 µs and 4 µs. The short peaking times allow input count rates of several hundreds of kcps per channel without loss in performance. For even shorter processing times, input count rates of 1 Mcps per channel and above can be handled.

The KETEK VA560 7-channel SDD Array allows an independent switch-on/off and readout of the individual SDDs, which provides the user additional position information. The system includes the supply electronics for all necessary detector bias voltages, temperature and pressure control, low-noise pre-amplifiers positioned close to the detector head and digital pulse-processing based read-out electronics, thus, the system can be used in “plug-and-play” mode.

SESAME Infrared Beamline: Design and Progress

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ABSTRACT

SESAME is the only synchrotron light source in the Middle East constructed in Jordan. SESAME current Members are: Bahrain, Cyprus, Egypt, Iran, Israel, Jordan, Pakistan, the Palestinian Authority and Turkey. Whereas, Brazil, China, the European Union, France, Germany, Greece, Italy, Japan, Kuwait, Portugal, the Russian Federation, Spain, Sweden, Switzerland, the United Kingdom and the United States are its Observers.

The necessity to have a light source in the region was highly propagated many years ago due to the powerful capabilities of the Synchrotron radiation as a leading-edge for huge number of challenges. With an equivalent success, Infrared Microspectroscopy established a recognizable competence among the most demanded techniques in all the synchrotron facilities all over the world. In this context, and as expressed by letters of interests, the selection and approval to build an Infrared beamline at SESAME was recognized, and accordingly was scheduled as a "Day-1" beamline. The beamline is the first completely new designed beamline at SESAME implemented in the framework of a collaboration agreement with SOLEIL Synchrotron, France. The main focus is to allow Synchrotron Radiation Infrared Microspectroscopy and imaging, with the reliability to address the requirements of the Infrared Users within the scientific community of the Middle-East and neighboring regions. Thus, it will allow Infrared Microspectroscopy and imaging experiments, covering miscellaneous applications such as Life Sciences, Biomedicine and Pharmaceuticals, Environmental Science, Surface and Material Science, Archaeology, Cultural Heritage, Art restoration, Geology, and others.

The technical design of the beamline components is demonstrated, together with some examples of the experiments conducted at the beamline using the IR Thermal source. Coupling with the synchrotron radiation is expected in Spring 2017.

The Multi-technique X-ray Scanning Imaging Station of Nanoscopium for RNA Visualization within Cells

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ABSTRACT

Mitochondria are involved in energy production, reactive oxygen species (ROS) signaling and apoptosis in eukaryotes. Their genome encodes components necessary for translation and to partly build up the five respiratory chain complexes while the other components are encoded by the nuclear genome, which sets the ground for continuous cross-talk. Consequently, many proteins and RNAs are imported into mitochondria. Defects in the synthesis of mitochondrial components or in the crosstalk invariably leads to serious myopathies and/or neurodegenerative diseases mustered under the generic name of "mitochondrial disorders". While protein import is fairly well understood, RNA import knowledge is scarce.

In our laboratory, we have demonstrated that the import of RNAs occurs in human cells and can be used as a potential therapeutic application. Indeed, sequences complementary to mutant DNA can be inserted within the imported RNA in order to decrease the replication of the ill-defined DNA molecules. Proof of principles of this promising strategy has been obtained recently [1-3]. In order to better understand and optimize the process, we need to study the dynamics of the RNA mitochondrial import process on intact and living cells. Our first attempts using confocal microscopy proved to be jeopardized by the fluorophores labeling the RNAs, which may interfere with RNA trafficking. The novel and original approach of tracking selenium- or bromine-derivatized RNAs by X-ray fluorescence (XRF) scanning spectro-microscopy seems to be promising in this perspective.

Both continuous fast scanning with millisecond dwell times and high precision step-scan mode operation are foreseen at the 155 meters-long Nanoscopium beamline (Soleil Synchrotron) for scanning imaging and tomography. Multi-scale and multi-technique imaging provide unprecedented information on metal concentration and distribution together with sample morphology by coupling modalities such X-ray fluorescence, absorption, phase contrast and dark field [4,5].

We present here the first results of experiments obtained on biological samples performed at the multi-technique station of Nanoscopium, which has been starting operating in February 2016. The images from human cells in culture transfected with brominated RNAs obtained at the beamline demonstrate the future possibilities offered by Nanoscopium in biology.

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Coherent Diffractive Imaging Techniques at the Nanoscopium Beamline

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ABSTRACT

The coherent flux that became available at increasingly brilliant X-ray sources motivated the development of alternative microscopy approaches, such as coherent diffractive X-ray imaging techniques. These techniques exploit the coherence of the X-ray beam in order to measure both absorption and phase quantitatively and in parallel, providing quantitative information about the sample morphology (electron density variation).

The Nanoscopium beamline of Synchrotron Soleil is especially well suited to such coherent X-ray imaging techniques in the 5–20 keV energy range due to its 150 m beamline length and the possibility of tailoring the coherence properties of the X-ray beam by the secondary source. Moreover, scanning coherent diffractive imaging (ptychography) provides a useful complement to the scanning X-ray imaging modalities implemented at the beamline, such as X-ray Fluorescence, X-ray phase contrast and X-ray dark field contrast. Since the spatial resolution obtained by ptychography is not limited by the size (~400 nm) of the probing beam, morphological details of 100 nm dimensions are becoming detectable with this coherent based technique.

This poster presents the first test experiments of coherent based imaging at Nanoscopium from the field of the main scientific fields of the beamline, geology and environmental sciences. These techniques will be available for hierarchical length-scale 2D/3D electron density and multimodal imaging.

Caractérisation de Films Minces par Analyse Combinée XRR-GIXRF

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ABSTRACT

Les films minces ou empilements multi-couches associant différents matériaux sont d'un grand intérêt pour les applications de haute technologie, par exemple, dans le développement d'électrodes transparentes pour les cellules photovoltaïques. Les performances de ces matériaux sont étroitement liées à la qualité des interfaces entre les différentes couches, leur rugosité et le profil de concentration des différents éléments. Pour ces caractérisations à l'échelle nanométrique, les techniques par fluorescence X en incidence rasante (GIXRF) présentent l'avantage d'être non-destructives et de fournir des informations quantitatives sur les épaisseurs et les propriétés des interfaces.

Pour développer les méthodes de caractérisation des nouveaux matériaux, le Laboratoire National Henri Becquerel a installé un nouveau goniomètre nommé CASTOR (Chambre d'Analyse par Spectrométrie en Transmission Ou en Réflexion) sur la ligne de métrologie du synchrotron SOLEIL. Ce goniomètre se compose d'une chambre à vide incluant un manipulateur à 7 axes comprenant quatre translations et trois rotations. Cet ensemble permet de déplacer l'échantillon dans les différentes orientations requises par les diverses méthodes d'analyse: réflectométrie (X-Ray Reflectivity - XRR), fluorescence X, (X-Ray Fluorescence - XRF), fluorescence X en réflexion totale (Total X-Ray Fluorescence - TXRF) ou sous incidence rasante (Grazing Incidence X-Ray Fluorescence GIXRF). La technique d'analyse combinée XRR-GIXRF a été appliquée à divers échantillons déposés sur substrat Si en couches minces (Ge, Te, Sb, GeTe et Ge₂Sb₂Te₅) et empilements multicouches (Al/ZrC/Al/W). Les données GIXRF ont été analysées par le logiciel PyMCA et les données XRR ont été simulées avec le logiciel PYXCEL développé au CEA-LETI. Cette analyse a permis de déterminer différents paramètres comme la composition de l'échantillon, l'épaisseur du film, la densité et la rugosité de chaque couche.

Le goniomètre a été récemment équipé d'un porte-échantillons thermo-régulé, développé par le LNE, afin de soumettre l'échantillon à des variations contrôlées de température jusqu'à 300°C. Les premiers essais ont porté sur le chauffage d'échantillons de GeTe et de Ge₂Sb₂Te₅ dans le but d'observer un changement de phase se traduisant par un changement dans la réflectivité. Les transitions de phase recherchées se produisent respectivement à 239°C et 170°C. Ce nouveau développement doit permettre d'améliorer la compréhension des propriétés des matériaux en lien avec leur structure.

Ces études sont menées dans le cadre des projets européens EMRP ENG53 (ThinErgy) et EMPIR 14IND01 (3DMetChemIT).

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Ligne de lumière française IF-BM32 à l'ESRF – Opportunités d'utilisation de la nouvelle source 2020

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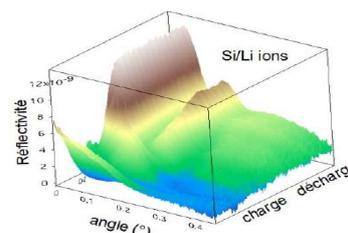
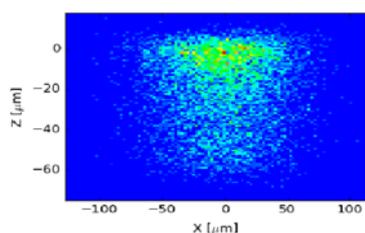
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ABSTRACT

La ligne de lumière InterFaces (IF) mène des études structurales fondamentales et appliquées à l'aide du rayonnement synchrotron dans le domaine des nanosciences, des micro- et nanotechnologies. Les matériaux peuvent être étudiés *ex situ* ou *in situ* durant leur élaboration sous ultra-vide, en cours de fonctionnement ou sous sollicitations diverses (ex : thermique, mécanique, électrique). Elle est composée de trois instruments avec un faisceau monochromatique submillimétrique ($0.3 \times 0.5 \text{ mm}^2$) d'énergie ajustable comprise entre 5 et 30 keV ou polychromatique (de 5 à 22 keV) et de taille submicrométrique ($300 \times 300 \text{ nm}^2$).

L'instrument **In situ Nanostructures et Surfaces (INS)** sous ultra-vide permet de déterminer la structure atomique, la morphologie et la composition d'objets à l'échelle nanoscopique (îlots, nanofils, graphène, matériaux 2D) des surfaces et interfaces (alliage, hétérostructures, catalyse). Grâce à un EquipeX, il permet d'étudier les mécanismes de croissance par épitaxie par jet moléculaire (MBE) et par dépôt chimique en phase vapeur (UHV-CVD). Le **goniomètre multitechnique (GMT)** accueille des échantillons à l'air ou avec leur environnement spécifique. Avec des photons X pénétrant (30 keV) il est particulièrement utile aux études structurales des interfaces solide/solide (adhésion, implantation) ou liquide/solide souvent *operando* (microfluidique, altération de surface, batterie Li-ions), des couches minces et les déformations dans les matériaux fonctionnels (relation propriétés-structure). L'instrument de **microdiffraction Laue (μ Laue)** permet de cartographier l'orientation et l'état de déformation des cristaux à l'échelle submicronique : mesures fines des déformations en microélectronique (intégration 3D, ingénierie du gap), de contrôle de la dispersion des contraintes internes dans des matériaux pour l'énergie. Des tests mécaniques réalisés *in situ* sur des micro- et nano-objets sont aussi effectués sur le rôle fondamental des défauts (dislocations, joints de grains) sur l'élasticité et la plasticité.

Dans la perspective de l'emploi de la nouvelle source X pourvue par l'ESRF en 2020, la ligne prépare la conception d'une optique et d'une instrumentation optimales. Ainsi la performance de chaque instrument bénéficiera pleinement de la brillance accrue de la source (x15) ainsi que d'une nouvelle panoplie de détecteurs 2D rapides adaptés aux mesures effectuées.



Les développements sur la ligne IF vont permettre de disposer d'un faisceau au niveau de l'échantillon très inférieur à $100 \mu\text{m}$ en taille (gauche) sur INS renoué (milieu) et GMT, et de 100 nm sur le μ Laue. Les mesures s'appuieront de plus sur de nouveaux détecteurs rapides et performant à haute énergie, par exemple en CdTe pour les expériences *in situ* sur les batteries (droite).

Bandgap Opening Induced by the Structural Periodicity on Buffer Layer Graphene

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ABSTRACT

The promise and pitfall of graphene for nanoelectronic applications stems from its inherent property such as zero bandgap in its electronic structure. Several methods have been proposed to open a bandgap in monolayer graphene [1, 2]. Recently, for the first time, we have shown that on SiC(0001) substrate, under adequate growth conditions, a well ordered first single layer graphene (i.e. the buffer layer) exhibits a bandgap of more than 0.5eV [3], twice the previous value in epitaxial graphene samples [4]. The origin of this bandgap was unclear.

To understand the bandgap opening in buffer layer, we used different experimental techniques such as scanning tunneling microscope (STM), high-resolution scanning transmission electron microscope (HR-STEM) and Angle-resolved photoemission spectroscopy (ARPES). Using STEM, we have shown that the majority of carbon atoms in buffer layer are decoupled from the substrate and thus we discard the possibility of bandgap opening due to the strong covalent bonding with the substrate. Our STM images clearly reveal the honeycomb structure of graphene without any defects. Thus we elucidate the bandgap is not due to the periodic inclusion of heptagon-pentagon-hexagon defects. Finally from ARPES we confirm that the bandgap opening is due to the super periodicity induced by the substrate. This has been further corroborated with our calculations [5].

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Dealing with Capillary Fouling, and Extraction of Pure Component Patterns from Poorly Resolved SEC-SAXS Data using the US-SOMO Software

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ABSTRACT

Size-exclusion chromatography directly coupled with SAXS using a flow-through capillary should allow direct collection of monodispersed sample data, and is increasingly offered at major SAXS beamlines.^{1,2} However, capillary fouling issues and not baseline-resolved peaks can hamper its efficacy. The UltraScan SOLUTION MOdeler³ (US-SOMO) HPLC-SAXS module provides a comprehensive framework to analyze such data, starting with a simple linear baseline correction and symmetrical Gaussian decomposition tools⁴. In addition to several new features, substantial improvements to both routines have now been implemented,⁵ comprising the evaluation of outcomes by advanced statistical tools. The novel integral baseline correction procedure is based on the more sound assumption that the effect of capillary fouling on scattering increases monotonically with the intensity scattered by the material within the X ray beam. Overlapping peaks, often skewed because of sample interaction with the column matrix, can now be accurately decomposed using non-symmetrical modified Gaussian functions. As an example, the analysis of a polydispersed solution of aldolase will be presented: from heavily convoluted peaks, individual SAXS profiles of tetramers, octamers, and dodecamers are extracted and reliably modeled.

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Hierarchical Length-scale Imaging at the Nanoscopium Beamline of Synchrotron SOLEIL

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ABSTRACT

The Nanoscopium beamline of Synchrotron SOLEIL is dedicated to scanning multi-technique X-ray imaging in the 5–20 keV energy range. It aims to offer 2D/3D quantitative information on the elemental composition and electronic density of samples with sub-micrometer spatial resolution and analytical sensitivity, i.e. trace, sub-parts-per-million detection limit. The beamline is especially well suited for hierarchical length-scale studies of highly heterogeneous samples providing simultaneous morphological, elemental and chemical information at multiple length scales. Indeed, the scanning range can be scaled from millimetres to micrometres with spatial resolution down to 400 nm.

The main scientific fields of application at the beamline are biology, life sciences, geo-biology and environmental sciences. The multi-technique ‘FLYSCAN’ data acquisition scheme developed at Synchrotron SOLEIL, based on the specific technical features of Nanoscopium, is crucial for such multi-length scale scanning imaging. Obviously, on-line and off-line data processing is a crucial part of the success of the experiments. In order to cope with these challenges, we have developed a dedicated data processing tool, the MMX-I freeware, at the Nanoscopium beamline, which is available for users for data treatment of scanning multimodal imaging.

This poster presents the first measured performance of the Nanoscopium beamline followed by the proof of principle multi-technique fast scanning imaging and tomography experiments performed with ms dwell time per pixel in geo-biological applications.

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Projet Dichro50 : Une Révolution des Outils de Mesure du Dichroïsme Magnétique

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ABSTRACT

DICHOÏSME MAGNETIQUE A 50mK SOUS ULTRA VIDE ET CHAMP MAGNETIQUE INTENSE

Les mesures d'absorption x reposent sur plusieurs méthodes de détection, parmi lesquelles le rendement total d'électrons (TEY, pour *Total Electron Yield*) qui est la méthode privilégiée aux basses énergies. Elle s'obtient grâce à la mesure du courant échantillon, ce qui suppose que celui-ci est isolé électriquement de la masse. Ce photo-courant est directement relié à l'absorption de l'échantillon.

Les propriétés magnétiques de la matière dépendent essentiellement de la température. Les molécules-aimants présentent des propriétés exceptionnelles à très basses températures. Pour atteindre leur caractérisation magnétique il faut un dispositif permettant de refroidir la molécule tout en garantissant une isolation électrique parfaite, pour des mesures, en particulier, de dichroïsme magnétique.

Le descriptif de la technologie mise en oeuvre pour le **Projet Dichro50**, regroupant la ligne **DEIMOS** du Synchrotron Soleil et l'entreprise **CryoConcept**, est de créer un outil de mesure original avec comme caractéristiques essentielles :

- une très bonne isolation électrique (de l'ordre de 200GΩ).
- des températures avoisinant les 50mK (dilution 3He-4He).
- Un champ magnétique pouvant atteindre 7T.

Pour se faire, un certain nombre de points clés devront être réalisés :

- Réaliser un outil compatible avec l'UHV.
- Améliorer l'écrantage du Cryostat existant afin de garantir les très basses températures tout en garantissant l'accessibilité de l'outil.
- Atténuer l'impact des courants de Foucault.
- Garantir un bruit de mesure infime.
- Garantir une facilité d'utilisation pour tous les types d'utilisateurs.
- Obtenir plusieurs modes de fonctionnement en fonction des gammes de températures.

Les objectifs globaux de l'outil tournent autour de trois axes :

- Obtenir un rapport H/T de 140 (7T/50mK) ce qui correspond à **un rapport 5 fois supérieur à l'existant**.
- Obtenir un rapport signal sur bruit **20 fois supérieur à l'existant** permettant d'accéder à des quantités de matière encore plus faible (environ 0.1% d'une monocouche).
- Avoir un changement de température

Role of Local Structure Modification on Phase Transition Behavior of Functional Materials

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ABSTRACT

Fascinating properties emerges when materials subjected to external conditions such as high pressure, chemical pressure driven by local defects or in the presence of high electric and magnetic field. Numerous properties of materials correlated to its crystal structure tailored when the inherent symmetric arrangement modifies under the influence of these external attributes that often drives a material into a new state. If the associate structural variances are aperiodic or having sizes in the regime which cannot be probed by techniques that provide information on the average long range structure, their correlation to material properties are difficult to establish. In this respect, the EXAFS technique provides information complementary to these techniques in its sensitivity to local structure. We now present EXAFS results on two types of functional material that are important to investigate for their current technological applications. First EXAFS results are presented on ionic liquid (IL) gated epitaxial MoO_3 thin film oriented along c -axis. IL as the gate dielectric can, in principle, electrostatically induce higher carrier densities in the transistor channel than is possible using solid state dielectric materials. During the IL gating metal to insulator transition (M-I) in this material are speculated to occur by enhanced carrier density created by oxygen vacancies. However, the role of structural modification occurs due to O vacancies on M-I phase transition was not well studied. Using the polarization of synchrotron source EXAFS measurements was performed on this sample in two geometries i.e. perpendicular and parallel to c -axis. MoO_3 has an orthorhombic structure which consists of layers of corner sharing and edge sharing MoO_6 octahedra, which are highly asymmetric. IL gating results in reduction of terminal Mo(VI) to Mo(V) which resemble to symmetric octahedra in metallic MoO_2 and hence may lead to observed enhance metallization after IL gating. Next, EXAFS results are presented in Se deficient 3D topological insulator (TI) Bi_2Se_3 that displays the 3D Dirac semi-metallic type behavior in the bulk transport measurements. Bi_2Se_3 has a rhombohedral structure in which $\text{Se}_2\text{-Bi-Se}_1\text{-Bi-Se}_2$ quintuple layers (QLs) stacked along $[0001]$ direction via weak van der Waals bonding. Local defects created in the lattice by the presence of natural se vacancies generates local strain that may easily modifies van der Waal separation which causes the tuning of bulk band topology and may drive the material in a different state. Anisotropic EXAFS measurements reveal preservation of structure within the QLs however, shows compression along the c -axis, which are absent in the bulk diffraction study. It suggests that local strained regions are embedded in the material which are likely to be at the critical regime of TI phase to Dirac type 3D semi-metallic phase transition.

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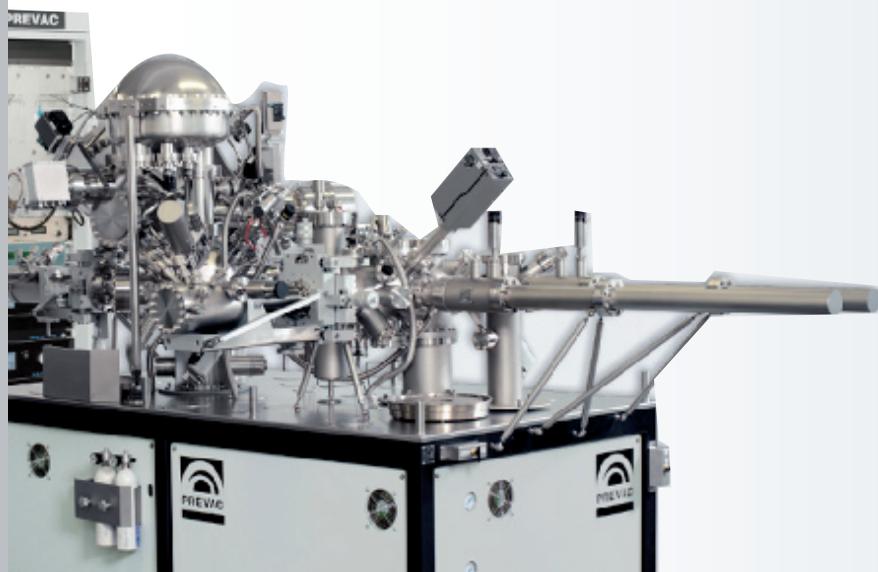
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