



HAL
open science

Unraveling isomeric structures of oligosaccharides by VUVPD and VUVEPD experiments: Towards an unambiguous and complete sequencing of isomers

David Ropartz, Alexandre Giuliani, Marie-Christine Ralet-Renard, H el ene Rogniaux

► To cite this version:

David Ropartz, Alexandre Giuliani, Marie-Christine Ralet-Renard, H el ene Rogniaux. Unraveling isomeric structures of oligosaccharides by VUVPD and VUVEPD experiments: Towards an unambiguous and complete sequencing of isomers. Synchrotron SOLEIL Users Meeting, Jan 2014, Saclay, France. hal-01580668

HAL Id: hal-01580668

<https://hal.science/hal-01580668>

Submitted on 5 Jun 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destin ee au d ep ot et  a la diffusion de documents scientifiques de niveau recherche, publi es ou non,  emanant des  tablissements d'enseignement et de recherche fran ais ou  trangers, des laboratoires publics ou priv es.

9th SOLEIL Users' Meeting



January 23rd and 24th, 2014

**Arago Amphitheatre
Ecole Polytechnique, Palaiseau
& SOLEIL, Saint-Aubin**


SUM Scientific Committee

Elise BERRIER (*UCCS, Villeneuve d'Ascq*)
Valérie BIOU (*LBPCPM, Paris*)
Vincent BOUDON (*Lab Interdisciplinaire Camot, Dijon*)
Isabelle BROUTIN (*Univ. Paris-Descartes, Paris*)
Matteo D'ASTUTO (*IMPMC, Paris*)
Emmanuel GUILLON (*ICM, Reims*)
Sandrine LYONNARD (*INAC/SPrAM-CEA, Grenoble*)
Judith MONNIER (*ICMPE, Paris*)
Sandra NINET (*IMPMC, Paris*)
Francis PENENT (*LCPMR, Paris*)
Stéphanie ROSSANO (*LGE, Marne la Vallée*)
Antonio TEJEDA (*IJA, Nancy*)

**Morning Satellite Session dedicated to
Crystallography on January 23
Organized by SOLEIL and LLB**

Satellite Session Scientific Committee

Christiane ALBA-SIMONESCO (LLB)
Jean DAILLANT (SOLEIL)
Béatrice GILLON (LLB)
Jean-Paul ITIE (SOLEIL)
Florence PORCHER (LLB)
Jean-Pierre SAMAMA (SOLEIL)



9th SOLEIL Users' Meeting

January 23 and 24, 2014

FOREWORD

2014 has been proclaimed **International Year of Crystallography** and has been inaugurated during a ceremony at UNESCO headquarters in Paris, on January 20th and 21st, 2014.

SOLEIL and LLB has pointed out the interest in enhancing this theme before the Users' Meeting 2014 program, with a **morning satellite session SOLEIL - LLB** composed of **four plenary lectures** dedicated to Crystallography, **on January 23rd a.m.**

The **9th Users' Meeting** takes place on **January 23rd p.m. and 24th a.m., 2014** at the "Ecole Polytechnique" and at SOLEIL.

It provides an invaluable forum for the synchrotron radiation user community, presenting an important opportunity to hear about the latest and most exciting results obtained at SOLEIL.

The morning of the second day consists in **parallel sessions**, with original scientific presentations **selected from submitted abstracts for Oral Presentation**.

During the **poster session**, the best student poster is awarded a prize.

A social program with a buffet reception is held at SOLEIL in the afternoon of January 23rd in conjunction with the commercial exhibitions and the visit of the slicing, the long beamline and IPANEMA.

AVANT-PROPOS

L'année 2014 a été proclamée **Année Internationale de la Cristallographie** et a été inaugurée lors d'une cérémonie au siège de l'UNESCO à Paris, les 23 et 24 janvier 2014.

SOLEIL et le LLB ont souligné l'intérêt de valoriser cette thématique avant le programme du Colloque des utilisateurs 2014, avec une matinée consacrée à une **session satellite SOLEIL - LLB** composée de **quatre conférences plénières** dédiées à la cristallographie, le **23 janvier 2014 au matin**, à l'Ecole Polytechnique (Palaiseau).

Le **9ème Colloque des Utilisateurs de SOLEIL** se tiend le **jeudi 23 janvier après-midi et le vendredi 24 janvier au matin**, à l'Ecole Polytechnique et à SOLEIL.

Ce rendez-vous incontournable pour la communauté des utilisateurs du rayonnement synchrotron est l'occasion de recueillir les plus récents résultats obtenus à SOLEIL.

Le matin de la deuxième journée est consacré aux **sessions parallèles**, composées d'exposés scientifiques originaux, **sélectionnés à partir des résumés soumis pour les présentations orales**.

Lors de la **session posters**, un prix est décerné au meilleur poster étudiant.

Un **temps de convivialité** est organisé à SOLEIL le jeudi 23 janvier après-midi avec les stands d'entreprises et la visite du Slicing, de la Ligne Longue et d'IPANEMA.

SOLEIL Users' Meeting 2014

January 23rd - 24th, 2014

École Polytechnique Palaiseau, and Synchrotron SOLEIL France

Summary

- Programme
- Crystallography Satellite Session to SOLEIL Users' Meeting 2014
- 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
- Posters Session
 - List of Student Posters
 - List of Other Posters
- List of Participants
- List of Commercial Exhibitors
- Companies Advertisements

SOLEIL Users' Meeting 2014

January 23rd - 24th, 2014

Auditorium ARAGO, École Polytechnique,
Palaiseau, France

Programme

Thursday, January 23rd

Crystallography Satellite Session to SOLEIL Users' Meeting 2014

Ecole Polytechnique (Palaiseau) Arago Auditorium

- 08:30 - 09:30 Registration & coffee
- 09:30 - 09:40 Welcome / Introduction SOLEIL / LLB
- 09:40 - 10:25 Quasicrystals: Structure and dynamics
Marc De Boissieu - Laboratoire Sciences de l'Ingénierie, des Matériaux et Procédés
Grenoble (France)
- 10:25 - 11:10 2D crystallography, a unique tool for unraveling surface and interface atomic structures
Michèle Sauvage – Synchrotron SOLEIL (France)
- 11:10 - 11:30 Coffee break
- 11:30 - 12:15 Integrated Structural Biology of RNA Polymerase I and III Transcription
Christoph Mueller - EMBL - Heidelberg (Germany)
- 12:15 - 13:00 Neutron and x-ray scattering studies of correlated-electron materials
Bernhard Keimer - Max Plank Institut (Germany)

SOLEIL Users' Meeting 2014

Ecole Polytechnique (Palaiseau) Arago Auditorium

- 13:00 - 14:30 Lunch
- 14:30 - 14:45 Welcome - Introduction
Elise Berrier, ORGUES Chairperson
- 14:45 - 15:15 Using a multi-disciplinary synchrotron approach to analyse the original marine iodide metabolism
Myriam Czjzek - Station Biologique de Roscoff (France)
- 15:15 - 15:45 Unveiling the electronic structure of complex materials: Electrons and photons "à la carte"
Marco Grioni, - Institut de Physique des Nanostructures - EPFL, Lausanne (Suisse)

SOLEIL Users' Meeting 2014

January 23rd - 24th, 2014

Synchrotron SOLEIL Orme des Merisiers,
Saint-Aubin, France

Programme

Thursday, January 23rd

- 15:45 - 16:00 *Transfer to SOLEIL*
- 16:00 - 16:30 *Coffee break*
- 16:30 - 20:00 Posters Session / Commercial Exhibitors / Web TV
- 17:00 - 20:00 Visit of Slicing - Long beamline - IPANEMA
- 20:00 - 21:30 *Buffet / Best Poster Prize Award*

Friday, January 24th

SYNCHROTRON SOLEIL

- 9:00 - 10:50 Parallel sessions (see detailed programme here after)
- 10:50 - 11:20 *Coffee break*
- 11:20 - 13:10 Parallel sessions (see detailed programme here after)
- 13:10 – 14:30 *Lunch*

Parallel Sessions Schedule

Biology - Health

(BLOC Auditorium, CEA, Orme des Merisiers)

Chairpersons: Valérie BIOU and Isabelle BROUTIN

- 09:00 - 09:30 Structural flexibility revealed by three nitric oxide sensors
Pierre Nioche - invited speaker (UFR Biomédicale - Paris, France)
- 09:30 - 09:50 Deciphering the binding mode of Trm112 activator with four structurally related methyltransferases involved in protein synthesis
Juliette Létoquart (Laboratoire de Biochimie - Palaiseau, France)
- 09:50 - 10:10 Function of Fap7 in the maturation of the ribosome small subunit
Magali Blaud (Université Paris Descartes - Paris, France)
- 10:10 - 10:30 Structural studies of bacterial effectors hijacking cellular Arf GTPases
Marcia Folly-Klan (LEBS - Gif-sur-Yvette, France)
- 10:30 - 10:50 The periplasmic binding protein AccA from agrobacterium tumefaciens
Abbas El Sahili (LEBS - Gif-sur-Yvette, France)
- 10:50 - 11:20 *Coffee break*
- 11:20 - 11:50 How random are Intrinsically Disordered Proteins? A Small Angle X-Ray Scattering perspective
Véronique Receveur-Brechot - invited speaker (Centre Recherche Cancérologie - Marseille, France)
- 11:50 - 12:10 A comprehensive mechanism of fibrin network formation involving early branching and delayed single-to double-strand transition from coupled time-resolved SAXS and MALS
Mattia Rocco (Biopolimeri e Proteomica - Genova, Italy)
- 12:10 - 12:30 Synchrotron deep UV fluorescence microspectroscopy: An efficient method for muscle fibers characterization
Caroline Chagnot (INRA - Saint-Genes Champanelle, France)
- 12:30 - 12:50 Unraveling isomeric structures of oligosaccharides by VUVPD and VUVEPD experiments: Towards an unambiguous and complete sequencing of Isomers
David Ropartz (INRA - Nantes, France)
- 12:50 - 13:10 Near-infrared imaging in living cells with lanthanides based nanoMOFs
Alexandra Foucault-Collet (CBM CNRS - Orléans, France)

Parallel Sessions Schedule

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

(Conference Room, Reception Building, Ground floor, SOLEIL)

Chairpersons: Sandrine LYONNARD and Elise BERRIER

- 09:00 - 09:30 Amorphous to crystal conversion as a mechanism governing oxide nanoparticle
David Carrière - invited speaker (CEA - Saclay, France)
- 09:30 - 09:50 Quick-EXAFS-Raman and SAXS study of formation and growth of SnO₂ nanoparticles
Bruno Caetano (UPMC - Paris, France)
- 09:50 - 10:10 Controlling nanoparticles dispersion in ionic liquids by tuning the pH
Clément Guibert (UPMC - Paris, France)
- 10:10 - 10:30 The electrochemical mechanism of Na insertion in Sb-based negative electrode materials for innovative Na-ion batteries: The first discharge
Lorenzo Stievano (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 10:30 - 10:50 Connectivity of water molecules confined in nafion
Simona Dalla Bernardina (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 10:50 - 11:20 Coffee break
- 11:20 - 11:50 Understanding the nature and transformations of dispersed phases: Synchrotron radiation and heterogeneous catalysts
Eric Marceau - invited speaker (Laboratoire de Réactivité de Surface - Ivry-sur-Seine, France)
- 11:50 - 12:10 New insights on the impact of Co-components on the formation of the active supported Pd/TiO₂ catalysts during the gas phase acetoxylation obtained with operando XAS
Joerg Radnik (LIKAT - Rostock, Deutschland)
- 12:10 - 12:30 In-situ study of silicon oxide growth from tetraethoxysilane (TEOS) using near-ambient pressure XPS
Giorgia Olivieri (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 12:30 - 12:50 Study of uranyl and thorium complexation with phosphorylated biomolecules
Gaëlle Creff (Institut de Chimie de Nice, France)
- 12:50 - 13:10 Ionization and enhanced photochemistry of nitric acid on ice
Philippe Parent (CINaM - Marseille, France)

Parallel Sessions Schedule

Cultural Heritage, Archaeology, Environment, Geosciences

(Conference Room PA.1.12. Reception Building, 1st floor, SOLEIL)

Chairpersons: Stéphanie ROSSANO and Emmanuel GUILLON

- 09:00 - 09:30 X-ray absorption spectroscopy to elucidate the behavior of heavy metal in organic waste agricultural recycling
Samuel Legros - invited speaker (CIRAD - Paris, France)
- 09:30 - 09:50 Alteration of green copper-based pigments in model and masterpieces paintings by a multi-analytical approach
Anne-Solenn Le Hô (C2RMF - Paris, France)
- 09:50 - 10:10 Phytostabilization of mining soils by the plant anthyllis vulneraria
Marie-Pierre Isaure (LCABIE- IPREM - Pau, France)
- 10:10 - 10:30 Study of chromium in pigments and enamels produced at the “Sèvres cité de la céramique”
Louisiane Verger (IMPMC - Paris, France)
- 10:30 - 10:50 Application of microscopic and synchrotron-based techniques in microbe/radionuclide interaction studies
Mohammed L. Merroun (University of Granada, Spain)
- 10:50 - 11:20 *Coffee break*
- 11:20 - 11:50 Abiotic synthesis of prebiotic molecules in the recesses of the oceanic lithosphere: a SR-Deep UV, SR-FTIR and ToF-SIMS multimodal approach
Bénédicte Menez - invited speaker (Institut de Physique du Globe - Paris, France)
- 11:50 - 12:10 Trace elemental imaging of rare earth elements discriminates tissues at microscale in flat fossils
Pierre Guériaux (MNHN - Paris, France)
- 12:10 - 12:30 Toxicity of Aluminum Nanophases
Armand Masion (CEREGE - Aix-en-Provence, France)

Parallel Sessions Schedule

Diluted Matter

(Conference Room PHENIX, A1.0.59, Main Building, SOLEIL)

Chairpersons: Vincent BOUDON and Francis PENENT

- 09:00 - 09:30 Gyroscopic Destabilization in a Polyatomic Molecule: An unusual Rotational Behaviour Revealed by the AILES Beamline of SOLEIL
Arnaud Cuisset- invited speaker (LPCA - Dunkerque, France)
- 09:30 - 09:50 Synchrotron-based high resolution Fourier transform spectroscopy of PAHs and derivatives
Sébastien Gruet (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 09:50 - 10:10 Multiple photoionization processes of the potassium atom
Pascal Lablanquie (LCP-MR - Paris, France)
- 10:10 - 10:30 Molecular isomer identification in organic aerosols by photoelectrons/photoions coincidence spectroscopy coupled to VUV Synchrotron Radiation: Application to Titan's tholins Analysis
Barbara Miranda (LCP - Orsay, France)
- 10:30 - 10:50 Photoionisation of Si⁺ and silicon hydride molecular ions (SiH⁺, SiH₂⁺, SiH₃⁺)
Eugene T. Kennedy (Dublin City University - Dublin, Ireland)
- 10:50 - 11:20 *Coffee break*
- 11:20 - 11:50 Action spectroscopy of biological ions
Alexandre Giuliani - invited speaker (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 11:50 - 12:10 Soft X-ray spectroscopies as a probe of TiO₂ nanoparticles solvation in the gas phase
Safia Benkoula (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 12:10 - 12:30 The 1s⁻¹2s⁻¹,2p⁻¹ shake up satellites in argon
Ralf Püttner (Freie Universität Berlin, Deutschland)
- 12:30 - 12:50 Spin-forbidden bands and extreme-ultraviolet photodissociation of N₂
Alan N. Heays (Leiden Observatory - Leiden, The Netherlands)
- 12:50 - 13:10 Near-edge X-ray absorption fine structures revealed in core ionization photoelectron spectroscopy
S. Carniato (LCPMR - Paris, France)

Parallel Sessions Schedule

Electronic & Magnetic Property of Matter, Surfaces and Interfaces

(Conference Room Libra, A2.1.32, Main Building, SOLEIL)

Chairpersons: Antonio TEJEDA and Matteo d'ASTUTO

- 09:00 - 09:30 Charge and spin density waves in the light of coherent x-rays
Vincent Jacques - invited speaker (Laboratoire de Physique des Solides - Orsay, France)
- 09:30 - 09:50 Band structure, polarization and switching dynamics in ferroelectrics
Nick Barrett (CEA DSM, IRAMIS - Gif-sur-Yvette, France)
- 09:50 - 10:10 Electronic structure of Metal/ferroelectric Interfaces under Polarization Switching
Julien E. Rault (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 10:10 - 10:30 Plasmon dispersion of titania polymorphs
Francesco Sottile (Ecole Polytechnique - Palaiseau, France)
- 10:30 - 10:50 Hydrogen/deuterium-induced nanotunnel opening within semiconductor sub-surface
Patrick Soukiassian (CEA - Saclay, France)
- 10:50 - 11:20 Coffee break
- 11:20 - 11:40 Structural Origin of the Band-gap in Graphene Armchair Nanoribbons
Irene Palacio (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 11:40 - 12:00 Dirac cone with helical spin polarization in ultrathin α -Sn(001) films
Yoshiyuki Ohtsubo (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 12:00 - 12:30 X-ray magnetic circular dichroism detected by resonant inelastic X-ray scattering: A 2D photon-in, photon-out magnetic spectroscopy
Amélie Juhin - invited speaker (IMPMC - Paris, France)
- 12:30 - 12:50 Co nanodot arrays grown on a ferromagnetic GdAu₂ template: Substrate/nanodot antiferromagnetic exchange
Laura Fernández (Donostia International Physics Center, Spain)
- 12:50 - 13:10 Magnetic anisotropies of ferrofluids measured by XMCD at Fe and Co L_{2,3} edges
Nieli Daffé (UPMC - Paris, France)

Parallel Sessions Schedule

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

(SOLEIL Auditorium, Main Building, SOLEIL)

Chairpersons: Judith MONNIER and Sandra NINET

- 09:00 - 09:30 Contribution from the Synchrotron radiation to the electronic and structural description of Prussian blue analogues
Julien Lejeune- invited speaker (University of Southampton, UK)
- 09:30 - 09:50 Combination of X-ray absorption spectroscopy and X-ray diffraction under high pressure using nano-polycrystalline-diamond anvils
Jean-Paul Itié (Synchrotron SOLEIL - Gif-sur-Yvette, France)
- 09:50 - 10:10 AlH₃: An example of the use of the infrared spectroscopy to study hydrides under pressure
Charles Pépin (Département de Physique Théorique et Appliquée, CEA/DAM - Bruyères-le-Châtel, France)
- 10:10 - 10:30 Abnormal operando structural behavior of sodium battery material: Influence of dynamic on phase diagram of Na_xFePO₄
Florent Boucher (Institut des Matériaux Jean Rouxel, Nantes, France)
- 10:30 - 10:50 First analyses at the MARS beamline above the exemption limits for radioactive materials: Experimental procedures and preliminary results obtained for irradiated ODS ferritic steel
Denis Menut (CEA, DEN, SRMA - Gif-sur-Yvette, France)
- 10:50 - 11:20 Coffee break
- 11:20 - 11:50 Structural and magnetic properties of LuFe₂O₄
Françoise Damay - invited speaker (LLB, CEA-CNRS - Gif-sur-Yvette, France)
- 11:50 - 12:10 Low-energy orbital excitations in FeCr₂S₄ using resonant inelastic X-ray scattering
Stefania Brignolo (LCPMR, Université Pierre et Marie Curie - Paris, France)
- 12:10 - 12:30 Structure of the Cd-Tb approximant to the quasicrystal
Dan Liu (SIMAP, Université de Grenoble - St Martin d'Hères, France)
- 12:30 - 12:50 In-situ tracking of AuCu nanoparticle structure at low pressure of reactant
Axel Wilson (Institut des Nanosciences de Paris, UPMC - Paris, France)
- 12:50 - 13:10 The effect of temperature and pressure on an active pharmaceutical ingredient: L-tyrosine ethyl ester
Béatrice Nicolai (Université Paris Descartes - Paris, France)

CRYSTALLOGRAPHY SATELLITE SESSION
TO SOLEIL USERS' MEETING 2014

SATELLITE SESSION TO SOLEIL USERS' MEETING 2014

PLENARY SESSION

- PT-01 Quasicrystals: structure and dynamics
M. De Boissieu
- PT-02 2D crystallography, a unique tool for unraveling surface and interface
atomic structures
M. Sauvage
- PT-03 Integrated Structural Biology of RNA Polymerase I and III Transcription
C. Mueller
- PT-04 Neutron and x-ray scattering studies of correlated-electron materials
B. Keimer

Quasicrystals: Structure and Dynamics

M. de Boissieu

SIMAP, Université de Grenoble, CNRS, BP 75 38402 St Martin d'Hères Cedex

ABSTRACT

The discovery of quasicrystals in 1982 by Dan Shechtman, who received the 2011 Nobel prize in chemistry, has been a breakthrough in crystallography which led to a paradigm shift and has deeply modified our understanding of long range ordered materials. Indeed, quasicrystals are materials which are long range ordered but without periodicity: their diffraction pattern presents sharp Bragg peaks but with symmetries, such as five-fold rotation axes, incompatible with lattice translation. After an introduction on quasicrystals, recent results on their atomic structure in the binary CdYb system will be presented. Does the long range quasiperiodic order brings in new physical properties? This question will be addressed through the study of dynamics in quasicrystals, both for phonons and phasons. The presentation will illustrate the importance of combining neutron and x-ray scattering techniques.

REFERENCES

1. T. Janssen, G. Chapuis and M. de Boissieu: *Aperiodic Crystals. From modulated phases to quasicrystals*, Oxford University Press, Oxford 2007
2. Takakura H, Gomez C P, Yamamoto A, de Boissieu M and Tsai A P 2007 *Nature Materials* **6** 58.
3. M. de Boissieu, S. Francoual, M. Mihalkovic, K. Shibata, et al. *Nature Materials*, **6**, 977-984, (2007).
4. H. Euchner, T. Yamada, H. Schober, S. Rols, M. Mihalkovic, et al. *J. Phys.: Condens. Matter*, **24**, 415403, (2012).
5. H. Euchner, T. Yamada, S. Rols, T. Ishimasa, Y. Kaneko, J. Ollivier, H. Schober et al. *J. Phys.: Condens. Matter*, **25**, 115405, (2013)
6. T. Yamada, H. Euchner, C. P. Gómez, H. Takakura, R. Tamura and M. de Boissieu *J. Phys.: Condens. Matter*, **25**, 205405, (2013).

2D Crystallography, a Unique Tool for Unraveling Surface and Interface Atomic Structures

M. Sauvage-Simkin², Y. Garreau^{3,1}, A. Coati¹, A. Vlad¹

¹*Synchrotron SOLEIL, Saint Aubin BP 48, 91192 Gif-sur-Yvette Cedex, France*

²*Synchrotron SOLEIL and UR1-CNRS, Saint Aubin BP 48, 91192 Gif-sur-Yvette Cedex, France*

³*Université Paris Diderot, Sorbonne Paris Cité, MPQ, UMR 7162 CNRS, Bâtiment Condorcet, Case courrier 7021, 75205 Paris Cedex 13, France*

ABSTRACT

An overview of the specificity of surface structure analysis using X-ray diffraction methods will be illustrated on several examples from the pioneering LURE experiments to the latest results obtained at SOLEIL on the SixS beamline. The importance of coupling X-ray diffraction with other techniques such as scanning tunneling microscopy together with the mandatory support of theory will be outlined.

Integrated Structural Biology of RNA Polymerase I and III Transcription

C. W. Müller

*European Molecular Biology Laboratory 69117 Heidelberg, Germany
e-mail: cmueller@embl.de*

ABSTRACT

RNA polymerase (Pol) I and Pol III synthesize non-translated RNAs including rRNA, 5S RNA, and tRNAs for ribosome assembly and protein synthesis. Pol I and Pol III transcription initiation machineries are carefully regulated in healthy cells, while misregulation of Pol I and Pol III transcription is observed in a variety of cancers. Our group studies the structure and dynamics of the Pol I and Pol III transcription initiation machineries using an integrated structural biology approach. Recently, we determined the crystal structure of the 14-subunit Pol I enzyme from *Saccharomyces cerevisiae* at 3.0 Å resolution using data mainly obtained at the Soleil synchrotron (1). Biological insights resulting from the Pol I crystal structure will be discussed. Furthermore, we will compare the Pol I structure with the Pol III structure (2) obtained by single-particle electron microscopy at 10 Å resolution and discuss similarities and differences between both enzymes and the way they initiate transcription.

REFERENCES

- (1) Crystal structure of the 14-subunit RNA polymerase I. Fernandez-Tornero C., Moreno-Morcillo M., Rashid U.J., Taylor N.M., Ruiz F.M., Gruene T., Legrand P., Steuerwald U. & Müller C.W. (2013). *Nature* 502, 644-9.
- (2) Conformational flexibility of RNA polymerase III during transcriptional elongation. Fernández-Tornero C., Böttcher B., Rashid U.J., Steuerwald U., Flörchinger B., Devos D.P., Lindner D., Müller C.W. (2010). *EMBO J.* 29, 3762-72.

Neutron and X-ray Scattering Studies of Correlated-electron Materials

B. Keimer

Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany

ABSTRACT

We will discuss complementary neutron and x-ray scattering experiments designed to explore spin, charge, and orbital ordering phenomena in correlated-electron materials. We will first focus on the recent discovery of charge density wave correlations in copper-oxide superconductors, their interplay with high-temperature superconductivity, and their influence on electronic and lattice vibrational excitations. [1-4] We will then discuss recent progress in manipulating such phenomena in metal-oxide heterostructures, with emphasis on nickel-oxide superlattices. [5-8]

REFERENCES

- [1] G. Ghiringhelli et al., *Science* 337, 821 (2012).
- [2] S. Blanco-Canosa et al., *Phys. Rev. Lett.* 110, 187001 (2013).
- [3] M. Le Tacon et al., *Nature Phys.* 10, 52 (2014).
- [4] R. Comin et al., *Science* (in press); DOI: 10.1126/science.1242996.
- [5] A.V. Boris et al., *Science* 332, 937 (2011).
- [6] E. Benckiser et al., *Nature Mater.* 10, 189 (2011).
- [7] A. Frano et al., *Phys. Rev. Lett.* 111, 106804 (2013).
- [8] M. Wu et al., *Phys. Rev. B* 88, 125124 (2013).

SOLEIL USERS' MEETING 2014
PLENARY SESSION

SOLEIL USERS' MEETING 2014

PLENARY SESSION

- PT-05 Using a multi-disciplinary synchrotron approach to analyse the original
marine iodide metabolism
M. Czjck
- PT-06 Unveiling the electronic structure of complex materials: Electrons and
photons "à la carte"
M. Grioni

When Crystallography Meets Marine Biology: The Structure and Evolution of a Marine Bacterial Vanadium Dependant Iodo-peroxidase

J.-B. Fournier^{1,2}, L. Delage^{1,2}, M. Czjzek^{1,2}, E. Rebuffet^{1,2}, R. Grijol^{1,2},
S. Le Panse^{3,4}, L. Meslet-Cladière^{1,2}, J. Rzonca^{1,2}, P. Potin^{1,2},
G. Michel^{1,2} and C. Leblanc^{1,2}

¹UPMC University Paris 6, UMR 7139 Marine Plants and Biomolecules, Station Biologique de Roscoff, F-29682 Roscoff, ²CNRS, UMR 7139 Marine Plants and Biomolecules, Station Biologique de Roscoff, F-29682 Roscoff, ³UPMC University Paris 6, FR2424, Station Biologique de Roscoff, F-29682 Roscoff, ⁴CNRS, FR2424, Station Biologique de Roscoff, F-29682 Roscoff, Bretagne, France

ABSTRACT

Halogenated compounds are abundantly found in nature, and play various biological functions, ranging from chemical defense to signaling molecules. Indeed halogenation is an efficient strategy used to increase the biological activity of secondary metabolites [1] and involves many different halogenating-enzymes [2]. Vanadium-dependent haloperoxidases (VHPO) differ strongly from heme peroxidases in substrate specificity and stability, and instead of a heme group they contain the bare metal oxide vanadate as a prosthetic group. These enzymes catalyze, in the presence of hydrogen peroxide, the oxidation of halides according to the following reaction: $H_2O_2 + X^- + H^+ \rightarrow H_2O + HOX$, wherein X^- represents a halide ion and may be Cl^- , Br^- or I^- . A variety of halocarbons can subsequently be generated if the appropriate nucleophilic acceptors are present.

Since the first discovery of a VBPO in the brown alga *Ascophyllum nodosum* thirty years ago [3], structural and mechanistic studies were focused on two types of eukaryotic VHPO, namely the vanadium-dependent chloroperoxidase (VCPO) from the pathogenic fungus *Curvularia inaequalis* [4], and the vanadium-dependent bromoperoxidases (VBPO) from *A. nodosum* [5], and from red algae *Corallina* sp. [6]. Exponentially-increasing databases of bacterial genomes and metagenomes allow the prediction of VHPO-like genes in numerous bacterial lineages [7]. However the *in vivo* biochemical function of bacterial VCPO were only demonstrated for two marine *Streptomyces* sp. strains, where they are involved in the chlorination cyclization steps of antibiotic biosynthesis [8,9]. A functional VBPO was also reported in two strains of the marine cyanobacterium *Synechococcus* sp., and gene homologs detected in cyanobacterial environmental DNA samples [10].

A genome sequencing project on the marine flavobacterium *Zobellia galactanivorans* provided us with new VHPO homologous sequences. This presentation will focus on the enzymatic and structural analysis of the first iodide specific VIPO from *Z. galactanivorans*, using a multi-disciplinary synchrotron approach. Phylogenetic analyses combined with functional and structural data shed a new light on the history of the vanadium dependent HPO and on the evolution of iodine specificity among both bacterial and algal phyla.

REFERENCES

1. Butler A, Sandy M. *Nature*. **2009**, 460 (7257):848-54
2. Wagner C, El Omari M, König GM. *J Nat Prod*. **2009**, 72 (3):540-53
3. Vilter, H. *Le Jol Bot. Mar.* **1983**, 26 (9): 429-435
4. Messerschmidt A, Wever R. *Proc Natl Acad Sci U S A*. **1996**, 93 (1):392-6
5. Weyand M, Hecht H, Kiess M, Liaud M, Vilter H, Schomburg D. *J Mol Biol*. **1999**, 293 (3):595-611
6. Isupov MN, et al. & Littlechild JA. *J Mol Biol*. **2000**, 299(4):1035-49
7. Winter JM, Moore BS. *J Biol Chem*. **2009**, 284 (28):18577-81
8. Winter JM, et al. & Moore BS. *J Biol Chem*. **2007**, 282 (22):16362-16368
9. Kaysser L, Bernhardt et al. & Moore BS. *J Am Chem Soc*. **2012**, 134(29):11988-91
10. Johnson, TL, Palenik B, Brahmsha B. *J. of Phycol.* **2011**, 47:792-801.

Unveiling the Electronic Structure of Complex Materials: Electrons and Photons “à la carte”

M. Grioni

Institute of Condensed Matter Physics – EPFL – Lausanne (Switzerland)

ABSTRACT

Synchrotron radiation (SR) is a uniquely powerful tool to probe the electronic structure of matter. Indeed, spectroscopic techniques such as angle-resolved photoelectron spectroscopy (ARPES) thrived and gained in relevance following the dramatic improvements in SR sources. Using result from recent literature, I will briefly show that modern SR ARPES provides information of unprecedented accuracy on the crucial quasiparticle excitations of electronic materials.

Still, useful as (photo-)electrons may be, perhaps the most exciting recent developments in the field come from a technique where “photons do it all”. Resonant Inelastic x-ray Scattering (RIXS) fully exploits the performances of 3rd generation SR sources. I will flash some recent examples of the original insight that RIXS offers in the electronic and magnetic properties of matter.

PARALLEL SESSIONS

PARALLEL SESSION

Biology - Health

Chairpersons: Valérie BIOU and Isabelle BROUTIN

- IT-01 Structural Flexibility Revealed by Three Nitric Oxide Sensors
P. Nioche
- OC-01 Deciphering the binding mode of Trm112 activator with four structurally
related methyltransferases involved in protein synthesis
J. Létouquart
- OC-02 Function of Fap7 in the maturation of the ribosome small subunit
M. Blaud
- OC-03 Structural studies of bacterial effectors hijacking cellular Arf GTPases
M. Folly-Klan
- OC-04 The periplasmic binding protein AccA from agrobacterium tumefaciens
A. El Sahili
- IT-02 How random are intrinsically disordered proteins? A small angle X-ray
scattering perspective
V. Receveur-Brechot
- OC-05 A comprehensive mechanism of fibrin network formation involving early
branching and delayed single-to double-strand transition from coupled time-
resolved SAXS and MALS
M. Rocco
- OC-06 Synchrotron deep UV fluorescence microspectroscopy: An efficient method
for muscle fibers characterization
C. Chagnot
- OC-07 Unraveling isomeric structures of oligosaccharides by VUVPD and
VUVEPD experiments: Towards an unambiguous and complete sequencing
of Isomers
D. Ropartz
- OC-08 Near-infrared imaging in living cells with lanthanides based nanoMOFs
A. Foucault-Collet

Structural Flexibility Revealed by Three Nitric Oxide Sensors

P. Nioche

*INSERM UMR-S747 Pharmacologie, Toxicologie et Signalisation cellulaire,
UFR Biomédicale des Saints-Pères, IFR 95 75005 Paris, France*

ABSTRACT

In the past four decades, nitric oxide (NO) has become a key signaling molecule because of its ability to regulate several biological processes like blood pressure. Soluble Guanylate Cyclase (sGC), a heme-containing protein, is the only known, specific, NO receptor in human. Therefore, it is an excellent candidate to address NO-related diseases like hypertension and erectile dysfunction. However, despite years of study, the molecular mechanism responsible for activating sGC upon NO binding remains elusive, essentially due to sample instability and lack of crystal structure. The discovery of a molecule capable of efficiently activating this enzyme would have a great potential in clinics.

In order to address these challenges, we have identified biological systems homolog to sGC in prokaryotes. SONO (Sensor Of Nitric Oxide), a NO binding heme-containing domain, is an excellent model for the sGC heme domain with up to 40% sequence identity. We will present our structural results from three different bacterial SONO.

Deciphering the Binding Mode of Trm112 Activator with Four Structurally Related Methyltransferases Involved in Protein Synthesis

J. L etoquart¹, C. Vonny¹, A. Alexandrov¹, V. Heurgu -Hamard³,
E. Huvelle³, D. Lafontaine⁴, N. Lazar², H. van Tilbeurgh²,
D. Liger² and M. Graille¹

¹Laboratoire de biochimie-Ecole Polytechnique-Route de Saclay-91128 Palaiseau cedex,

²IBBMC-Universit  Paris-sud11-B t430-91405 Orsay cedex,

³IBPC-13 rue Pierre et Marie Curie 75005Paris,

⁴ULB-12 Avenue des professeurs Jeener & Brahet-B-6041 Gosselies-Belgique
juliette.letouart@polytechnique.edu

ABSTRACT

In Eukaryotes, Trm112 is a small protein (15kDa) which interacts with and activates four Methyltransferases (MTases): Mtq2, Bud23, Trm11 and Trm9. These four complexes are involved in translation.

The Mtq2-Trm112 complex methylates translation termination factor eRF1 on the universally conserved GGQ motif which is involved in release mechanism of newly synthesized protein (Liger et al, 2011). The Bud23-Trm112 complex is implicated in ribosome biogenesis by methylating guanosine 1575 of 18S rRNA. The Trm11-Trm112 complex methylates guanosine 10 of many tRNAs in yeast, improving their stability. The Trm9-Trm112 complex participates in the modification of wobble uridine 34 of some tRNAs. It catalyses the methylation of the cm5U (5-carboxymethyl Uridine) into mcm5U (5-methoxycarbonylmethyl Uridine) which is the final product of the modification. The full process requires the activity of at least 15 proteins, including the Elongator complex. This methylation enhances the decoding accuracy of specific codons highly represented in some key genes of DNA damage response (Begley et al, 2007).

Despite the low sequence identity, these 4 MTases should adopt a similar fold and should compete to interact with Trm112. Structural and functional studies of the Trm112 complexes will allow us to decipher the mechanism of action of Trm112 and the regulation of this activating hub protein.

As part of my PhD, I have solved the crystal structures of two out of four Trm112 complexes. Moreover, I am particularly interested in characterizing the mechanism of tRNA recognition and modification by Trm9-Trm112 as well as deciphering the biological impact of this modification. Indeed, the human Trm9 orthologue is over-expressed in various types of cancer, including bladder cancer.

I will present a structural comparison of the Trm112 complexes and the functional studies of some mutants of the Trm9-Trm112 complex *in vitro* as well as *in vivo*. These studies pave the road to the mapping of the active site and substrate binding sites in order to understand the mechanism of action of the enzyme and to design potential inhibitors.

REFERENCES

Begley U, Dyavaiah M, Patil A, Rooney JP, DiRenzo D, Young CM, Conklin DS, Zitomer RS, Begley TJ (2007) Trm9-catalyzed tRNA modifications link translation to the DNA damage response. *Mol Cell* **28**: 860-870

Liger D, Mora L, Lazar N, Figaro S, Henri J, Scrima N, Buckingham RH, van Tilbeurgh H, Heurgu -Hamard V, Graille M (2011) Mechanism of activation of methyltransferases involved in translation by the Trm112 'hub' protein. *Nucleic Acids Res* **39**: 6249-6259

Function of Fap7 in the Maturation of the Ribosome Small Subunit

M. Blaud¹, S. Réty¹, J. Loc'h¹, S. Lebaron¹, C. Charenton¹,
S. Grannemann³, D. Tollervey², P. Deschamps¹, J. Jombart¹,
J. Bareille¹ and N. Leulliot¹.

*1 LCRB, UMR 8015 CNRS, Faculté de Pharmacie, Université Paris Descartes,
75270 Paris Cedex 06, France.*

2 Wellcome Trust Centre for Cell Biology, The University of Edinburgh, Scotland

3 SynthSys Edinburgh, The University of Edinburgh, Scotland

ABSTRACT

Over 200 pre-ribosomal factors are involved in the maturation of ribosomes. Most of these factors are essential to cell survival, but their precise function remains elusive. One of the last steps of maturation of the ribosome small subunit is the cleavage of 20S pre-rRNA in 18S rRNA in the cytoplasm. This cleavage is carried out by the endonuclease Nob1 and also requires the presence of other factors such as the methyltransferase Dim1, and a plethora of NTPases including the Rio protein kinases, Prp43 and its cofactor Pfa1, the Ltv1 GTPase and the Fap7 NTPase.

The function of Fap7 is especially intriguing since the human homologue bears adenylate activity, an enzymatic activity not usually found during ribonucleoprotein biogenesis. In addition, the function of Fap7 is intimately linked to its interaction with the Rps14 ribosomal protein. The Rps14 C-terminal domain is essential for D-site cleavage and is located in proximity to the 18S rRNA 3'-extremity in the mature ribosome. The deletion of this protein causes the 5q syndrome that is phenotypically close to Diamond Blackfan anemia. The link between the enzymatic activity of Fap7 and its role in ribosome biogenesis remains enigmatic.

We have conducted functional and structural characterisation of the Fap7 protein alone and in complex with Rps14 and nucleotides. Using a combination of structural studies by X-ray crystallography, small angle X-ray scattering (SAXS) in solution, enzymatic studies on purified proteins, and *in vitro* D site cleavage reaction assays on purified pre-ribosomes, we were able to uncover the function of Fap7 within pre-40S ribosomes. We show that the Fap7/Rps14 interaction is involved in a major conformational change at the heart of the pre-ribosomes and that this structural rearrangement is necessary to expose the D-site for cleavage by the endonuclease Nob1. The link between the enzymatic activity and the conformational switch both before and after cleavage is currently being investigated.

Structural Studies of Bacterial Effectors Hijacking Cellular Arf GTPases

M. Folly-Klan¹, E. Alix², D. Stalder³, P. Ray¹, L.V. Duarte¹, A. Delprato¹,
M. Zeghouf¹, B. Antony³, V. Campanacci¹, C.R. Roy², J. Cherfils¹

¹ Laboratoire d'Enzymologie et Biochimie Structurales, Centre de Recherche de Gif,
CNRS, Gif-sur-Yvette, France,

² Department of Microbial Pathogenesis, Yale University School of Medicine, New Haven,
Connecticut, United States of America,

³ Institut de Pharmacologie Moléculaire et Cellulaire, Université de Nice-Sophia Antipolis
et CNRS, Valbonne, France

ABSTRACT

The intracellular gram-negative bacterium *Legionella pneumophila* is responsible of Legionnaires diseases. These bacteria invade and proliferate within macrophages after taking control of host cell trafficking processes, leading to the establishment of the *Legionella*-containing vacuole (LCV) where the pathogen hides and replicates. To that purpose, the pathogen translocated several bacterial effectors in the host cell using a Type IV secretion system. One of these effectors, RalF, recruits the small GTP-binding protein (GTPase) Arf1 to the LCV. RalF is made up of two domains: a Sec7 domain related to cellular guanine nucleotide exchange factors (ArfGEFs), whose active site is auto-inhibited by a capping domain unrelated to any eukaryotic domain.

We found that membranes activate LpRalF and identified the membrane-binding region as the region that inhibits the Sec7 active site. It is enriched in aromatic and positively charged residues, which establish a membrane sensor to control the GEF activity in accordance with specific lipid environments. A similar mechanism of activation is found in RalF from *Rickettsia prowazekii* (Rp), with a different aromatic/charged residues ratio that results in divergent membrane preferences. We demonstrated that RalF proteins are regulated by a membrane sensor that functions as a binary switch to derepress ArfGEF activity when RalF encounters a favorable lipid environment, thus establishing a regulatory paradigm to ensure that Arf GTPases are efficiently activated at specific membrane locations. I will also show the preliminary structural studies highlighting the functional differences between LpRalF and RpRalF.

REFERENCES

Folly-Klan M, Alix E, Stalder D, et al. (2013) A Novel Membrane Sensor Controls the Localization and ArfGEF Activity of Bacterial RalF. *PLoS Pathog* 9(11): e1003747

The Periplasmic Binding Protein AccA from *Agrobacterium tumefaciens*

A. El Sahili¹, D. Faure², S. Morera¹

1-LEBS UPR 3082, CNRS, Avenue de la Terrasse, Gif Sur Yvette, 91198

2-ISV UPR 2355, CNRS, Avenue de la Terrasse, Gif Sur Yvette, 91198

ABSTRACT

Agrobacterium tumefaciens is a soil bacterium that is pathogenic for several plants causing the crown gall disease, which is characterized by tumour formation at the infection site. The infection mechanism is well known and composed of 4 steps:

- 1- The wound on the plant activates *A. tumefaciens*' virulence plasmid.
- 2- T-DNA, a piece of the pTi is transferred to the plant's cell and integrated to its genome.
- 3- The plant secretes hormones, triggering the tumour formation, tumours which are colonized by *A. tumefaciens*. The plant also secretes opines including agrocinopine used as energy source by the bacterium.
- 4- Agrocinopine also activates the quorum sensing mechanisms in *A. tumefaciens* leading to the propagation of the pTi to non-virulent bacteria¹.

Agrocinopine is imported in the bacteria by the Acc system². Acc is composed of an ABC transporter and a periplasmic binding protein namely AccA which recognizes agrocinopine. Genetic studies³ have shown that AccA is also responsible for the import of Agrocin 84, a lethal toxin, produced by the bacteria *A. radiobacter* K84.

The subject of my thesis is to understand the interaction specificity of the PBP AccA with agrocinopine and agrocin 84, combining structural and biochemical studies. We determined the first 3D structure of a PBP in complex with its opine ligand and in complex with the toxin Agrocin 84 allowing us to identify the interactions with each ligand. Using microcalorimetry and structural analysis, we characterized the Acca specificity towards ligands leading to their cytoplasm import by the specific Acc ABC transporter.

REFERENCES

1. Beck von Bodman, S., Hayman, G. T. & Farrand, S. K. Opine catabolism and conjugal transfer of the nopaline Ti plasmid pTiC58 are coordinately regulated by a single repressor. *Proceedings of the National Academy of Sciences of the United States of America* 89, 643–7 (1992).
2. Kim, H. & Farrand, S. K. Characterization of the acc operon from the nopaline-type Ti plasmid pTiC58, which encodes utilization of agrocinopines A and B and susceptibility to agrocin 84. Characterization of the acc Operon from the Nopaline-Type Ti Plasmid pTiC58, Which Encodes. *Journal of bacteriology* 179, 7559 (1997).
3. Vicedo, B., Peñalver, R., Asins, M. J. & López, M. M. Biological Control of *Agrobacterium tumefaciens*, Colonization, and pAgK84 Transfer with *Agrobacterium radiobacter* K84 and the Tra Mutant Strain K1026. *Applied and environmental microbiology* 59, 309–15 (1993).

How Random are Intrinsically Disordered Proteins ? A Small Angle X-ray Scattering perspective

V. Receveur-Bréchet

*Cancer Research Center of Marseille (CRCM) UMR7258 CNRS-INSERM-AMU-IPC
27 Boulevard Leï Roure BP30059 F-13273 Marseille Cedex 9, FRANCE*

ABSTRACT

Intrinsically disordered proteins (IDPs) are currently in the limelight of the most recent and exciting structure-function relationship studies. These proteins have overthrown the long-lived idea that a definite 3D structure of a protein dictates its function. Far from being the exception that proves the rule, they have revealed to be extremely abundant in the cell, especially in eukaryotes, and have been shown to fulfill numerous essential functions in the cellular cycle. They are often at the crossroad of interaction networks and cellular signaling pathways, as they may be implicated in molecular recognition processes with multiple partners, sometimes through an induced folding mechanism. Deciphering their molecular mode of action at the structural level still remains highly challenging and requires a combination of many biophysical approaches. Among them, small angle X-ray scattering (SAXS) has been extremely successful in the last decade and has become an indispensable technique for addressing many of the fundamental questions regarding the activities of IDPs^{1,2}.

After a general introduction on IDPs, I will present as examples recent results that we obtained on several IDPs. A special emphasis will be made on integrated computational approaches that now enable the generation of ensembles of conformers to translate the unique flexible characteristics of IDPs by taking into consideration the constraints of more and more various complementary experiment. In particular, a combination of SAXS with high-resolution techniques, such as x-ray crystallography and/or NMR, allow us to gain unique structural insights about the protein over multiple structural scales.

REFERENCES

1. Receveur-Bréchet V. & Durand D. (2012) How random are intrinsically disordered proteins ? A Small Angle Scattering perspective. *Curr Prot. Pept. Science*, 13(1), 55-75.
2. Czjzek M., Fierobe HP, Receveur-Bréchet V (2012) Small angle X-ray scattering and crystallography, a winning combination for exploring the multi-modular organisation of cellulytic macromolecular complexes, *Methods in Enzymology*, 510, 183-210.

A Comprehensive Mechanism of Fibrin Network Formation Involving Early Branching and Delayed Single-to Double-Strand Transition from Coupled Time-resolved SAXS and MALS

M. Rocco¹, M. Molteni², M. Ponassi¹, G. Giachi³,
A. Koutsioubas⁴, A. Profumo¹, D. Trevarin⁴, B. Cardinali⁵,
P. Vachette⁶, F. Ferri^{2,4}, and J. Pérez⁴

¹*Biopolimeri e Proteomica, IRCCS AOU San Martino-IST, Genova, Italy;*

²*Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria, Como, Italy;*

³*Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Firenze, Italy;*

⁴*SWING beamline, Synchrotron SOLEIL, Gif-sur-Yvette, France;*

⁵*Department of Pathology and Laboratory Medicine, University of North Carolina at Chapel Hill, Chapel Hill, NC, USA;*

⁶*IBBMC, CNRS-Université Paris-Sud UMR8619, Orsay, France*

ABSTRACT

The formation of a fibrin network after enzymatic activation of fibrinogen is the central event in the vertebrates' blood coagulation. It is also involved in several pathologies, such as thrombosis and cancer metastasis, and has widespread biomedical/biotechnological applications. It basically consists of two complementary processes: elongation/branching generates an interconnected 3D scaffold of relatively thin fibrils, cooperative lateral aggregation thickens them more than ten fold. The early stages up to the gel point were studied by fast fibrinogen:enzyme mixing experiments using simultaneous SAXS and multi-angle light scattering (MALS) detection. The coupled evolution of the weight-average molecular weight $\langle M \rangle_w$, z-average square radius of gyration $\langle R_g^2 \rangle_z$, and z-average square cross-section radius of gyration $\langle R_c^2 \rangle_z$ of the growing fibrils were thus recovered. Extensive modeling suggests the rapid elongation of single-bonded "Y ladder" polymers that undergo a delayed transition to the classic half-staggered, double-stranded fibrils. Consistent with the data, this mechanism can generate frequent, random branching points in each growing fibril. Branches in these expanding "lumps" will eventually interconnect, forming the pervasive 3D network. The proposed mechanism further predicts that, while still growing, other branches will undergo a Ca⁺⁺/length-dependent cooperative collapse on the resulting network scaffolding filaments, explaining their sudden thickening, low final density, and basic mechanical properties. Besides the present application, the SAXS/MALS combination developed in the present study could be profitably employed to study the structural dynamics of other biological relevant processes involving the formation, elongation and thickening of fibrous-like structures, such as, e.g., intermediate filaments, microtubules, collagen, and β -amyloid.

Synchrotron Deep UV Fluorescence Microspectroscopy: An Efficient Method for Muscle Fibers Characterization

C. Chagnot^{a, b}, A. Vénien^a, F. Peyrin^a, F. Jamme^{c, d},
M. Réfrégiers^c, M. Desvaux^b and T. Astruc^{a*}

^aUR370 Qualité des Produits Animaux, INRA, F-63122 Saint-Genès Champanelle, France.

^bUR454 Microbiologie, INRA, F-63122 Saint-Genès Champanelle, France

^cSynchrotron SOLEIL, BP48, L'Orme des Merisiers, F-91120 Gif sur Yvette, France

^dINRA, UAR1008 CEPIA, Rue de la Géraudière, F-44316 Nantes, France

*Thierry.Astruc@clermont.inra.fr

Tel.(33) 4 73 62 41 56

ABSTRACT

Mammals skeletal muscles are generally composed of 4 muscle fibers types (identified I, IIA, IIX & IIB) characterized by the combination of their metabolic pathway which could be oxidative (type I & IIA) or glycolytic (IIX & IIB) and their contraction speed which could be slow (type I) or fast (type IIA, IIX & IIB). Muscles generally comprise various proportions of each muscle fiber type depending on the muscle's function. This fiber composition is of great importance in a wide range of scientific fields, such as clinical research, biomechanics studies or muscle food science. Usually, muscle fibers types are identified by histoenzymological or immunohistochemical techniques (**Figure 1**). However, these techniques are quite time consuming, expensive and require a skilled laboratory personnel. For the first time in the world, we have explored the relevance of Deep UltraViolet Fluorescence (DUV) microspectroscopy to characterize the different muscle fibers types previously identified by immunohistochemistry. Two rat muscles were chosen for this experiment : the Extensor Digitorum Longus muscle (EDL) containing the four fiber types and the Soleus muscle containing only I and IIA muscle fiber types. Muscle fibers were excited at 275 nm and the emission response was acquired from 290 to 540 nm. Multivariate analyzes showed a discrimination of oxidative fibers (I, IIA) from glycolytic fibers (IIB, IIX) and between fast (I) and slow (II) contraction speed fibers in the two muscles at 305 nm and 330 nm respectively assigned to Tyrosine and Tryptophan and at 410 nm from an unidentified fluorophore. Separation is clearer on the soleus than on the EDL muscle which is composed of four fiber types (**Figure 2**). Deep UV Fluorescence Microspectroscopy could discriminate directly the various types of muscle fibers in histological sections without the use of dyes or probes. These results are very encouraging and suggest that muscles typing can be done by acquiring fluorescence map of muscle tissue sections.

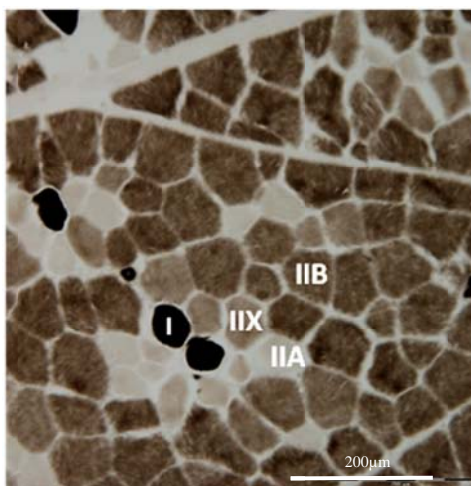


Figure 1: Identification of muscle fiber type (I, IIA, IIX and IIB) by histoenzymology based on the ATPase activity of myosin heavy chains.

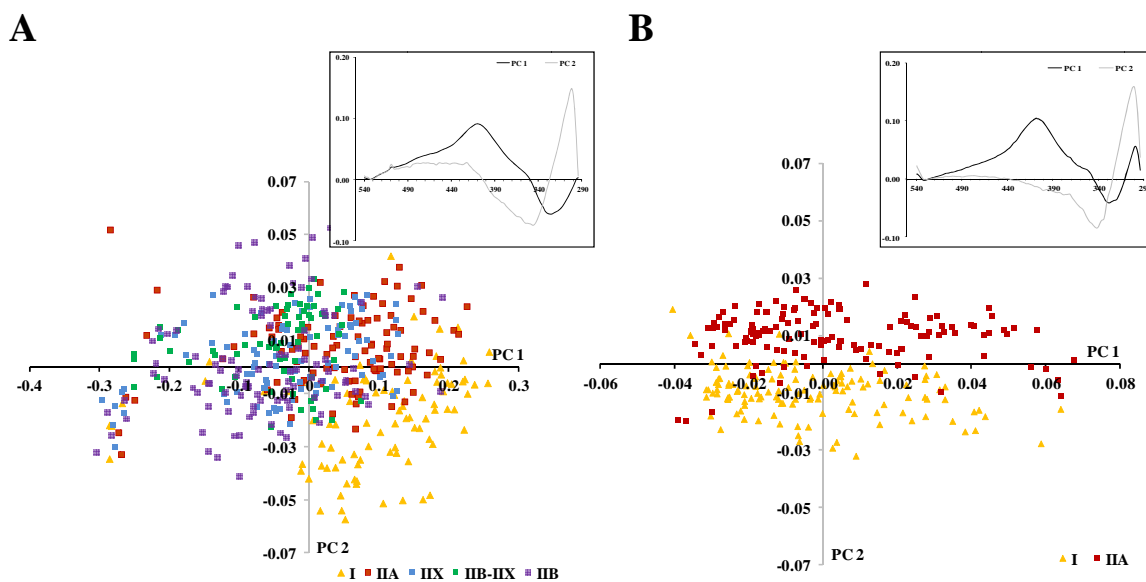


Figure 2 : Scores and loadings (PC1 and PC2) of autofluorescence response of fiber types I, IIA, IIX, IIB and IIX-IIB hybrid fibers found in EDL muscle (A) and fiber types I and IIA composing the soleus muscle (B).

Unraveling Isomeric Structures of Oligosaccharides by VUVPD and VUVEPD Experiments: Towards an Unambiguous and Complete Sequencing of Isomers

D. Ropartz¹; A. Giuliani^{2,3}; J. Lemoine⁴; M.C. Ralet¹; H. Rogniaux¹

¹.INRA, UR1268 Biopolymers Interactions Assemblies F-44316 NANTES, France

²Synchrotron SOLEIL, L'Orme des Merisiers, F-91190 Gif-sur-Yvette, France

³UAR 1008 CEPIA, INRA, F-44316 NANTES, France

⁴.Institut des Sciences Analytiques, UMR 5280, Université Lyon 1-CNRS, Université de Lyon F-69622 Villeurbanne cedex, France

ABSTRACT

Structural characterization of carbohydrates is of key importance to better understand the structure/property relationships of these molecules, as well as to tailor compounds with enhanced functionalities. Mass spectrometry, with its remarkable sensitivity, rapidity and high information content, is a forefront method for that purpose. However, classical tandem mass spectrometry based on low-energy collision-activated dissociation (LE-CAD) fails in many cases to achieve definitive structural assignments.

In this work, we investigated Vacuum Ultra-violet (VUV) synchrotron radiation as activation process for tandem mass spectrometry in positive and negative ion mode. A very interesting setup is implemented on the DISCO beamline which couples the synchrotron radiation with an ion trap mass spectrometer and enables the tuning of the photons energy between 5 and 22 eV.

This study is the first one reporting the use of photo-activated dissociation in the VUV for large oligosaccharides. The features of the fragmentation spectra are remarkable and bring straightforward and rich structural information. This led to the comprehensive identification of a large number of structures, including many isomers. This enabled to reach by far the most complete description of the products released from the enzymatic degradation of polysaccharides, bringing insights both on the structure of these polymers as well as on the enzyme specificity. In that context, we believe that the advances brought by VUV activation in tandem MS will meet a widespread interest in the field of structural chemistry of carbohydrates.

REFERENCES

1. Ropartz, D.; Lemoine, J.; Giuliani, A.; Bittebiere, Y.; Enjalbert, Q.; Antoine, R.; Dugourd, P.; Ralet, M.-C.; Rogniaux, H. *Analytica Chimica Acta*. In Press, Accepted Manuscript
2. Milosavljevic A.R., Nicolas C., Gil J. F., Canon F., Refregiers M., Nahon L., Giuliani A.: *Journal of Synchrotron Radiation*, 19, 174-178 (2012).

Near-infrared Imaging in Living Cells with Lanthanides based NanoMOFs

A. Foucault-Collet^a, K.A. Gogick^b, N.L. Rosi^b, S. Petoud^{a,b}

^a*Centre de Biophysique Moléculaire, CNRS, rue Charles Sadron, 45071 Orléans, France*

^b*Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260*

ABSTRACT

We have created novel near-infrared-emitting nanoscale metal-organic frameworks (nano-MOFs) incorporating a high density of Yb³⁺ lanthanide cations and sensitizers derived from phenylene. We establish here that these nano-MOFs can be incorporated into living cells for near-infrared (NIR) imaging.

The use of near-infrared (NIR) photons is beneficial for improved detection sensitivity in biological systems because 1) biological systems have lower autofluorescence in the NIR, resulting in higher signal-to-noise ratios and detection sensitivity; and 2) the lower scattering of NIR photons allows for the acquisition of higher resolution images. Furthermore, the luminescence of NIR emitting lanthanide cations is very attractive due to its emission wavelength and the photostability of the luminescent reporters. In order to take advantage of such luminescence, lanthanide cations need to be sensitized. In order to maximize the number of photons per unit volume, we have chosen to create a nanomaterial incorporating a high density of lanthanide cations and lanthanide sensitizers.

We present here a new nanoscale metal-organic framework (nanoMOF) based on a (PVDC)sensitizer-ligand and Yb³⁺NIR-emitting lanthanide cation. This material has been structurally characterized, its stability in various media has been assessed, and its luminescent properties have been studied. We demonstrate that it is stable in certain specific biological media, does not photobleach, and has an IC₅₀ of 100 µg/mL, which is sufficient to allow live cell imaging. Confocal microscopy and ICP measurements reveal that nano-Yb-PVDC-3 can be internalized by cells with a cytoplasmic localization. Despite its relatively low quantum yield, nano-Yb-PVDC-3 emits a sufficient number of photons per unit volume to serve as a NIR-emitting reporter for imaging living HeLa and NIH 3T3 cells. NIR microscopy allows for highly efficient discrimination between the nanoMOF emission signal and the cellular autofluorescence arising from biological material. This work represents one of the first demonstrations of the possibility of using NIR lanthanide emission for biological imaging applications in living cells with single photon excitation.

Acknowledgements : La Ligue Régionale contre le Cancer, Le Cancéropôle Grand-Ouest, La Région Centre.

PARALLEL SESSION

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

Chairpersons: Sandrine LYONNARD and Elise BERRIER

- IT-03 Amorphous to crystal conversion as a mechanism governing oxide nanoparticle
D. Carrière
- OC-09 Quick-EXAFS-Raman and SAXS study of formation and growth of SnO₂ nanoparticles
B.L. Caetano
- OC-10 Controlling nanoparticles dispersion in ionic liquids by tuning the pH
C. Guibert
- OC-11 The electrochemical mechanism of Na insertion in Sb-based negative electrode materials for innovative Na-ion batteries: The first discharge
L. Stievano
- OC-12 Connectivity of water molecules confined in nafion
S. Dalla Bernardina
- IT-04 Understanding the nature and transformations of dispersed phases: Synchrotron radiation and heterogeneous catalysts
E. Marceau
- OC-13 New insights on the impact of Co-components on the formation of the active supported Pd/TiO₂ catalysts during the gas phase acetoxylation obtained with operando XAS
J. Radnik
- OC-14 In-situ study of silicon oxide growth from tetraethoxysilane (TEOS) using near-ambient pressure XPS
G. Olivieri
- OC-15 Study of uranyl and thorium complexation with phosphorylated biomolecules
G. Creff
- OC-16 Ionization and enhanced photochemistry of nitric acid on ice
P. Parent

Amorphous to Crystal Conversion as a Mechanism Governing Oxide Nanoparticle Structure

B. Fleury,^{a,b} M.A. Neouze,^{a,b} J.M. Guigner,^c N. Menguy,^c
O. Spalla^b, T. Gacoin^a and D. Carriere^{*b}

^a *Groupe de Chimie du Solide, Laboratoire de Physique de la Matière Condensée, UMR CNRS 7643, École Polytechnique, 91128 Palaiseau, France.*

^b *CEA Saclay, IRAMIS, UMR CEA/CNRS 3299 SIS2M, 91191 Gif sur Yvette, France*

^c *IMPMC, UMR 7590 CNRS, Université Pierre et Marie Curie, 75252 Paris*

ABSTRACT

The development of functional materials by taking advantage of the physical properties of nanoparticles needs an optimal control over their size and crystal quality. In this context, the synthesis of crystalline oxide nanoparticles in water at room temperature is a versatile and industrially appealing process, but lacks control especially for “large” nanoparticles (> 30 nanometres), which commonly consist of agglomerates of smaller crystalline primary grains. Improvement of these syntheses is hampered by the lack of knowledge on possible intermediate, non-crystalline stages, although their critical importance has already been outlined in crystallisation processes.

Here, we combined time-resolved, in situ SAXS/WAXS and EXAFS to demonstrate that during the synthesis of luminescent Eu-doped YVO₄ nanoparticles, a transient amorphous network forms with a two-level structuration. These two pre-structuration scales constrain topologically the nucleation of the nanometre-sized crystalline primary grains, and their aggregation in nanoparticles, respectively. The amorphous network, which forms within 40 ms, therefore determines the nanocrystalline structure, which forms in the minute range.

This template effect not only clarifies why the crystal size is found independent of the nucleation rate, in contradiction with the classical nucleation models, but also supports the possibility to control the final nanostructure with the amorphous phase.

Quick-EXAFS-Raman and SAXS Study of Formation and Growth of SnO₂ Nanoparticles

B.L. Caetano^{a,b}, F. Meneau^b, M. Magnani^a, C.V. Santilli^a,
S.H. Pulcinelli^a, V. Briois^b

^a*Instituto de Química UNESP¹, PO Box 355, 14800-900 Araraquara, SP, Brazil*

^b*Synchrotron SOLEIL, L'Orme des Merisiers, BP48, Saint Aubin, 91192 Gif-sur Yvette, France*

ABSTRACT

Tin dioxide (SnO₂) is an important n-type semiconductor (3.6 eV band gap at 300 K) with wide range of applications such as solar cells, catalysts, transparent electrodes, gas sensor, and thermoelectric materials among others^{1,2}. Although a deep understanding of formation and growth mechanisms of these systems provides guidance to the control of properties during synthesis³, the mechanisms that allow to obtain SnO₂ nanoparticles are not yet well known. This work describes the formation and growth of SnO₂ nanoparticles from tin tetrachloride pentahydrate (SnCl₄.5H₂O) ethanolic solutions by water addition, [H₂O]/[Sn] = 105. Simultaneous Sn K-edge quick-EXAFS and Raman measurements were carried out at the SAMBA beamline for unravelling the local order around Sn whereas SAXS investigation at the SWING beamline was used for structural characterisation at the nanoscopic scale. Each quick-EXAFS spectrum is described by a linear combination of the spectrum of the SnO₂ powder extracted at the end of the reaction and a representative EXAFS spectrum of monomeric species in solution. From the beginning to the end of the reaction the composition evolved from 0% to ~30% of SnO₂ nanoparticles. Before water addition, SAXS and Raman evidence the formation of a solution composed of monomeric species [SnCl_x(H₂O)_{6-x}]^{4-x} with x= 6, 5, 4 and Guinier radius R_g equal to 1.9 Å. The results show that the formation of SnO₂ nanoparticles is a stepped process composed from three main stages: i) during the ageing at RT, the exchange of chlorine by oxygen was clearly verified by the modifications of Sn-Cl and Sn-O EXAFS coordination numbers that result from the partial consumption of the [SnCl_x(H₂O)_{6-x}]^{4-x} with x= 6 and 5. Concomitantly the R_g radii of scattering species gradually increase to 10.7Å with variation suggesting the successive association of monomeric species; ii) during heating (RT<T<70°C), an uptake of chlorine ions by tin coordination sphere evidenced by both Raman and quick-EXAFS spectroscopies gives rise to the slight decrease of R_g indicating that the equilibria between species in solution is a key parameter driving the growth process; iii) during the isothermal treatment at 70°C, the growth of SnO₂ particles restarts, SAXS pattern showing that the R_g of well defined (Porod slope = -3) particles reaches 12.5 Å. Otherwise, the Sn-Cl coordination number decreases indicating the further exchange of Cl by O shifting the reaction equilibrium.

REFERENCES

1. J. Phys. Chem. C.2011, 115, 118–124.
2. J. Am. Chem. Soc. 2012, 134, 6785 – 679.
3. J. Am. Chem. Soc. 2012, 134, 16228– 16234.

Controlling Nanoparticles Dispersion in Ionic Liquids by Tuning the pH

C. Guibert^a, F. Cousin^b, F. Meneau^c, V. Dupuis^a, J. Fresnais^a, V. Peyre^a

^a *Laboratoire Physico-Chimie des Electrolytes, Colloïdes et Sciences Analytiques (PECSA)
UMR 7195 Université Pierre & Marie Curie – CC 51, 4, place Jussieu,
75252 PARIS Cedex 5 – France*

^b *Laboratoire Léon Brillouin, UMR 12, CEA Saclay, 91191 Gif-sur-Yvette Cedex – France*

^c *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette Cedex – France*

ABSTRACT

Ionic liquids (ILs) are nowadays of uttermost interest to develop new materials. Among them, dispersions of nanoparticles (NPs) in ILs are promising combinations, e.g. for catalyst and batteries, but remain a challenging task since the electrostatic stabilisation often occurring in molecular liquids is likely to differ in ILs. Hence, keeping NPs dispersed in an IL arises ticklish problems of colloidal stability.

On the one hand, we used ethylammonium nitrate (EAN), a well characterised IL that shares many similarities with water; in particular, it is a protic IL.

On the other hand, magnetic NPs give way to numerous promising applications such as magnetic hyperthermia or catalysis. Synergetic behaviours could occur by combining those two components. In our work, we demonstrated that poly(acrylic acid) (PAA) coated maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs give stable dispersions in salted aqueous solutions as well as in EAN. In water, this coating displays an interesting response with the pH leading to reversible flocculation/redispersion of the coated NPs [1]. It is due to the protonation/deprotonation of the acidic groups of the polymer (figure 1) and it has been fully characterised with the help of SAXS experiments on SWING beamline at the SOLEIL synchrotron.

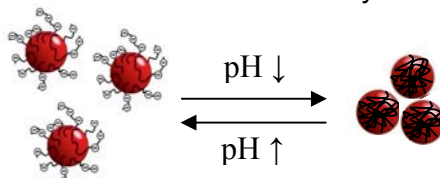


Fig. 1. Reversible mechanism of flocculation/redispersion of PAA coated NPs

Surprisingly, this interesting and reversible transition is preserved in EAN. SAXS experiments shed light upon the mechanisms responsible both for colloidal stability and for this reversible flocculation in EAN (figure 2). These results give a brand new insight on the use of pH for tuning the dispersion state of NPs in protic ILs and an interesting example of similarities between EAN and water.

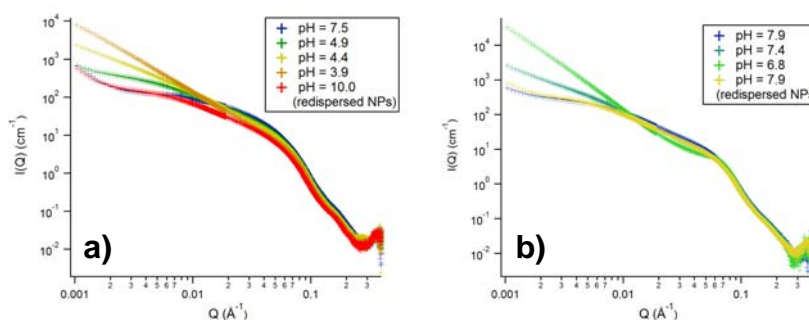


Fig. 2 Spectra of PAA2k coated 6nm maghemite NPs for different pH a) in water, b) in EAN.

REFERENCES

1. J. Fresnais, M. Yan, J. Courtois, T. Bostelmann, A. Bee, J.F. Berret, , *J Colloid Interface Sc.*, **395**, 24-30 (2013)

The Electrochemical Mechanism of Na Insertion in Sb-based Negative Electrode Materials for Innovative Na-ion Batteries: The First Discharge

A. Darwiche¹, M.T. Sougrati¹, B. Donnadieu¹, C. La Fontaine², S. Belin²,
B. Fraisse¹, L. Monconduit¹ and L. Stievano¹

¹ ICG-AIME, UMR 5253, Univ. Montpellier 2, place E. Bataillon, 34095 Montpellier cedex 5 (France)

² Synchrotron SOLEIL, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette cedex (France)

ABSTRACT

Na-ion batteries is a viable substitute for lithium in large-scale systems (e.g., storage systems in smart grids) because of the widespread abundance and low cost of sodium-containing precursors.[1] For these reasons, Na-based storage systems working at ambient temperature have recently regained a certain interest.[2-3]

Alloy materials have shown lately to be a valid alternative to hard carbon as negative electrode materials, and in particular antimony-based electrodes were shown to be very promising, sustaining over 160 cycles at C/2 without any capacity fading vs. Na, whereas the same material vs. Li shows a constant decrease of the capacity upon cycling. [4] In particular, it was shown that the reaction mechanism of Sb with Na can neither be trivially deduced from that with Li nor from the reading of the phase diagrams, in line with similar results recently shown also on tin electrode materials. [5]

To shed more light in the electrochemical mechanism of Sb-based systems during electrochemical reaction with Na, we have undertaken a detailed study of the physico-chemical state of Sb during electrochemical cycling in Na-based batteries. To this end, Sb K-edge X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) were used under *operando* conditions together with other *ex situ* techniques. However, the Sb-Na species formed during cycling were found to be partially amorphous, and until now could not be identified by XRD. On the contrary, XAS was a particularly valuable tool to follow in detail the changes in oxidation state and coordination environment of Sb centres during the first discharge.

The collected results, supported by previous *ex situ* ¹²¹Sb Mössbauer spectroscopy measurements, allowed us to have a more complete and precise description of the first discharge of Sb vs. Na. These results have potentially a very high impact for the promotion of alloy materials as stable negative electrode materials for Na-ion batteries.

REFERENCES

1. B. L. Ellis, W. R. M. Makahnouk, Y. Makimura, K. Toghill, L. F. Nazar, *Nature Mater.* **6**, 749-753 (2007).
2. V. L. Chevrier, G. Ceder, *J. Electrochem. Soc.* **158**, A1011-A1014 (2011).
3. S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, *Adv. Energy Mater.* **2**, 710-721 (2012).
4. A. Darwiche, C. Marino, M. T. Sougrati, B. Fraisse, L. Stievano, L. Monconduit, *J. Am. Chem. Soc.* **134**, 20805-20811 (2012).
5. L. D. Ellis, T. D. Hatchard, M. N. Obrovac, *J. Electrochem. Soc.* **159**, A1801-A1805 (2012).

Connectivity of Water Molecules Confined in Nafion

S. Dalla Bernardina¹, J.B. Brubach¹, P. Roy¹, Q. Berrod²,
P. Judeinstein^{3,4}, J.M. Zanotti^{3,4}, A. Guillermo², S. Lyonard²

¹Société civile Synchrotron SOLEIL, AILES beamline, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 GIF-sur-YVETTE Cedex, France,

²CEA Grenoble, INAC SPrAM, Lab Polymeres Conducteurs Ion, CEA CNRS UJF, UMR 5819, F-38054 Grenoble 9, France,

³CEA, Lab Leon Brillouin, DSM, IRAMIS, F-91191 Gif Sur Yvette, France, ⁴CEA Saclay, CNRS UMR 12, F-91191 Gif Sur Yvette, France

ABSTRACT

Perfluorosulfonic acid ionomeric membranes are used in proton exchange membrane fuel cells (PEM-FCs) as electrolytes, enabling proton conduction from the anode to the cathode to derive electrical energy directly from a chemical fuel. Currently the best PEM in fuel cells is Nafion due to its unchallenged proton conductivity at temperatures below 80°C. Nafion consists in a hydrophobic fluorocarbon backbone chain with pendent hydrophilic side chains which terminate with sulfonic acid groups. These terminations give to the membrane the ionic properties. Proton conductivity is directly related to the water content in Nafion, therefore a molecular understanding of the proton conduction mechanisms and the structure/transport interplay is required to improve fuel cells performances.

The interaction between water molecules and Nafion membrane was studied by Fourier Transform Infrared Spectroscopy (FTIR) at the AILES beamline in both the far and mid infrared regions during *in situ* absorption and desorption of water molecules. Far infrared region provides information about the hydrogen bond O-H...O between different water molecules (connectivity and libration bands) while in mid infrared region we observe the intramolecular modes of water molecules (stretching and bending bands).

To monitor the effect of water molecules on Nafion at different levels of relative humidity (RH), the sample was placed in a cell, designed at the AILES beamline, which allows to control the level of hydration. The cell is connected to a water reservoir through a valve system which enables to set the desired hydration level even in low humidity ranges (down to 0.15 mbar, that correspond to 0.5% of relative humidity). Variations in vibrational modes, during hydration and dehydration cycles, provide information about proton transport inside Nafion channels since IR spectroscopy allows to clearly distinguish the protonic species involved in the process as well as the changes in the membrane structure during water sorption and desorption.

The influence of water on the protons was revealed by comparing vibrational spectra of Nafion-H and Nafion-Na, which differ in the counter-ion of the side chains, at several hydration levels.

REFERENCES

1. K.-D. Kreuer et al. Transport in Proton for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology. *Chemical Reviews*, 104, 4637-4678 (2004)
2. Brubach J.-B. et al, *Signatures of the hydrogen bonding in the infrared bands of water*, *J. Chem. Phys.* 122, 184509 (2005).
3. Laporta, M et al, *Perfluorosulfonated membrane (Nafion): FT-IR study of the state of water with increasing humidity*. *Phys. Chem. Chem. Phys.*, 1, p. 4619-4628 (1999)

Understanding the Nature and Transformations of Dispersed Phases: Synchrotron Radiation and Heterogeneous Catalysts

E. Marceau

Laboratoire de Réactivité de Surface (UMR 7197 CNRS), UPMC, site d'Ivry, 3 rue Galilée, 94200 Ivry-sur-Seine, France. eric.marceau@upmc.fr

ABSTRACT

Heterogeneous catalysts are multicomponent materials that can be described at different scales. They often consist of millimeter-sized grains of a porous material, called support, inside which molecular complexes or nanometric particles of active phase, themselves containing one or several metal elements associated at the atomic level, are fixed and dispersed. Unlike bulk materials, heterogeneous catalysts cannot be characterized using a single technique. X-ray diffraction usually provides the identification of the support and supported phase, but may be of no use when the supported phase is too well dispersed. Similarly, the spatial distribution of the active phase throughout the grains is difficult to assess precisely and chemical promoters, introduced in very small amounts, cannot be traced easily. Finally, it is not just the as-prepared catalyst that should be characterized, but the catalyst while performing the catalytic reaction, since the active phase may transform or even form in operating conditions.

Synchrotron radiation thus appears as an invaluable tool to study heterogeneous catalysts. X-ray absorption spectroscopy is element-specific and can be implemented for the characterization of low quantities of elements, including elements that do not respond to routine characterization techniques. Measurements can be carried out in real time in reactors, under various gas atmospheres, at atmospheric pressure or at high pressure, and kinetics of transformation can be established. X-rays can also be used for tomography, allowing detection of heterogeneities in the material.

The examples presented in this communication include results obtained at synchrotron Soleil on beamline Samba, on cobalt and ruthenium-doped cobalt catalysts, as well as results taken from the recent literature, in particular from Bert M. Weckhuysen (Utrecht University) and Burtron H. Davis (University of Kentucky) groups.

New Insights on the Impact of Co-components on the Formation of the Active Supported Pd/TiO₂ Catalysts during the Gas Phase Acetoxylation Obtained with Operando XAS

J. Radnik¹, J. Rabeah¹, S. Gatla², V. Briois³ and A. Brückner¹

¹ Leibniz Institute for Catalysis, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

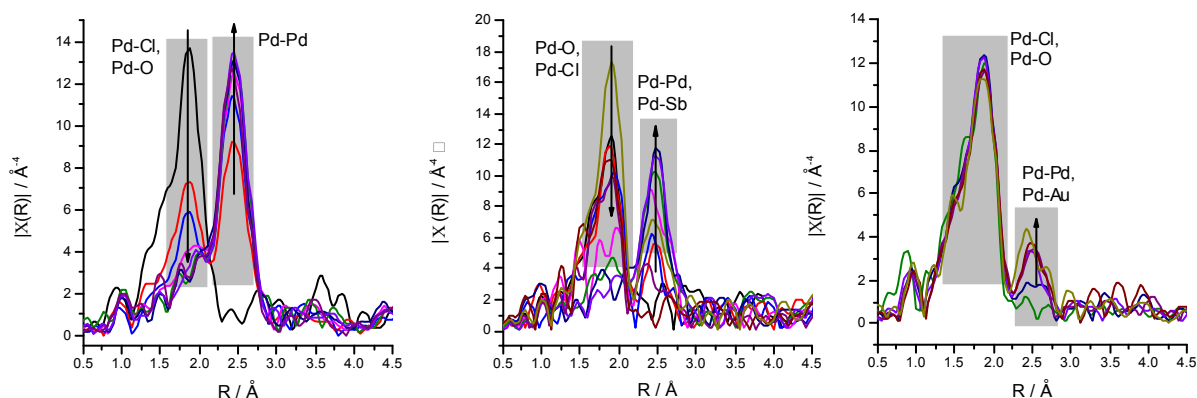
² ESRF, 6 rue Juels Horowitz, 38000 Grenoble, France

³ Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, Cedex, France

ABSTRACT

Co-components or promoters are often crucial for the performance of catalysts, but it is often unclear, how they work. In former investigations it could be shown that the redox potential of the chosen co-component influences the Pd/PdO ratio of catalysts in the gas phase acetoxylation of the toluene, and, hereby, the activity and selectivity of the supported Pd catalysts¹.

With operando quick XAS at the SAMBA beamline it was possible to follow the reduction of the oxidic Pd(II) in calcined catalyst to Pd(0) in the active catalyst in dependence of the less noble Mn and Sb and the noble Au as co-components. In presence of Mn a fast reduction of Pd(II) to Pd(0) was observed, whereas Au led to a slight reduction of the Pd. Sb is the most suitable co-component to obtain the wished Pd/PdO ratio. Additionally, it was possible to reveal the changes of the co-components during the reaction, which was not possible with other methods. Mn remains oxidic during time-on-stream, whereas the metallic Au formed during the preparation is stable during the reaction. The changes of Sb correlate to the observation at the Pd K edges for the Pd-Sb catalyst: only a small part of Sb is reduced during time on stream. These different redox properties are reflected in the catalyst properties: active catalysts with Mn as co-components, highly selective with Au. Sb as co-component is the best compromise between these two extremes.



k³ weighted Fourier-transformation of the EXAFS spectra at the Pd K edge of Pd-Mn (left), Pd-Sb (center) and Pd-Au (right) catalysts during 8 h on stream.

This study shows clearly the benefit of such investigations for the optimization of catalysts in view of activity and selectivity.

REFERENCES

1 S. Gatla, N. Madaan, J. Radnik, V.N. Kalevaru, B. Lücke, A. Martin, U. Bentrup, A. Brückner, ChemCatChem 3 (2011) 1-10

In-situ Study of Silicon Oxide Growth from Tetraethoxysilane (TEOS) using Near-ambient Pressure XPS

G. Olivieri[†], H. Tissot^{†§}, J.J. Gallet^{§†}, F. Bournel^{§†}, F. Sirotti[†], F. Rochet^{§†}

[†]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif sur Yvette, France

[§]Laboratoire de Chimie Physique Matière et Rayonnement (UMR 7614), Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France

ABSTRACT

Organosilanes as tetraethoxysilane (TEOS, $(\text{Si}[\text{OCH}_2\text{CH}_3]_4)$) are used as precursors for chemical vapor deposition (CVD) of silicon dioxide (SiO_2) on clean silicon surfaces.¹ In presence of an adsorbed water layer, they form self-assembled monolayers (SAMs) on hydroxylated silica surfaces. Other applications include the adhesion of polymers or the fixation of biological molecules on surfaces.

The early stages of adsorption of TEOS on silicon surfaces have been studied using synchrotron radiation X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM).^{2,3} The results show that TEOS dissociatively adsorbs on the surface via the scission of all Si-O bonds.³ However standard XPS is not suitable to follow in-situ the CVD of SiO_2 since the TEOS pressure used for the oxide growth process is in the order of the TEOS vapour pressures (1.5 mbar).

The new Near Ambient Pressure (NAP) XPS end station on TEMPO beamline in SOLEIL synchrotron can solve the previous problem since it allows to measure normal XPS spectra with a gas pressure inside the analyzer chamber that can go up to 25 mbar. The kinetic of the SiO_2 growth from TEOS is then studied following the evolution of both Si 2p and C 1s peaks while the TEOS pressure increases from 10^{-9} to 1 mbar. A comparison between hydroxylated and non hydroxylated surfaces is also proposed. The results elucidate the role of the gas phase reactions in the SiO_2 growth and show also the potentiality of the new NAP-XPS.

REFERENCES

1. Doering, R.; Nishi, Y. *Handbook of Semiconductor Manufacturing Technology*, 2007, CRC Press
2. Spitzmüller, J.; Braun, J.; Rauscher, H.; Behm, R.J. *Surface Science* **1998**, 400, 356-366.
3. Tissot, H.; Gallet, J.-J.; Bournel, F.; Naïtabdi, A.; Pierucci, D.; Bondino, F.; Magnano, E.; Rochet, F.; Finocchi, F. *J. Phys. Chem. C*, in press.

Study of Uranyl and Thorium Complexation with Phosphorylated Biomolecules

G. Creff^{1,2,3}, S. Safi¹, A. Jeanson¹, J. Roques¹, P. L. Solari⁴,
E. Simoni¹, C. Vidaud², C. Den Auwer

¹ Institut de Physique Nucléaire d'Orsay (IPNO) – UMR 8608 - FRANCE

² Laboratoire d'étude des protéines cibles - DSV/IBEB/SBTN – CEA Centre de Marcoule - FRANCE

³ Institut de Chimie de Nice (ICN) – UMR 7272 Université Nice Sophia Antipolis- FRANCE

⁴ Synchrotron SOLEIL– France

ABSTRACT

In case of accidental release of actinides in the environment, contamination of the living organisms can occur and induce radiological and chemical toxicities. Whatever the way of integration (inhalation, ingestion or cutaneous), the actinide is absorbed, and then either directly excreted, or transported by blood, linking with different biological ligands (amino acids, peptides, proteins), toward target organs. Once absorbed by the organs, these heavy elements might take the place of essential elements by analogy (Calcium and Iron for example), leading to a serious alteration of the organ activity. Excretion rates as the nature of the target organs (mainly bone, kidney, and liver for actinides) depends on the nature of the actinide and on its oxidation state¹: U (VI) is widely excreted in urinary (65% after one day) while Np is more moderately eliminated (until 40% for Np (V) and 15% for Np (IV) after 1 day). Pu (IV) and actinides (III) retention rate are very important: only 0.4% of Pu is excreted after 1 day and the elimination rate of Am and Cm is less than 1% after 1 day. Regarding the target organs and based on several different studies, the bone matrix appears as a privileged target for most of the An².

At the molecular scale, the study of the actinides in interaction with biological molecules is essential in order to obtain a better description of the toxicological processes associated with these elements. Despite a significant number of studies on the interaction of these elements with living organisms, most of the available data are from a physiological point of view of the toxicology. In fact, there is very few data concerning the bioactinidic approach at the molecular level. Even so, the acquisition of structural information on complexes of radionuclides with molecules of biological interest (proteins) is essential to have a better understanding of the mechanisms of transfer (transport, storage and absorption) of these elements in the living cycles.

Among the different techniques used to probe the structure of the complexes between actinides and their biological environment (molecule, protein, matrix), X-ray Absorption Spectroscopy performed on MARS beamline is a preferential tool. By probing the local environment of the cation which is targeted, this spectroscopy allows to overcome the size, chemical and physical forms of the considered system.

We have selected the interaction of uranyl and thorium with biological molecules of increasing complexity: an amino acid (p-Ser) and a phosphorylated peptide (His-p-Ser-Asp-Glu-p-Ser-Asp-Glu-Val) biomimetic of osteopontin (OPN) which is a hyper-phosphorylated protein particularly important in the process of osteogenesis and which is also studied in this work³. The study of the interaction of Th (IV) with the same peptides allowed us to better understand the devenir of actinides (IV) using a less radioactive surrogate with simpler RedOx chemistry than for the other An (IV) (such as Pu).

Molecular models of the different complexes: actinides-pSer, actinides-peptide and actinides-OPN have been determined on the basis of EXAFS data in combination with quantum chemical calculations⁴.

REFERENCES

1. P. W. Durbin, Actinides in animals and man, in *The chemistry of the actinide and transactinide elements*, 4th edition, L. R. Morss, N. M. Edelstein, J. Fuger, J. J. Katz, Ed. Springer, 2011, Vol. 5, p. 3339
2. C. Vidaud, D. Bourgeois, D. Meyer, *Chem. Res. Toxicol.*, 2012, 25, 1161–1175
3. J. Sodek, B. Ganss, M.D. McKeel, *Crit. Rev. Oral Biol. Med.*, 2000, 11(3), p.279–303
4. S. Safi, G. Creff, A. Jeanson, J. Roques, P. L. Solari, E. Simoni, C. Vidaud, C. Den Auwer, *Chem. Eur. J.*, 2013, 19, 34, 11261–11269.

Ionization and Enhanced Photochemistry of Nitric Acid on Ice

G. Marcotte,¹ P. Ayotte,¹ S. Pronovost,¹ P. Marchand,¹
C. Laffon² and P. Parent²

1 - Département de chimie, Université de Sherbrooke, Sherbrooke, CANADA J1K 2R1;

2 - Centre Interdisciplinaire de Nanoscience de Marseille (CINaM : UMR 7325), Université Aix-Marseille, Campus de Luminy, Case 913, Marseille, Cedex 9, France 13288

ABSTRACT

Nitric acid HNO_3 is an important player in a plethora of environmental heterogeneous processes involving atmospheric aerosols, icy particulates and snow. Whether nitric acid adsorbs in its molecular form HNO_3 or dissociated form NO_3^- (nitrate) on these environmental surfaces is a key question in the formation, stability, and reactivity of nitrates in urban particulate matter, the formation and lifetime of cirrus clouds, and the budget of atmospheric nitrogen oxides over snow-covered regions. (1). X-ray photoabsorption (NEXAFS) spectroscopy at the N and O K-edge on TEMPO (2), we show that nitric acid is mostly dissociated upon its adsorption onto, and its dissolution in ice at temperatures as low 20K. By irradiation in the environmentally relevant $n \rightarrow \pi^*$ transition, we also observe that the photolysis rate are significantly higher for surface-bound nitrates compared to that of dissolved nitrates. Surface-enhanced photolysis rates on ice may contribute to the intense photochemical NO_x fluxes observed to emanate from the sunlit snowpack upon polar sunrise.

REFERENCES

1. F. Dominé, P.B. Shepson, *Science*, 297, 1506-1510 (2002).
2. G. Marcotte, P. Ayotte, A. Bendouan, F. Sirotti, C. Laffon and P. Parent, *J. Phys. Chem. Lett.* 4, 2643-2648 (2013).

PARALLEL SESSION

Cultural Heritage, Archaeology, Environment, Geosciences

Chairpersons: Stéphanie ROSSANO and Emmanuel GUILLON

- IT-05 X-ray absorption spectroscopy to elucidate the behavior of heavy metal in organic waste agricultural recycling
S. Legros
- OC-17 Alteration of green copper-based pigments in model and masterpieces paintings by a multi-analytical approach
A.S. Le Hô
- OC-18 Phytostabilization of mining soils by the plant *anthyllis vulneraria*
M.P. Isaure
- OC- 19 Study of chromium in pigments and enamels produced at the “Sèvres cité de la céramique”
L. Verger
- OC-20 Application of microscopic and synchrotron-based techniques in microbe/radionuclide interaction studies
M.L. Merroun
- IT-06 Abiotic synthesis of prebiotic molecules in the recesses of the oceanic lithosphere: a SR-Deep UV, SR-FTIR and ToF-SIMS multimodal approach
B. Menez
- OC-21 Trace elemental imaging of rare earth elements discriminates tissues at microscale in flat fossils
P. Guériau
- OC-22 Toxicity of aluminum nanophases
A. Masion

X-ray Absorption Spectroscopy to Elucidate the Behavior of Heavy Metal in Organic Waste Agricultural Recycling

S. Legros¹, M. Tella¹, B. Collin², C. Levard², M. Guiresse⁶,
J. Rose², A. Masion², O. Proux⁴, J-L. Hazeman³,
V. Briois⁵, J-Y. Bottero², E. Doelsch¹

¹ CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France ;

² CEREGE, Interfast, F-13545 Aix en Provence, France ;

³ CNRS, OSUG, 414 rue de la piscine, 38400 St Martin d'Hères, France ;

⁴ CNRS, Institut Néel, 25 avenue des Martyrs, 38042 Grenoble, France ;

⁵ Synchrotron SOLEIL L'Orme des Merisiers, Saint-Aubin - BP 48, Gif-sur-Yvette F-91192.

⁶ Campus ENSAT Ensatecolab, Avenue de l'Agrobiopole, BP 32607, Auzeville tolosane, 31326 Castanet-Tolosan

ABSTRACT

In the past century, waste production has risen tenfold, and by 2025 it will double again to reach 6 million tonnes per day¹. Solutions have then to be found to this waste problem. Organic waste (e.g. pig slurry, sewage sludge etc.) represent a significant part of the world waste production and can be valorized following two routes. The first one is agricultural recycling. Organic wastes (OW) have fertilizing properties and can be used as an alternative to chemical fertilizers². The second one is an energetic valorization. OW can be digested to produce biogas used to generate electricity and heat. Besides, this digestion produces a by-product than can also be recycled in agriculture³.

However, OW can have high pollutant concentration among which heavy metal (HM) is particularly concerning. Indeed, soils that have been amended with OW can present HM accumulation at their surface layers⁴. This accumulation could induce phytotoxicity and groundwater quality degradation. Consequently, the fate of HM in the cultivated soil system after OW amendment is a key issue, and it can better be predict by determining their speciation in the OW.

Studies that investigate heavy metal speciation in OW with X-ray absorption spectroscopy (XAS) are presented. In the first study, pig slurry spreading on a tropical soil is used as an example (agricultural recycling valorization). Pig slurry present high concentration of Cu and Zn. Field experiment showed Cu and Zn accumulation in soil at different layers⁴. XAS permitted to elucidate the Cu and Zn speciation in pig slurry⁵ and explain their behavior on the field. The second study deals with anaerobic digestion of OW (energetic valorization). The anaerobic digestion of the studied OW permitted the production of methane, but increased the Cu and Zn concentration in the by-product. XAS was used to compare the Cu and Zn speciation in the OW (before digestion) and in the by-product (after digestion). Results shows that the anaerobic digestion tends to modify the Cu and Zn speciation.

REFERENCES

1. D.Hoornweg, P. Bhada-Tata and C. Kennedy, *Nature* **502**, 615-617 (2013).
2. M.J. Goss, A. Tubeileh and D. Goorahoo, *Adv. Agri.* **120**, 275-379 (2013).
3. L. Appels, J. Baeyens, J. Degre' ve and R. Dewil, *Progress Eneg. Comb. Sci.* **34**, 755-781 (2008).
4. S. Legros, E. Doelsch, F. Feder, G. Moussarda, J. Sansoulet, J.-P. Gaudet, S. Rigaud, I. Basile Doelsch, H. Saint Macary, and J.-Y. Bottero, *Agri. Ecosyst. Environ.* **164**, 70-79 (2013).
5. S. Legros, P. Chaurand, J. Rose, A. Masion, V. Briois, J.-H. Ferrasse, H. Saint Macary, J.-Y. Bottero, E. Doelsch *Environ. Sci. Technol.* **44**, 6926-6932 (2010)

Alteration of Green Copper-based Pigments in Model and Masterpieces Paintings by a Multi-analytical Approach

S. Reguer¹, C. Santoro^{2,3}, A.-S. Le Hô², F. Mirambet², D. Gourier²,
L. Binet², S. Pagès-Camagna², K. Zarkout², S. Mirabaud⁴,
P. Griesmar⁵, N. Lubin-Germain³, M. Menu³

¹ Ligne DIFFABS synchrotron SOLEIL,

² C2RMF Centre de Recherche et Restauration des Musées de France/Institut de Recherche de Chimie Paris – IRCP – UMR8247,

³ SOSCO laboratoire de Synthèse Organique Sélective et de Chimie bioOrganique – EA 4505 CNRS – Université de Cergy-Pontoise,

⁴ Institut National du Patrimoine,

⁵ Laboratoire SATIE Système de l'Application des Technologies de l'Information et de l'Energie UMR 8029 CNRS – ENS – Université de Cergy-Pontoise

ABSTRACT

Among the various painting materials used during the XVth and XVIth centuries, some green copper-based pigments as verdigris and resinate have been widely used for their transparent and pure green tones. Unfortunately chromatic modifications like browning or darkening can be observed on those green painted layers. The understanding of the degradation process is the key factor to evaluate potential evolution of the damages through time.

Despite several previous studies pursued on this question during the last 20 years, the mechanism responsible for the darkening of green copper-based pigments remains unknown. Several contradictory hypotheses were formulated: oxidation of binders due to a high chemical reactivity of copper when present in the form of verdigris or resinate, poor stability with other pigments, reduction of Cu(II), formation of inorganic copper oxides, effects of outer SO₂ and NO₂ pollutants, diffusion of copper ions from verdigris by fatty and resin acids, variation in the hydration of Cu complex [1-3]. Up to now, no clear and definite explanation of the degradation process has been proposed and the debate remains still unsolved.

An original but crucial approach has been developed based on the comparison on data collected on both model samples simulating the ancient paintings and real samples issued from Old masters paintings. Model samples have undergone artificial ageing (RH, T, light) to reproduce the color change effect. They were characterised before and after accelerated ageing tests by XAS spectroscopy correlated to a complementary set of classical techniques UV-visible, EPR and SEM-EDS [4].

The darkening is clearly promoted by the unsaturation degree of the siccativ oil. XANES experiments have demonstrated that incorporation of copper acetate or resinate pigments in the linseed oil binder and the following accelerated ageing induces a rearrangement of the bridge binuclear structure of the copper atoms generally observed for the pure pigments. The chromatic change has been evidenced and characterized by UV-visible spectroscopy. Moreover EPR experiments allowed us to demonstrate that incorporation of copper acetate in oil favours the monomeric copper-carboxylate structure due to the lability of Cu-carboxylate ligand bonds. Nevertheless, it is not responsible for the browning mechanism. The formation of Cu(I) in the copper complexes of the pigment/oil system is considered. It could be initiated by ambient light absorption through LMCT leading to the reduction of Cu(II) into Cu(I) and a drastic change in the optical properties. The partially decarboxylated Cu(I)-Cu(I) pairs are thought to react with oxygen, promoting the formation of copper bridged by peroxide bonds and a darkening of samples.

REFERENCES

¹Altavilla C. and Ciliberto E., *Appl. Phys.A*, **83**, 699-703 (2006).

²Gunn M. and Chottard G. and Rivière E., and Girerd J., and Chottard J.-C., *Studies in Conservation*, **47**, 1, 12-23 (2002).

³Ioakimoglou E. and Boyatzis S. and Argitis P., and Fostiridou A. and Papapanagiotou K. and Yannovits N., *Chem. Mater.*, **11**, 2013-2022 (1999).

⁴ Santoro C. and Zarkout K. and Le Hô A.-S. and Mirambet F. and Gourier D. and Binet L. and Pagès-Camagna S. and Reguer S. and Mirabaud S. and Le Du Y. and Griesmar P. and Lubin-Germain N. and Menu M., *Appl. Phys.A*, under preparation

Phytostabilization of Mining Soils by the Plant *Anthyllis vulneraria*

M.P. Isaure¹, S. Huguet¹, N. Trcera², J.C. Cleyet-Marel³

¹ Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux (LCABIE/IPREM, UPPA/CNRS - UMR 5254), Université de Pau et des Pays de l'Adour, Technopôle Hélioparc Pau-Pyrénées, 2 Av. Président Angot, 64053 Pau Cedex 9, France.

² Beamline LUCIA, Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif sur Yvette Cedex, France.

³ Laboratoire des Symbioses Tropicales et Méditerranéennes (LSTM, INRA/Montpellier SupAgro/IRD/CIRAD /UM2 - UMR-113), Campus International de Baillarguet, TA A-82/J, 34398 Montpellier Cedex 5, France.

ABSTRACT

Mine tailings are typical highly metal contaminated areas, which are affected by intensive rain and wind erosion processes, thus representing a source of environmental and health hazard. Due to their large area and high contamination, conventional remediation techniques are not appropriate, and phytostabilization has emerged as an alternative technique during the last decade¹. The legume plant *Anthyllis vulneraria* has been identified as a pioneer plant to revegetalize a mine tailing from South of France where an experimental site has been set up for 10 years². Our objective was to clarify the role of *Anthyllis vulneraria* in the distribution and speciation of Cd in the soil. For that, we used a combination of micro X-ray fluorescence (μ XRF) and Cd L_{III}-edge micro X-ray Absorption Near Edge Spectroscopy (μ XANES) combined to bulk Cd K-edge Extended X-ray Absorption Fine Structure (EXAFS).

Observation of cross-sections of soils showed that the top of the rhizosphere was highly enriched with organic matter after 10 years of vegetalization. Cd form, mainly identified as CdCO₃ in the unvegetalized soil, did not change significantly in the bulk rhizosphere but investigations at the micrometer scale allowed the identification of Cd organic phases in the upper part, probably related to the shoots decomposition. At the close vicinity of the roots, some minor organic Cd forms were found whilst CdCO₃ minerals were still present, thus highlighting the low direct impact of the roots in the soil. Finally, this study indicated that the direct impact of the plant on Cd speciation in the soil was weak, while an indirect effect resulting from shoots decomposition could be observed.

REFERENCES

1. E.L. Arthur, P.J. Rice, T.A. Anderson, S.M. Baladi, K.L.D. Henderson, and J.R. Coast JR, Critical Reviews in Plant Sciences, 24, 109-122 (2005).
2. H. Frérot, C. Lefèvre, W. Gruber, C. Collin, A. Dos Santos and J. Escarré, Plant and Soil, 282, 53-65 (2006).

Study of Chromium in Pigments and Enamels Produced at the “Sèvres Cité de la Céramique”

L. Verger^{a,b}, L. Cormier^a, O. Dargaud^b

*a : Institut de Minéralogie et de Physique des Milieux Condensés,
Université Pierre et Marie Curie, CNRS, 4 place Jussieu Case 115, 75005 Paris*

b : Cité de la céramique, Sèvres et Limoges

ABSTRACT

Chromium was introduced for the first time at the “Manufacture of Sèvres” in 1804, a few years after its discovery by Vauquelin. It is now the most common element used to produce green, pink and brown decorations on porcelain. Colorants and enamels were studied on beam line LUCIA by X-Ray absorption near edge spectroscopy (XANES) at the Cr K edge. The colorants studied are crystallised compounds synthesized at the “Manufacture of Sèvres”. The mixture of these colorants with a colourless frit is applied on the porcelain and fired at high temperature (1280°C) to form an enamel, *i.e.* a glassy layer. Observations under a scanning electron microscope (SEM) revealed that the enamels are composed of small grains of colorant (between 5 to 30µm) embedded in a glassy matrix. The aim is to follow the environment and the oxidation state of chromium from the colorant to the final product, the decorative enamel. The analysis is focussed on the investigation of the pre-edge feature which is sensitive to both the redox and coordination. The spatial resolution of the X-Ray beam on LUCIA beam line (4x4µm²) was mandatory to characterise the grains of pigment embedded in the glassy matrix:

- Phases which are not detectable by XRD in the colorant rich in Cr₂O₃ were investigated,
- Variability of Cr speciation and environment in malayaite doped with Cr was shown,
- The mechanism of colour change occurring with the pigment ZnAl₂O₄:Cr fired in the frit was understood.

-
Combined with SEM, UV-visible spectroscopy and X-Ray diffraction analyses, this experiment is a first step to understand the origin of the colouration of enamels composed of chromium.

Application of Microscopic and Synchrotron-based Techniques in Microbe/Radionuclide Interaction Studies

M.L. Merroun^a, M. López-Fernández^a, I. Sánchez-Castro^a,
A. Guenther^b, P.L. Solari^c

^a*Department of Microbiology, University of Granada, Spain*

^b*Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Dresden, Germany*

^c*Synchrotron SOLEIL, L'Orme des Merisiers, Gif-sur-Yvette Cedex, Saint-Aubin, France*

ABSTRACT

The presence of the actinides uranium, plutonium, neptunium, americium and curium in radioactive wastes is of major concern because of their potential for migration from the waste repositories and long-term contamination of the environment. It was demonstrated that abiotic processes strongly affect the migration of these elements in the environment. However, it is becoming increasingly evident that microbial processes are of importance as well. Microbial processes will act immobilizing or mobilizing radionuclides, depending on the type of process and the state of the microbes. This paper deals with the speciation of U(VI) associated with the cells of a yeast, *Rhodotorula mucilaginosa* R8, isolated from Clay formations using a multidisciplinary approach combining X-ray absorption spectroscopy (XAS), time-resolved laser-induced fluorescence spectroscopy (TRLFS), High-Angle Annular Dark Field (HAADF), Scanning Transmission Electron Microscope (STEM), and High Resolution Transmission Electron Microscope (HRTEM). XAS analysis indicated that the cells of the yeast strain are able precipitate uranium as uranium phosphate mineral phase with a structure similar to that of meta-autunite. STEM combined with Energy Dispersive X-ray (EDX) element-distribution maps of U and P showed these elements located on the surface and within bacterial cytoplasm, in addition to the extracellular space. The results of this work will help in understanding the role of microbiological process in the chemical behaviour of actinides in geological and environmental context for future nuclear waste disposals as well as in the optimization of bioremediation processes using these natural microbes.

Abiotic Synthesis of Prebiotic Molecules in the Recesses of the Oceanic Lithosphere: A SR-deep UV, SR-FTIR and ToF-SIMS Multimodal Approach

B. Ménez^a, C. Pisapia^a, V. Pasini^{a,b}, M. Réfrégiers^c, F. Jamme^c,
Q. Vanbellingen^d, A. Brunelle^d, D. Touboul^d, P. Dumas^e, M. Andreani^f

^a Institut de Physique du Globe de Paris, Univ. Paris Diderot, Sorbonne Paris Cité, UMR7154,
1, rue Jussieu, 75238 Paris cedex 05, France (menez@jggp.fr)

^b Università di Modena e Reggio Emilia, largo St. Eufemia 19, 41100 Modena, Italy

^c DISCO Beamline, SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48,
91192 Gif-sur-Yvette cedex, France

^d Institut de Chimie des Substances Naturelles, CNRS UPR2301, Centre de Recherche de Gif, 1 avenue de
la Terrasse, 91198 Gif-sur-Yvette cedex, France

^e SMIS Beamline, SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48,
91192 Gif-sur-Yvette cedex, France

^f Laboratoire de Géologie de Lyon : Terre, Planète, Environnement, UMR5276, Univ. Claude Bernard, 2, rue
Raphaël Dubois, 69622 Villeurbanne cedex, France

ABSTRACT

Serpentinites resulting from the hydration of mantle rock-forming minerals are now increasingly regarded as an attractive prebiotic venue. The key point here is the capacity of serpentinization reactions to continuously produce molecular hydrogen over a wide range of temperatures (from 350-400°C as low as 50°C). This lets us suspect carbon reduction to occur from deep levels where solely abiotic reactions (*i.e.* pure chemical processes) can account for the generation of organic compounds of putative prebiotic interest, up to colonizable depths where this hydrogen represents an invaluable source of energy for the inhabiting chemolithoautotrophic microbial communities. In accordance, serpentinization concurs since ancient times where plate tectonics started, to highly reducing and alkaline conditions, potentially allowing the formation and the stabilization of life's 'building blocks', along with the creation of viable geochemical niches where these reactions could have provided the first energy-harnessing biochemical pathways underpinning microbial growth¹. Additionally, it was recently stated that, if the last universal common ancestor emerged in such environments, it retained an obligate endolithic lifestyle². The initial organisms are thereby suspected to have emerged as cloistered within micrometric pore spaces, having minerals acting like cell membrane³. Embedding minerals could also have provided, in addition to protective porous space, reactive surfaces acting as template and catalyzing mineral species.

To properly explore putative environmental niches nested in serpentinites, a compatible observation scale is thus mandatory. We deployed a combination of high-resolution techniques (*i.e.* coupled CLSM/Raman spectroscopy, SEM, TEM, synchrotron-based deep UV and FTIR μ imaging, ToF-SIMS imaging) to track organic molecules at the pore level in serpentinized rocks from the oceanic lithosphere, considered as a relevant analog of the primitive Earth. Their ability to reveal chemical, mineralogical and metabolic diversity at the micrometric scale first provides new approaches for tackling the biological affinities of the detected organic molecules and tracking viable ecological niches⁴. Altogether these approaches thus helps unveiling the molecular and mineralogical mechanisms involved at depth in abiotic and biological carbon reduction within the serpentinizing oceanic lithosphere and establishing a first inventory of the diversity and stability of the produced organic molecules, with the potential to deeply modify our view on the possible mechanisms and the range of physical and chemical conditions under which complex organic molecules can be synthesized and preserved over geological times.

REFERENCES

- ¹ Martin W., Baross J., Kelley D., Russell M. J. (2008) Hydrothermal vents and the origin of life. *Nat. Rev. Microbiol.* 6, 805–814.
- ² Sleep N., Bird D. K., Pope E. C. (2011) Serpentinite and the dawn of life. *Phil. Trans. R. Soc. B* 366, 2857–2869.
- ³ Russell M. J., Hall, A. J. (2009) The hydrothermal source of energy and materials at the origin of life. In *Chemical evolution II: from the origins of life to modern society* (eds L. Zaikowski, J. Friedrich & S. R. Seidel), pp. 45–62. Washington, DC: American Chemical Society.
- ⁴ Ménez B., Pasini V., Brunelli D. (2012) Life in the hydrated suboceanic mantle. *Nat. Geosci.* 5(2), 133-137.

Trace Elemental Imaging of Rare Earth Elements Discriminates Tissues at Microscale in Flat Fossils

P. Gueriau^{1,2}, C. Mocuta³, D.B. Dutheil¹, S.X. Cohen², D. Thiaudière³,
S. Charbonnier¹, G. Clément¹ and L. Bertrand^{2,3}

¹ CR2P, UMR 7207 CNRS, MNHN, UPMC, 57 rue Cuvier, CP 38, F-75005, Paris, France

² IPANEMA CNRS, MCC, USR 3461, BP48 Saint-Aubin, F-91192 Gif-sur-Yvette, France

³ Synchrotron SOLEIL, BP48 Saint-Aubin, F-91192 Gif-sur-Yvette, France

ABSTRACT

The interpretation of flattened fossils remains a major challenge due to compression of their complex anatomies during fossilization, making critical anatomical features invisible or hardly discernible. Key features are often hidden under greatly preserved decay prone tissues, or an unpreparable sedimentary matrix. A method offering access to such anatomical features is of paramount interest to resolve taxonomic affinities and to study fossils after a least possible invasive preparation. Unfortunately, the widely-used X-ray micro-computed tomography, for visualizing hidden or internal structures of a broad range of fossils, is generally inapplicable to flattened specimens, due to the very high differential absorbance in distinct directions. Here we show that synchrotron X-ray fluorescence spectral raster-scanning coupled to spectral decomposition or a much faster Kullback-Leibler divergence based statistical analysis provides microscale visualization of tissues. We imaged exceptionally well-preserved fossils from the Late Cretaceous without needing any prior delicate preparation. The contrasting elemental distributions greatly improved the discrimination of skeletal elements material from both the sedimentary matrix and fossilized soft tissues. Aside content in alkaline earth elements and phosphorus, a critical parameter for tissue discrimination is the distinct amounts of rare earth elements. Local quantification of rare earths may open new avenues for fossil description but also in paleoenvironmental and taphonomical studies.

Toxicity of Aluminum Nanophases

A. Masion¹, C. Santaella², L. Shintu³, W. Liu¹, M. Auffan¹, J. Rose¹

1: CEREGE UMR CNRS-AMU, Europole Arbois, BP 80, 13545 Aix-en-Provence, France.

2: LEMIRE, CEA Cadarache, 13115 Saint-Paul-lès-Durance, France.

3: ISM2 UMR AMU-CNRS, Campus Scientifique de St Jérôme, , 13397 Marseille cedex 20, France

ABSTRACT

Aluminum is an ubiquitous element in the environment where it is mainly present in the form of a variety of minerals as well as short range ordered and amorphous structures. The toxicity of Aluminum is considered to be linked essentially to soluble Al species, the "free" Al cations being considered as the most toxic species. Al included in solid phases is generally considered as non-toxic. However, it has been demonstrated that some nano-sized Al structures are up to 60 times more toxic than the Al³⁺ cation.

Here we investigate the influence of the Al speciation and morphology on the toxicity towards bacteria and human skin cells. The Al species used here are the Al₁₃ polymer, nano-boehmite, and aluminosilicate nanotubes of various lengths.

As expected, Al₁₃ exhibited more severe toxic effects towards *P. Brassicacearum* than nano-boehmite. However, it appears that the metabolic routes affected depend on the nature of the Al species.

For the Al fibers, our results suggest that the toxicity is not a simple function of the tube lengths.

PARALLEL SESSION

Diluted Matter

Chairpersons: Vincent BOUDON and Francis PENENT

- IT-07 Gyroscopic destabilization in a polyatomic molecule: An unusual rotational behaviour revealed by the AILES beamline of SOLEIL
A. Cuisset
- OC-23 Synchrotron-based high resolution Fourier transform spectroscopy of PAHs and derivatives
S. Gruet
- OC-24 Multiple photoionization processes of the potassium atom
P. Lablanquie
- OC-25 Molecular isomer identification in organic aerosols by photoelectrons/photoions coincidence spectroscopy coupled to VUV Synchrotron Radiation: Application to Titan's tholins Analysis
B. Miranda
- OC-26 Photoionisation of Si^+ and silicon hydride molecular ions (SiH^+ , SiH_2^+ , SiH_3^+)
E.T. Kennedy
- IT-08 Action spectroscopy of biological ions
A. Giuliani
- OC-27 Soft X-ray spectroscopies as a probe of TiO_2 nanoparticles solvation in the gas phase
S. Benkoula
- OC-28 The $1s^{-1}2s^{-1}, 2p^{-1}$ shake up satellites in argon
R. Püttner
- OC-29 Spin-forbidden bands and extreme-ultraviolet photodissociation of N_2
A.N. Heays
- OC-30 Near-edge X-ray absorption fine structures revealed in core ionization photoelectron spectroscopy
S. Carniato

Gyroscopic Destabilization in a Polyatomic Molecule: An unusual Rotational Behaviour Revealed by the AILES Beamline of SOLEIL

A. Cuisset^a, M. A. Martin-Drumel^a, G. Mouret^a, F. Hindle^a,
O. Pirali^b, D. A. Sadovskii^a

^a *Laboratoire de Physico-Chimie de l'Atmosphère, EA 4493, Université du Littoral Côte d'Opale, 59140 Dunkerque, France, E-mail: arnaud.cuisset@univ-littoral.fr*

^b *Institut des Sciences Moléculaires d'Orsay, CNRS, UMR 8214, Université Paris XI, bat. 210, 91405 Orsay Cedex, France; SOLEIL Synchrotron, AILES beamline, L'orme des Merisiers, Saint-Aubin, 91192 Gif-Sur-Yvette, France.*

ABSTRACT

Many of us have enjoyed the spectacle of a spinning top influenced by friction: rotating rapidly about a stable stationary axis, the top loses slowly its angular momentum j (and energy), slows down gradually, and then, suddenly, its axis becomes unstable, the top wobbles, and an abrupt change of the top's position follows. In other words, the system undergoes a bifurcation. In the case of the tippe-top, rotation about its lower point is stable at low values of angular momentum J and becomes unstable at large J . Something quite similar occurs in a freely rotating dimethylsulfoxide (DMSO, $(\text{CH}_3)_2\text{SO}$) molecule. For the first time in such large polyatomic molecule, a quantum bifurcation induced by a gyroscopic destabilization was observed. [1,2] This unusual phenomenon in rotational dynamics was discovered in the rovibrational states of the asymmetric bending fundamental ν_{23} band of DMSO whose high-resolution gas phase absorption spectrum was observed along with that of the symmetric bending ν_{11} by Cuisset et al. [2,3] using the exceptional properties of AILES in the Far-Infrared domain (300 - 400 cm^{-1} spectral region). [4]

In order to explain this phenomenon, we looked for the system bifurcation in the pure rotational transitions in the lowest vibrationally excited states of DMSO. Therefore the high-resolution ground state THz spectrum of DMSO has been recorded with a sub-THz spectrometer based on a frequency multiplication chain. [5] We obtained rotational constants and centrifugal corrections to order J^8 of all low frequency fundamental vibrational states of DMSO, specifically those corresponding to the two methyl rocking modes ν_{13} and ν_{24} , the absorption inactive symmetric methyl bending mode ν_{12} of the OSC_2 frame, as well as the other symmetric and the only asymmetric bending modes ν_{11} and ν_{23} of OSC_2 . Neglecting splittings due to the internal rotation of methyl groups, the spectrum was reproduced to the subMHz experimental accuracy. [6] We have found that the state ν_{23} is the only low frequency vibrational state with the "anomalous" rotational structure uncovered in [1]

REFERENCES

- [1] A. Cuisset *et al.*, *Phys. Rev. Lett.*, **109**, 9, 094101, (2012).
- [2] A. Cuisset *et al.*, *J. Chem. Phys.* **138**, 234302 (2013).
- [3] A. Cuisset *et al.*, *Chem. Phys. Lett.*, **492**, 30, (2010).
- [4] J. B. Brubach *et al.*, *AIP Conf. Proc.*, **1214**, 81, (2010).
- [5] G. Mouret *et al.*, *IEEE Sensors Journal*, **13**, 1, (2013).
- [6] A. Cuisset *et al.*, *Chem. Phys. Lett.* **586**, 10, (2013).

Synchrotron-based High Resolution Fourier Transform Spectroscopy of PAHs and Derivatives

S. Gruet^a

^a AILES Beamline, Synchrotron SOLEIL Saint-Aubin, 91192 Gif-sur-Yvette, France.
Tel.: +33 (0)169358172, E-mail: sebastien.gruet@synchrotron-soleil.fr

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) have long been suspected to be the carriers of so called Unidentified Infrared Bands (UIBs) [1,2]. A better understanding of the carriers' nature of these broad and unresolved emission features requires an extensive range of experimental and theoretical studies. Most of the results published in the literature report rotationally unresolved spectra of pure carbon as well as heteroatom-containing PAHs species in different conditions (phase, temperature, degree of ionization state and of hydrogenation, ...). To date, high resolution measurements reporting rotational structure of the infrared (IR) vibrational bands are very scarce.

Recently, some high resolution techniques provided interesting new results to rotationally resolve the IR and far-IR bands of these large carbonated molecules of astrophysical interest [3]. One of them is to use the bright synchrotron radiation as IR continuum source of a high resolution Fourier transform (FTIR) spectrometer [4]. At SOLEIL, synchrotron-based high resolution FT spectroscopy using both room temperature long absorption cell and a continuous supersonic jet experiment provided the first rotationally resolved spectra of several FIR bands of relatively large C-bearing molecules [5].

We report the rotational analysis of the most intense c-type bands in the 50-900 cm⁻¹ range of several two rings PAHs and the spectra of larger species under jet-cooled conditions. Particular attention will be given on the 1,6-Naphthyridine (a N-bearing PAH) for which we recorded the microwave (MW) spectrum in collaboration with the PhLAM laboratory at Lille. MW spectroscopy provided highly accurate rotational constants in the ground state to perform Ground State Combinations Differences (GSCD) allowing the analysis of the FT-FIR bands. The rotational analysis of these IR/FIR bands might help to search these species in space and to model the IR emission responsible for the UIBs.

REFERENCES

- [1] A. Leger, J. L. Puget, *A&A* **137**, L5-L8 (1984).
- [2] L. J. Allamandola, A. G. G. M. Tielens, J. R. Barker, *ApJ* **290**, L25-L28 (1985).
- [3] B. E. Brumfield, J. T. Stewart, B. J. McCall, *Phys. Chem. Lett.* **3**, 1985-1988 (2012).
- [4] S. Albert, K. K. Albert, P. Lerch, M. Quack, *Faraday Discuss.* **150**, 71-99 (2011).
- [5] O. Pirali, M. Goubet, T. R. Huet, R. Georges, P. Souillard, P. Asselin, J. Courbe, P. Roy and M. Vervloet, *PCCP* **15**, 10141 (2013).

Multiple Photoionization Processes of the Potassium Atom

P. Lablanquie^{1,2}, L. Andric^{1,2}, K. Ito^{1,2}, J. Palaudoux^{1,2},
F. Penent^{1,2}, J-M. Bizau^{3,4}, D. Cubaynes^{3,4}, S. Sheinerman⁵,
S.-M. Huttula⁶, M. Huttula⁶

¹ UPMC, Université Paris 06, LCPMR, 11 rue P. & M. Curie, 75231 Paris cedex 05, France

² CNRS, LCPMR (UMR 7614), 11 rue P. & M Curie, 75231 Paris Cedex 05, France

³ ISMO, CNRS UMR 8214, Université Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France

⁴ Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, F-91192 Gif-sur-Yvette cedex, France

⁵ Dept. of Physics, St. Petersburg State Maritime Technical University, 198262 St. Petersburg, Russia

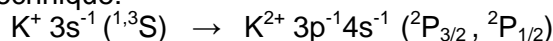
⁶ Department of Physics, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland

ABSTRACT

Multiple photoionization of isolated atoms or molecules consists in the ejection of two or more electrons by a single high energy photon. Such a process is only possible due to electron correlations and can result from the simultaneous ejection of electrons from valence or core shells or from cascade processes. Single and multiple Auger decays also depend on electrons interactions in the intermediate highly excited state formed after inner shell ionization. A way to study directly such processes is to detect in coincidence all the ejected electrons analyzed in energy. We have extensively studied multiple photoionization processes in the Argon atom, including Auger decay processes after 2p [1] or 2s [2] inner-shell ionization, different Post Collision Interaction (PCI) processes after 2p ionization [3], valence triple ionization [4], and core-valence double ionization which allows us to simulate the Auger decay of a 2p hole in an Ar⁺ ion [5]. The aim here is to extend these studies to the Potassium atom. Its [Ar] 4s configuration predicts similarities with the Ar atom and new phenomena, associated to its open shell character. For these studies of metallic vapors, an oven was developed and tested at the laboratory and used for the first time in June 2013 in SOLEIL.

The experiment was carried out at the PLEIADES beam line. It uses the HERMES setup (High Energy Resolution Multi electron spectrometer), [6] which is a 2m long magnetic bottle time of flight electron spectrometer, based on the original design by J Eland; tested in Super ACO, it was developed in BESSY and used in SOLEIL since 2010. Its advantage is a 4 π collection angle for electrons up to at least 200eV kinetic energy which ensures a very high efficiency (up to 70%) for coincidences experiments.

Preliminary results on K multiple ionization will be presented at the meeting. First, as the outer 4s electron is weakly bound (4.34eV), the double ionization threshold to K²⁺ 3p⁻¹4s⁻¹ (²P_{3/2}) occurs at low excess energy (35.97eV). It follows that, in contrary to Argon, the K⁺ 3s⁻¹ 'inner-valence' hole can undergo Auger decay with emission of a ~5eV electron. Multiplet states arise and are filtered by the coincidence technique:



PCI distortion has been measured and estimated by theory in this case.

Inner shell ionization of the K 2p and 2s orbitals and their subsequent Auger decays have been observed and will be compared to those of the Argon atom.

REFERENCES

- [1] P. Lablanquie, et al, Journal of Electron Spectroscopy and Related Phenomena 156-158 (2007) 51
- [2] P. Lablanquie, et al PCCP 13, 18355 (2011)
- [3] S Sheinerman, et al J. Phys. B 43 (2010) 115001
- [4] Y. Hikosaka, et al Phys. Rev. Lett, 102, 013002 (2009)
- [5] S.-M. Huttula, et al Phys. Rev. Lett. 110, 113002 (2013)
- [6] J. Palaudoux, et al, Phys. Rev. A, 82, (2010) 043419

Molecular Isomer Identification in Organic Aerosols by Photoelectrons/Photoions Coincidence Spectroscopy Coupled to VUV Synchrotron Radiation: Application to Titan's Tholins Analysis

B. Miranda¹, F. Gaie-Levrel^{1,2}, A. Mahjoub³, T. Gautier³,
N. Carrasco³, G. Garcia¹, L. Nahon¹, B. Fleury³, P. Pernot⁴

¹ *Synchrotron SOLEIL, DESIRS beamline, L'Orme des Merisiers, St Aubin
91192 Gif-sur-Yvette Cedex (France).*

² *Laboratoire National de Métrologie et d'Essais – LNE (National Metrology Institute and
Testing Laboratory), Chemistry and Biology Division, Air Quality and Gas Flowmetering
Department, 1 rue Gaston Boissier, 75724 Paris Cedex 15, France*

³ *Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), UVSQ,
11 Boulevard D'Alembert, 78280 Guyancourt, (France).*

⁴ *Laboratoire de Chimie Physique (LCP), Université Paris-Sud, 91405 Orsay Cedex (France).*

ABSTRACT

The chemical composition of Titan's atmospheric aerosols is poorly known. In order to access to a better knowledge, laboratory analogues named tholins are synthesized, then analyzed by methods requiring often an extraction process in a carrier solvent. These methods exclude the analysis of the insoluble tholin fraction and presume a hypothetical chemical equivalency between both soluble and insoluble fractions. In this work, we present a powerful analysis method recently developed on the DESIRS beamline¹ to improve the characterization of the chemical composition of tholins produced by the PAMPRE² plasma reactor (LATMOS) by a soft pyrolysis at 280°C. The use of an electron/ion coincidences spectrometer coupled to the tunability of the photon energy allowed to get more information concerning the correct isomer structure of selected observed compounds by comparison with theoretical calculations and OHR³ mass spectra.

REFERENCES

- 1 Nahon et al, Journal of Synchrotron Radiation, 19, 508, 2012.
- 2 Szopa et al, Planet. Space Sci, 54, 394, 2006.
- 3 Pernot et al ; Analytical Chemistry, 82 (4), 1371-1380, 2010.

Photoionisation of Si⁺ and Silicon Hydride Molecular Ions (SiH⁺, SiH₂⁺, SiH₃⁺)

J.M. Bizau^{2,3}, D. Cubaynes^{2,3}, S. Guilbaud², C. Blancard⁴, E.T. Kennedy¹,
J.P. Mosnier¹ and P. van Kampen¹

¹*School of Physical Sciences and NCPST, Dublin City University, Dublin 9, Ireland*

²*Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS UMR 8214, Univ Paris-Sud, Bat. 350, F-91405 Orsay cedex, France*

³*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP 48 F-91192 Gif-sur-Yvette cedex, France*

⁴*CEA-DAM-DIF, Bruyeres-le-Chatel, F-91297 Arpajon Cedex, France*

ABSTRACT

We report first time photoionisation measurements for silicon hydride molecular ions and absolute cross section data for singly ionized atomic silicon ions.

The MAIA¹ setup on the PLEIADES beamline was used for all the experiments reported here. Silicon atomic (Si⁺) and molecular hydride ions (SiH⁺, SiH₂⁺, SiH₃⁺) were produced from silane (SiH₄) in the ECR source via plasma heating by a 12.6-GHz microwave power supply.

For the atomic Si⁺ ions we carried out scans over the 2p-excitation 105-130 eV photon energy range, both for the single and double photoionisation channels. Data recorded for the metastable state allowed us to estimate the fraction of metastables present in the ion beam (of the order of a couple of per cent). Some of the resonance structures were scanned under high-resolution conditions (10 meV). Finally, the results were put on an absolute cross section basis for the first time.

We succeeded in obtaining the first photoionisation measurements for the molecular ion series (SiH⁺, SiH₂⁺, SiH₃⁺), in the 104-120 eV photon energy range, again corresponding to the 2p inner-shell excitation region. The results were recorded by detecting the Si²⁺ dissociation channel for each molecular ion species. The isolation of the individual ions in the initial ion beams was excellent as evidenced by the lack of cross-talk between the spectra. The photoionisation spectra show very clear systematic changes as the number of attached ligand H atoms is increased from zero (for Si⁺) to 3 (for SiH₃⁺).

No signal was observed in the H⁺ dissociation channel. We note that our set up does not allow detection of neutral fragments.

The overall results provide the first absolute measurements of the photoionisation cross section for the atomic ion and the first data on the molecular hydride ion series, which are of particular interest due to the astrophysical² abundance of both silicon and hydrogen and their role in industrial processing plasmas³.

The experiments demonstrate the versatility and performance of the MAIA-PLEIADES combination. We compare our experimental data with the results of different theoretical calculations.

REFERENCES

1. M. F. Gharaibeh, J.M. Bizau, D. Cubaynes, S. Guilbaud, N. El Hassan, M M Al Shorman, C. Miron, C. Nicolas, E. Robert, C. Blancard and B. M. McLaughlin *J. Phys. B: At. Mol. Opt. Phys.* **44** 175208 (2011)
2. Solar astrophysics, P.V. Foukal, Wiley-VCH Verlag GmbH and Co, Weinheim (2004)
3. S. G. Sayres, M. W. Ross and A. W. Castleman, Jr. *Phys Rev A* **82** 033424 (2010)

Action Spectroscopy of Biological Ions

A. Giuliani

Synchrotron Soleil L'Orme des Merisiers Saint-Aubin - BP 48 91192 GIF-sur-YVETTE CEDEX

ABSTRACT

Mass spectrometry in association with the so-called modern ionization techniques offers the unique ability to analyze heavy and fragile ions and assemblies in the gas phase. In specific arrangements, a photon source may be coupled with mass spectrometers to study the consequences of the irradiations of selected ions. Such a spectroscopic technique is usually referred to as action spectroscopy. Action spectroscopy is usually performed using lasers from the infrared to the near UV. The use of synchrotron radiation in that field is new, as the first coupling appeared in the beginning of the year 2000.

A portable setup based on a commercial linear ion trap has been coupled to the DESIRS, DISCO, and PLEIADES beamlines at SOLEIL, which deliver photons from the UV to the soft X-rays range.

Results on action spectroscopy of peptides ions will be presented along with the applications to analytical chemistry and protein sequencing.

Soft X-ray Spectroscopies as a Probe of TiO₂ Nanoparticles Solvation in the Gas Phase

S. Benkoula¹, O. Sublemontier², M. Patanen¹, F.-X. Ouf³, C. Nicolas¹, E. Antonsson¹, F.-A. Barreda^{1,2}, E. Robert¹, D. Aureau⁴, A. Etcheberry⁴, S. Wada⁵, K. Ueda⁶ and C. Miron¹

¹Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

²CEA/IRAMIS/SPAM/Laboratoire Francis Perrin, CEA Saclay, 91191 Gif-sur-Yvette, France

³Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SCA, LPMA, 91192 Gif-Sur-Yvette, France

⁴CNRS, Inst Lavoisier UVSQ, UMR 8180, F-78035 Versailles, France

⁵Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

⁶IMRAM, Tohoku University, Sendai 980-8577, Japan

ABSTRACT

In the last decades, TiO₂ surfaces have drawn a lot of attention due to their technological relevance to various fields, such as photocatalysis, electronic devices, biotechnologies, and self-cleaning materials. This interest evolved jointly with the emergence of nanosciences, making TiO₂ nanoparticles a new, attractive “target” for such applications. However, the use of this type of nanomaterial implies a good knowledge and control of its electronic structure, reactivity, and interfacial properties. Especially the water – TiO₂ surface interaction is crucial, and water sorption on TiO₂ materials, including nanoparticles and nanotubes, has been the topic of numerous theoretical and experimental studies [1, 2].

In this context, we performed X-ray spectroscopies to study the water layer shell on the surface of TiO₂ nanoparticles (mean sizes 25 and 100 nm). The experiment was performed at the PLEIADES beamline [3] by using a specific instrumentation, which allows the interaction of synchrotron radiation with a collimated beam of isolated nanoparticles [4]. This original and quite unique experimental approach offers the possibility to avoid interactions between the sample and a substrate.

We used two different ways to control the hydration level of the TiO₂ nanoparticles: the first method was based on the drying of solvated nanoparticles produced by atomization of a liquid suspension, and the second one was based on the hydration of dry nanoparticles generated by spark discharge with a commercial aerosol generator. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used to identify the signature of the water layer shell on the surface of the free TiO₂ nanoparticles, and made it possible to follow the evolution of the hydration state as well as to monitor size effects. A more quantitative analysis will however require a better control of the experimental conditions (especially during the hydration step) but the results obtained already allow to establish the method used at PLEIADES as a unique possibility to study the interfaces between isolated nano-objects and solvent layers.

REFERENCES

- [1] H. Perron, J. Vandenborre, C. Domain, R. Drot, J. Roques, E. Simoni, J.-J. Ehrhardt, H. Catalette, *Surf. Sci.* **601**, 518-527 (2006).
- [2] T. K. Sham, M. S. Lazarus, *Chem. Phys. Lett* **68**, 426-432 (1979).
- [3] <http://www.synchrotron-soleil.fr/Recherche/LignesLumiere/PLEIADES>
- [4] A. Linblad, J. Söderström, C. Nicolas, E. Robert, C. Miron, *Rev. Sci. Instrum.* **84**, 113105 (2013)

The $1s^{-1}2s^{-1},2p^{-1}$ Shake up Satellites in Argon

R. Püttner,¹ T. Marchenko,² R. Guillemin,² R. K. Kushawaha,²
L. Journal,² G. Goldsztejn,² D. W. Lindle,⁴ M. N. Piancastelli,^{2,5}
J.-P. Rueff,³ D. Céolin,³ and M. Simon^{2,3}

¹*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

²*Laboratoire de Chimie Physique-Matière et Rayonnement, CNRS and UPMC, UMR 7614,
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

³*Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, FR-91192 Gif-sur-Yvette Cedex, France*

⁴*Department of Chemistry, University of Nevada, Las Vegas, Nevada 89154-4003, USA*

⁵*Department of Physics and Astronomy, Uppsala University, SE-75120 Uppsala, Sweden*

ABSTRACT

Using a new experimental setup for high-resolution HAXPES in the gas phase, which is mounted at the GALAXIES beamline of SOLEIL [1], we investigated the $1s^{-1}2s^{-1},2p^{-1}$ shake up structures of Argon, i.e. an Ar $1s$ photoionization accompanied by a shake of a $2s$ or $2p$ inner shell electron into an unoccupied Rydberg orbital. The spectrum of the $1s^{-1}2p^{-1}$ shake up satellites is dominated by the np ($n=4$ to 7) Rydberg series converging towards the ionization thresholds 1P_1 and $^3P_{2,1,0}$, which are determined with high accuracy. These thresholds show an exchange splitting of approximately 10 eV as well as a spin-orbit splitting of the 3P threshold in the order of 1 eV. The obtained values agree reasonably well with theoretical predictions by Kuetgens and Hormes [2].

Below the $1s^{-1}2s^{-1}$ thresholds the spectrum is dominated by the broad $1s^{-1}2s^{-1}$ ($^1,^3S$) $4s$ Rydberg states which are split by approximately 16 eV. Moreover, a number of narrow lines are observed above the $1s^{-1}2p^{-1}$ ($^1,^3P$) thresholds. Based on linewidths and splittings similar to those of the $1s^{-1}2p^{-1}$ ($^1,^3P$) np Rydberg states, these narrow lines are assigned to $1s^{-1}2p^{-1}$ ($1,^3P$) $3p^{-1}$ $n'l'n''l'$ final states populated via double shake processes.

In addition, the $1s^{-1}2p^{-1}$ shake up satellites are also observed in molecules (S $1s^{-1}2p^{-1}$ in H_2S , Cl $1s^{-1}2p^{-1}$ in CH_3Cl and CCl_4) showing that this is a rather general effect. This observation opens the exciting new possibility to study single-site double core-hole (SS DCH) states in Si, P, S, and Cl containing molecules using conventional photoelectron spectroscopy at synchrotron radiation facilities.

REFERENCES

1. D. Céolin et al., *J. El. Spectr. Relat. Phenom.* **190**, 188 (2013)
2. U. Kuetgnes and J. Hormes, *Phys. Rev. A* **44**, 264 (1991)

Spin-forbidden Bands and Extreme-ultraviolet Photodissociation of N₂

A.N. Heays,^a B.R. Lewis,^b G. Stark,^c W. Ubachs,^d
S.T. Gibson,^b and N. de Oliveira^e

^aLeiden Observatory, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands

^bResearch School of Physics and Engineering, ANU, Canberra, ACT 0200, Australia

^cDepartment of Physics, Wellesley College, Wellesley, MA 02481, USA

^dLaserLaB, VU University, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

^eSynchrotron Soleil, Orme des Merisiers, St. Aubin, BP 48, 91192 Gif sur Yvette Cedex, France

ABSTRACT

A measurement program of N₂ photabsorption at extreme-ultraviolet (XUV) wavelengths was conducted on beamline DESIRS (Dichroïsme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron) using the Fourier-transform spectrometer permanent endstation. This is a uniquely high-resolution and broadband instrument with a maximum spectral resolution of $\sim 10^{-4}$ nm, a spectral range of 250-40 nm, and a single-measurement window of ~ 5 nm.^{1,2}

Here we present results of these experiments concerning the observation and characterisation of ${}^3\Pi_u \leftarrow {}^1\Sigma_g^+$ bands of ${}^{14}\text{N}_2$, ${}^{14}\text{N}{}^{15}\text{N}$, and ${}^{15}\text{N}_2$. These transitions appear despite being spin-forbidden, because of the perturbation of excited ${}^3\Pi_u$ and ${}^1\Pi_u$ states. Results are also presented for indirect predissociation above the dissociation energy of the optically-accessible $b{}^1\Pi_u$ state. The laboratory observations are interpreted by and inform a quantum-mechanical model³ of the excited states of N₂ and their perturbations. It is these perturbations which ultimately control the wavelength-dependent predissociation observed following N₂ photoabsorption.

The ultimate purpose of this combined experimental and theoretical study is a detailed and quantified characterisation of N₂ photoabsorption and photodissociation. The principal application of this work is to the study of photochemistry in interstellar space and planetary atmospheres.

REFERENCES

1. N. de Oliveira et al., *Nature Photonics* **5**, 149 (2011).
2. A. N. Heays et al., *J. Chem. Phys.* **135**, 244301 (2011).
3. B. R. Lewis et al., *J. Chem. Phys.* **122**, 144302 (2005).

Near-edge X-ray Absorption Fine Structures Revealed in Core Ionization Photoelectron Spectroscopy

P. Lablanquie^{1,2}, P. Selles^{1,2}, M. Nakano^{3,4}, Y. Hikosaka⁵,
E. Shigemasa⁶, K. Ito⁴, L. Andric^{1,2}, J. Palaudoux^{1,2},
F. Penent^{1,2}, S. Carniato^{1,2}

¹*UPMC Université Paris 6, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

²*CNRS, LCPMR(UMR 7614), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

³*Department of Chemistry, Tokyo Institute of Technology, Tokyo 152855, Japan*

⁴*Institute of Material Structural Science, Photon Factory, Tsukuba, Ibaraki 3050801, Japan*

⁵*Department of Environmental Science, Niigata University, Niigata 950-2181, Japan*

⁶*UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan*

ABSTRACT

Simultaneous core ionization and core excitation have been observed [1] in C_2H_n ($n=2,4,6$), C_6H_6 , and recently measured at SEXTANT beam line on N_2 and H_2O molecular series using synchrotron radiation and a magnetic bottle time-of-flight electron spectrometer. Rich satellite patterns corresponding to $(K^{-2}V)$ core excited states of the K^{-1} molecular ions have been identified by detecting in coincidence the photoelectron with the two Auger electrons resulting from the double core hole relaxation. A theoretical model is proposed providing absolute photoionization cross sections and revealing clear signatures of direct (monopolar) and conjugate (dipolar near-edge x-ray absorption fine structure) shakeup lines of comparable magnitude. For N_2 , analysis of absolute cross-sections modulations with photon energy recorded will be discussed.

REFERENCES

1-M. Nakano et al., Phys Rev. Lett. **111**, 123001 (2013)

PARALLEL SESSION

Electronic & Magnetic Property of Matter, Surfaces and Interfaces

Chairpersons: Antonio TEJEDA and Matteo d'ASTUTO

- IT-09 Charge and spin density waves in the light of coherent X-rays
V. Jacques
- OC-31 Band structure, polarization and switching dynamics in ferroelectrics
N. Barrett
- OC-32 Electronic structure of metal/ferroelectric interfaces under polarization switching
J.E. Rault
- OC-33 Plasmon dispersion of titania polymorphs
F. Sottile
- OC-34 Hydrogen/deuterium-induced nanotunnel opening within semiconductor sub-surface
P. Soukiassian
- OC-35 Structural origin of the band-gap in graphene armchair nanoribbons
I. Palacio
- OC-36 Dirac cone with helical spin polarization in ultrathin α -Sn(001) films
Y. Ohtsubo
- IT-10 X-ray magnetic circular dichroism detected by resonant inelastic X-ray scattering: A 2D photon-in, photon-out magnetic spectroscopy
A. Juhin
- OC-37 Co nanodot arrays grown on a ferromagnetic GdAu₂ template: Substrate/nanodot antiferromagnetic exchange
L. Fernández
- OC-38 Magnetic anisotropies of ferrofluids measured by XMCD at Fe and Co L_{2,3} edges
N. Daffé

Charge and Spin Density Waves in the Light of Coherent X-rays

V.L.R. Jacques¹, E. Pinsolle¹, S. Ravy², G. Abramovici¹, D. Le Bolloc'h¹

1. *Laboratoire de Physique des Solides, UMR8502 CNRS/Université Paris XI, Bât. 510, Université Paris XI, 91405 Orsay Cedex*

2. *Synchrotron SOLEIL, L'Orme des Merisiers, 91192 Gif-sur-Yvette Cedex*

ABSTRACT

Charge and spin density wave (CDW/SDW) phases are found in many systems amongst which some quasi-one dimensional materials, or in the proximity of superconducting phases of high-T_c superconductors. They also coexist in chromium, in which a nesting between electron and hole pockets leads to a magnetic instability in the form of a SDW with wavevector Q . Although this was found decades ago [1], the physical origin of the CDW is still not clearly understood. Two scenarios are found in the literature: either the CDW arises due to magnetostriction, or via a second nesting between hole pockets at $2Q$. Coherent and simultaneous x-ray diffraction have been used at the CRISTAL beamline of the Synchrotron SOLEIL to probe the CDW and the SDW orders independently. With a coherent x-ray beam, one gets information about the amount of phase defects of the probed modulation [2]. Interestingly, the SDW is perfect over micrometers in the sample, but the CDW contains a lot of defects. The use of simultaneous diffraction ensures to probe the same volume for the CDW and the SDW. These results provide information about the coupling between CDW and SDW. We show that the second nesting scenario is more appropriate to describe the CDW formation mechanism [3]. To go further, time-resolved experiments are planned to get the typical timescale of the CDW formation after laser excitation, which depends on the role of the lattice in the mechanism.

REFERENCES

1. E. Fawcett, Rev. Mod. Phys. 60, 209 (1988).
2. F. Livet, Acta Cryst. A 63, 87 (2007)
3. V.L.R. Jacques et al., submitted

Band Structure, Polarization and Switching Dynamics in Ferroelectrics

N. Barrett, J. Rault, J. Dionot, C. Mathieu, V. Feyer, C.M. Schneider,
G. Geneste, T. Maroutian, G. Angus, V. Pillard, Ph. Lecoeur,
G. Niu, B. Vilquin, M. Silly, A. Bendounan, F. Sirotti

CEA, DSM/IRAMIS/SPCSI, F-91191 Gif-sur-Yvette Cedex, France
Peter Gruenberg Institute (PGI-6), JARA-FIT, Research Center Jülich, 52425 Jülich, Germany
CEA, DAM, DIF, F-91297 Arpajon, France
Institut d'Electronique Fondamentale, CNRS UMR 8622, 91405 Orsay Cedex, France
Institut des Nanotechnologies de Lyon, F-69134 Ecully Cedex, France
Synchrotron-SOLEIL, Boîte Postale 48, Saint-Aubin, F91192 Gif-sur-Yvette Cedex, France

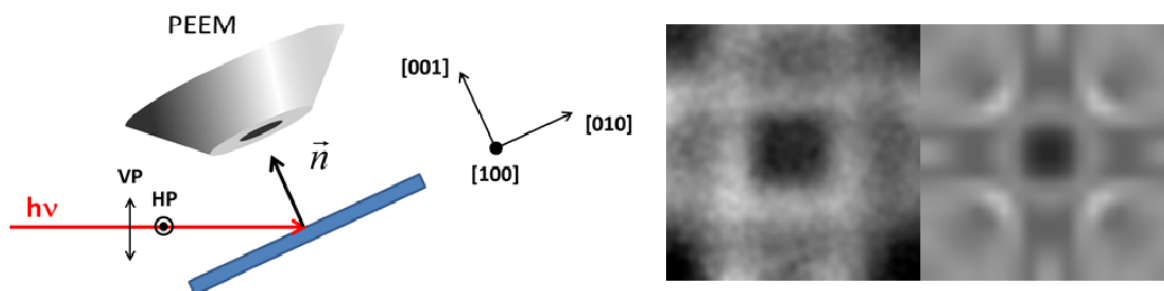
BAND STRUCTURE AND POLARIZATION SWITCHING

Amongst functional oxides, ferroelectrics (FE) have fascinating applications for post C-MOS electronics. Understanding the electronic structure on the micron- and sub-micron scale of domains and devices is a crucial in mastering their potential for fast switching speed, low power consumption and high storage densities.

We have investigated the band structure in microscopic FE domains of BaTiO₃ using wave-vector and energy resolved photoelectron emission microscopy (PEEM), revealing the polarization dependence of the electronic structure thanks to the use of polarized light.

In a second experiment, we have studied the dynamics of MHz polarization switching of a prototypical BaTiO₃ nano-capacitor using time-resolved photoemission, demonstrating the important role of the interface capacitance and its link to the electronic structure.

Finally, we will describe how these and other experiments on functional oxides could be developed in the perspective of advanced photoemission based techniques such as PEEM and near-ambient pressure photoelectron spectroscopy over a wide range of time-resolution.



REFERENCES

1. J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C.M. Schneider, G. Geneste, and N. Barrett, Phys. Rev. Lett. 111, 127602 (2013)
2. J. E. Rault, G. Angus, T. Maroutian, V. Pillard, P. Lecoeur, G. Niu, B. Vilquin, M. G. Silly, A. Bendounan, F. Sirotti, and N. Barrett, Phys. Rev. B 88, 155107 (2013).
3. N. Barrett, J. E. Rault, J. L. Wang, C. Mathieu, A. Locatelli, T. O. Montes, M. A. Niño, S. Fusil, M. Bibes, A. Barthélémy, D. Sando, W. Ren, S. Prosandeev, L. Bellaiche, B. Vilquin, A. Petraru, I. P. Krug and C. M. Schneider, Journal of Applied Physics 113, 187217 (2013)

Electronic Structure of Metal/ferroelectric Interfaces under Polarization Switching

J.E. Rault^{1,3}, G. Agnus², T. Maroutian², V. Pillard², P. Lecoeur², D. Ceolin³,
JP. Rueff³, M. Silly³, A. Bendounan³, F. Sirotty³, G. Niu⁴, B. Vilquin⁴,
D. Cooper⁵, N. Barrett¹

¹CEA, IRAMIS/SPCSI/LENSIS, F-91191 Gif-sur-Yvette, France

²Institut d'électronique fondamentale, Bât. 220, Université Paris-Sud, 91405 Orsay Cedex, France

³Synchrotron-SOLEIL, BP 48, Saint-Aubin, F91192 Gif sur Yvette CEDEX, France

⁴Institut des Nanotechnologies de Lyon (INL), 36, avenue Guy de Collongue,
69134 Ecully, France

⁵CEA, LETI, MINATEC Campus, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

ABSTRACT

In thin-film ferroelectric (FE) capacitors, the ability of the metallic electrodes to screen the depolarizing field is crucial to improve the performances of the devices [1]. Screening is directly related to the chemical and electronic structure of the electrode/FE interface. We investigated the electronic structure of a Pt/BaTiO₃/SrTiO₃:Nb [2, 3] and SrRuO₃/BaTiO₃/SrRuO₃ capacitors (Fig. 1a) using soft and hard x-ray photoemission spectroscopy with *in-situ* applied bias at TEMPO and GALAXIES beamlines of the SOLEIL synchrotron. The depth sensitivity of core-level photoemission is used to probe the electronic response across the upper electrode/ferroelectric interface to bias-induced polarization reversal. For both structures, we measure the energy shift of the electronic structure upon polarization reversal (Fig. 1b). The interface potential drop is a quantitative estimation of the screening capabilities of the electrodes. Surprisingly, the metallic oxide SrRuO₃ provides better screening than Pt, despite the fact that the latter is a better conductor (lower resistivity) with a higher density of free charges. Using high-resolution transmission electron microscopy, we observed that screening in SrRuO₃ is also provided by propagation of the polar distortion in the ferroelectric to the oxide electrode (interface rumpling), a mechanism which cannot be sustained in classic metals. The results agree well with theoretical calculations on SrRuO₃/BaTiO₃/SrRuO₃ capacitors which showed that interface rumpling is a very efficient screening mechanism in metallic oxide electrodes [4].



Figure 1: (a) Schematic of the SRO/BTO/SRO heterostructure, (b) Hard x-ray photoemission spectra for both polarization states in a SRO/BTO/SRO capacitor measured at 6.9 keV. The binding energy shift in the core-level of the FE layer (Ba 3d_{5/2} and Ti 2p_{3/2} here) is due to the different interface potential when switching polarization.

REFERENCES

1. J. F. Scott, *Science* **315**, 954 (2007).
2. J. E. Rault *et al.*, *Phys. Rev. B* **87**, 155146 (2013)
3. J. E. Rault *et al.*, *Phys. Rev. B* **88**, 155107 (2013)
4. G. Gerra, A. Tagantsev, N. Setter, and K. Parlinski, *Phys. Rev. Lett.* **96**, 107603 (2006)

Plasmon Dispersion of Titania Polymorphs

F.Sottile^{1,2} and L.Hung^{1,2} and M.Gatti^{1,2,3}
J.Ablett³ and J.-P. Rueff³

¹Laboratoire des Solides Irradiés, École Polytechnique, CNRS-CEA/DSM, F-91128 Palaiseau, France

²European Theoretical Spectroscopy Facility (ETSF)

³Synchrotron SOLEIL, L'Orme des Merisiers, BP 48 Saint-Aubin, 91192 Gif sur Yvette, France

ABSTRACT

TiO₂ has been shown to be a good photocatalyst in the UV range, and much research today concentrates on the effects of doping and microstructure to increase efficiency. It is nevertheless important to have an accurate characterization of defect-free TiO₂. By identifying the properties inherent to bulk structure, any trends due to defects can be better understood. Here, we use ab initio techniques to characterize and compare perfect crystals of the three most common polymorphs of TiO₂: rutile, anatase, and brookite. Kohn-Sham density-functional theory (DFT) is used to describe ground state properties, and time-dependent DFT and many-body perturbation theory techniques (GW approximation and Bethe-Salpeter) are used for optical properties. We present calculations that simulate momentum-transfer-resolved loss spectroscopy for the valence states of TiO₂. The spectra are interpreted in relation to the electronic properties of each polymorph. We also compare the calculations to preliminary Inelastic X-ray Scattering (IXS) experiments carried out at the GALAXIES beamline in SOLEIL and discuss the accuracy of theoretical techniques employed.

Hydrogen/Deuterium-induced Nanotunnel Opening within Semiconductor Sub-surface

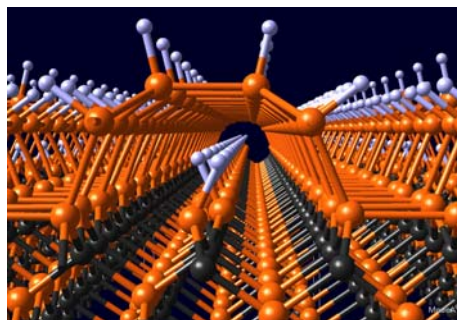
P. Soukiassian,^{1,2,3} E. Wimmer,^{4,5} E. Celasco,^{1,6} Cl. Giallombardo,⁶
 S. Bonanni,⁶ L. Vattuone,^{1,6} L. Savio,¹ A. Tejada,^{3,7} M. Silly,³
 M. D'angelo,⁸ F. Sirotti,³ M. Rocca^{1,6}

- 1) *Istituto Materiali per Elettronica e Magnetismo - CNR, 16146 Genova, Italy*
- 2) *Commissariat à l'Energie Atomique et aux Energies Alternatives, 91191 Gif sur Yvette, France*
- 3) *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif sur Yvette, France*
- 4) *Materials Design Inc., Santa Fe, NM 87501, USA*
- 5) *Materials Design Sarl., 92120 Montrouge, France*
- 6) *Dipartimento di Fisica dell'Università di Genova, 16146 Genova, Italy*
- 7) *Institut Jean Lamour, CNRS-Université de Lorraine, 54506 Vandoeuvre les Nancy, France*
- 8) *Institut des NanoSciences Paris, CNRS-Université Pierre et Marie Curie, 75251 Paris, France*

ABSTRACT

One of the key steps in nanoscience/nanotechnology is our ability to engineer/fabricate low dimensional nano-objects, such as quantum dots, nanowires, two-dimensional atomic layers or three-dimensional nano-porous systems. Here, we report the 1st evidence of nano-tunnels opening [1]. Such an effect, induced by selective adsorbate interaction at surfaces having intrinsic compressive stress, is demonstrated for hydrogen/deuterium atoms reacting with the sub-surface region of a wide band-gap semiconductor, silicon carbide. This finding is established combining synchrotron radiation-based photoemission, vibrational spectroscopy and *ab-initio* VASP computations within MedeA[®]. Hydrogen/deuterium-induced puckering of the sub-surface Si atoms marks the critical step in this nano-tunnel opening (Fig. 1). Nano-tunnels are either metallic or semiconducting, with semiconducting/metallic/semiconducting states transition depending on hydrogen/deuterium coverage. Indeed, the 1st example of hydrogen atoms leading to the metallization of a semiconductor surface was shown in the case of silicon carbide [2]. Dangling bonds generated inside the nano-tunnel offer a promising template to capture atoms or molecules [1]. These features open nano-tailoring capabilities toward advanced applications in electronics, chemistry, storage, sensors or biotechnology. Understanding and controlling such a mechanism opens routes toward selective surface and/or interface functionalization.

Figure 1: 3D Nanotunnel View. The nanotunnel opening induced by the interaction of hydrogen-atoms with the 3C-SiC(100)-3x2 surface is represented for the metallic structure. Note that, in the nanotunnel, the dangling bonds not terminated by a hydrogen atom are not shown.



REFERENCES

1. P. Soukiassian, E. Wimmer, E. Celasco, Cl. Giallombardo, S. Bonanni, L. Vattuone, L. Savio, A. Tejada, M. Silly, M. D'angelo, F. Sirotti, M. Rocca, *Nature Communications* **4**:2800 doi: 10.1038/ncomms3800 (2013).
 See: <http://www.nature.com/ncomms/2013/131121/ncomms3800/pdf/ncomms3800.pdf>
2. V. Derycke, P. Soukiassian, F. Amy, Y.J. Chabal, M. D'angelo, H. Enriquez, M. Silly, *Nature Materials* **2**, 253 (2003)
 See: <http://www.nature.com/nma>

Structural Origin of the Band-gap in Graphene Armchair Nanoribbons

I. Palacio¹, A. Celis¹, A. Gloter², M. S. Nevius³, A. Zobelli²,
M. Sicot⁴, D. Malterre⁴, C. Berger³, W. de Heer³, E.H. Conrad³,
A. Taleb-Ibrahimi¹, A. Tejeda^{1,4}

¹*Synchrotron SOLEIL, Saint-Aubin, 91192 Gif sur Yvette, France*

²*Laboratoire de Physique des Solides, UMR 8502, Université Paris Sud. 91405 Orsay, France*

³*School of Physics, The Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA*

⁴*Institut Jean Lamour, BP 70239, F-54506 Vandoeuvre-lès-Nancy, France*

ABSTRACT

Armchair graphene nanoribbons (GNRs) have been predicted to exhibit tunable gaps, a required property for electronic devices. This relies on edge regularity not achieved by lithography. However sidewall ribbons induced by lithography and annealing the Si-face of SiC are expected to have well defined edges¹. A deep understanding of the morphology of these GNRs will allow not only to improve the future electronic devices but also to link these properties to the electronic ones. In this work we present a detailed morphological characterization by Scanning Tunneling Microscopy (STM) and High Resolution cross-sectional Transmission Electron Microscopy (HR-XTEM) of these ribbons. One of our aims is to address the unknown origin of the gap opening that has been already observed in photoemission². The gap could be driven by either an sp^3 hybridization, by quantum confinement or by strain at the curved edge of the ribbon.

REFERENCES

1. M. Sprinkle *et al.* Nature Nanotech. **5**, 727 (2010)
2. J. Hicks *et al.* Nature Physics. Vol. **9**, 49 (2013)

Dirac Cone with Helical Spin Polarization in Ultrathin α -Sn(001) Films

Y. Ohtsubo¹, P. Le Fèvre¹, F. Bertran¹ and A. Taleb-Ibrahimi^{1,2}

1 Synchrotron SOLEIL, Saint-Aubin-BP 48, F-91192 Gif sur Yvette, France

2 UR1/CNRS Synchrotron SOLEIL, Saint-Aubin, F-91192 Gif sur Yvette, France

ABSTRACT

Topological insulators (TIs) are emerging as a new state of quantum matter with a bulk band gap and odd number of relativistic Dirac fermions, characterized by spin-polarized massless Dirac-cone (DC) dispersion of the edge or surface states (1-4). The unique properties of surface electrons of TIs are an encouraging playground to realize new electronic phenomena, such as the quantum spin-Hall effect (1, 5), and dissipationless electron or spin transport (5).

In this work, we observed two-dimensional (2D) electronic states on ultrathin α -Sn(001) films grown on InSb(001) substrates (6). α -Sn has the diamond-type lattice and topologically non-trivial bulk band structure. However, its bulk band structure does not have any band gap. One possibility to open a band gap in α -Sn and make it TI is to make an ultrathin film of α -Sn with quantum confinement of electrons in the film. Angle-resolved photoelectron spectroscopy (ARPES) performed on these films revealed Dirac-cone-like linear dispersion around the Γ point of the surface Brillouin zone, suggesting nearly massless electrons belonging to 2D surface states. The states disperse across a band gap between bulklike quantum well states in the films. Moreover, both circular dichroism of ARPES and spin-resolved ARPES studies show helical spin polarization of the Dirac-cone-like surface states, suggesting a topologically protected character as in a bulk TI.

Based on these results, we demonstrated a new opportunity to fabricate ultrathin TI films with thicknesses down to few nm on conventional semiconductors and to control the topological order of its electronic states. These results should offer new perspectives of applications in miniaturized electronic or spintronic devices with TI.

REFERENCES

1. M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L.W. Molenkamp, X.-L. Qi, and S.-C. Zhang, *Science* 318, 766 (2007).
2. L. Fu and C. L. Kane, *Phys. Rev. B* 76, 045302 (2007).
3. M. Z. Hasan and C. L. Kane, *Rev. Mod. Phys.* 82, 3045 (2010).
4. X. L. Qi and S. C. Zhang, *Rev. Mod. Phys.* 83, 1057 (2011).
5. S. Murakami, N. Nagaosa, and S. C. Zhang, *Science* 301, 1348 (2003).
6. Y. Ohtsubo, P. Le Fèvre, F. Bertran and A. Taleb-Ibrahimi, *Phys. Rev. Lett.* 111, 216401 (2013).

X-ray Magnetic Circular Dichroism Detected by Resonant Inelastic X-ray Scattering: A 2D Photon-in, Photon-out Magnetic Spectroscopy

A. Juhin

*Institut de Minéralogie et de Physique des Milieux Condensés,
CNRS & Université Pierre et Marie Curie, 75005 Paris, France*

ABSTRACT

XMCD is a powerful, well-established tool, for the element-specific study of the magnetic structure of complex systems. At absorption edges split by spin-orbit coupling (such as $L_{2,3}$ edges), it enables the determination of the spin and orbital magnetic moments by means of sum rules. The magnetic moments of $3d$ transition metal ions are generally studied at the $L_{2,3}$ absorption edges using soft X-rays whose short penetration depth is not compatible with demanding sample environments such as high pressure or liquid cells. X-rays are used at the K edge but the very weak XMCD signal and the absence of spin-orbit split edges do not allow for a detailed quantitative interpretation. Recently, we have developed a novel approach, which consists in coupling XMCD and RIXS spectroscopies at the K edge of $3d$ ions [1]. In particular, we have focused on $1s2p$ RIXS at the K pre-edge ($1s^2 2p^6 3d^N \rightarrow 1s^1 2p^6 3d^{N+1} \rightarrow 1s^2 2p^5 3d^{N+1}$). We have shown that the RIXS-MCD signal measured at room temperature at the Fe K pre-edge in iron oxides such as magnetite and Yttrium Iron Garnet is of the same order of magnitude as $L_{2,3}$ -edge XMCD.

In this talk, the new possibilities offered by the combination of RIXS and XMCD in the hard x-ray range will be discussed. RIXS-MCD can be applied in a quantitative way to investigate systems for which the use of soft x-rays is rather challenging, such as: (i) 15 nm-thick magnetite layers buried under 60 nm Au / Pt, for which element- and site- selective hysteresis loops were measured [2], and (ii) bimagnetic core-shell particles with nominal structure $\text{Fe}_2\text{O}_3 / \text{Mn}_3\text{O}_4$, for which RIXS-MCD directly evidenced the existence of a third layer and allowed to determine the thickness of the different layers [2,3].

REFERENCES

1. M. Sikora, A. Juhin, T.-C. Weng, P. Sainctavit, C. Detlefs, F. de Groot and P. Glatzel *Physical Review Letters*, **105**,037202 (2010).
2. M. Sikora, A. Juhin, G. Simon, M. Zaj.c, K. Biernacka, Cz. Kapusta, L. Morellon, M. R. Ibarra, and P. Glatzel *Journal of Applied Physics*, **111**, 07E301(2012).
3. A. Juhin, A. López-Ortega, M. Sikora, M. Estrader, S. Estradé, F. Peiró, M. D. Baró, P. Sainctavit, P.Glatzel, and J. Nogués, submitted

Co Nanodot Arrays Grown on a Ferromagnetic GdAu₂ Template: Substrate/Nanodot Antiferromagnetic Exchange

L. Fernández¹, M. Blanco-Rey^{1,2}, M. Ilyn³, L. Vitali^{2,4}, A. Correa¹, P. Ohresser⁵, J.E. Ortega^{1,2,3}, A. Ayuela^{1,3}, F. Schiller^{1,3}.

1 Donostia International Physics Center, 20018 Donostia-San Sebastián, Spain.

2 Departamento de Física de Materiales, Universidad del País Vasco UPV/EHU, 20018 Donostia-San Sebastián, Spain.

3 Centro de Física de Materiales (CSIC-UPV-EHU) and Materials Physics Center (MPC), 20018 San Sebastián, Spain.

4 Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain

5 Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin BP 48, 91192 Gif-sur-Yvette, France

ABSTRACT

Highly dense Co nanodot arrays are grown on a textured GdAu₂ surface alloy, which is used as a template. The magnetic behavior has been investigated with X-ray magnetic circular dichroism (XMCD), revealing a strong antiferromagnetic exchange coupling between Co and Gd substrate atoms. This coupling is explained by full-potential linearized augmented plane wave calculations, which additionally allow us to assess the magnetic anisotropy energy of Co layers in contact with the GdAu₂ nanotemplate. In agreement with XMCD observations, the theory finds high anisotropy values and out-of-plane easy-axis in 1ML thick Co layer grown on GdAu₂ and predicts the switch to in-plane easy-axis for 2ML of Co on GdAu₂.

Magnetic Anisotropies of Ferrofluids Measured by XMCD at Fe and Co L_{2,3} edges

N. Daffé^{1,2,3}, M.-A. Arrio¹, F. Choueikani², V. Dupuis³, A. Juhin¹,
S. Neveu³, Ph. Ohresser², Ph. Saintavit^{1,2}

[1] IMPMC, CNRS UMR 7590, Université Pierre et Marie Curie 75252 Paris Cedex 05, France.

[2] Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 91192 GIF-sur-YVETTE CEDEX.

[3] PECSA, UMR 7195, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France.

ABSTRACT

Ferrofluids are colloidal suspensions of magnetic nanoparticles embedded in a carrier liquid. Ferrofluids are well-known for their spectacular instabilities and their numerous applications : mechanical engineering [1], medicine [2], and optical waveguides [3]. The magnetic nanoparticles of the most common ferrofluids are nanospinels such as CoFe_2O_4 . In order to determine the spin and orbit magnetic moments, the magnetic couplings and the exchange magnetic anisotropies [4] of the nanospinels, we have performed X-ray magnetism circular dichroism (XMCD) at Co and Fe L_{2,3} edges on the DEIMOS beamline [5] at SOLEIL. CoFe_2O_4 nanoparticles are obtained from two different synthesis routes : co-precipitation process [6],[7] and polyol process synthesis pathways [8]. From XMCD, we have determined the relation between the particle sizes and the chemical order. The stoichiometry as well as the magnetic anisotropy of the CoFe_2O_4 nanospinels have been measured from XMCD detected magnetization curves. All these provide information on the site symmetry of Co(II) and Fe(III), i.e. octahedral vs tetrahedral sites. The comparison between the magnetization curves measured at either Co or Fe edges sitting either on the Tetrahedral sites or on the Octahedral sites provide a clear picture of the complex magnetic structure of these highly anisotropic nanospinels. This work is partially supported by a grant from the Labex MATISSE.

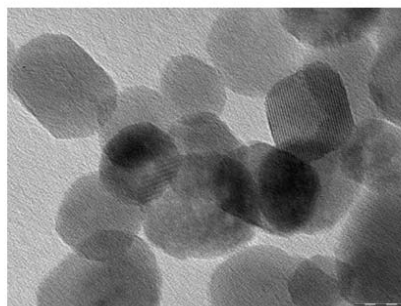


Figure. Left panel: Magnetic instability of ferrofluids; Right panel: CoFe_2O_4 nanospinels present in ferrofluids (scale bar 10nm).

REFERENCES

1. R.H. Kodama, *JMMM*, 1999, 200, 359.
2. Q.A. Pankhurst et al. *J. Phys. D*, 2003, 36, R167.
3. F. Choueikani et al., *Appl. Phys. Lett.*, 2009, 94, 05113.
4. J.F. Hochepped et al., *JMMM*, 2001, 231, 315-322.
5. P. Ohresser et al., Submitted to *Rev. Sci. Instrum.*
6. S. Neveu et al., *J. Coll. Int. Sc.*, 2002, 255, 293-298.
7. F. Tourinho et al., *J. Mat. Sci.*, 1990, 25, 3249-3254.
8. D. Caruntu et al., *Inorg. Chem.* 2002, 41, 6137-3146.

PARALLEL SESSION

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

Chairpersons: Judith MONNIER and Sandra NINET

- IT-11 Contribution from the synchrotron radiation to the electronic and structural description of Prussian blue analogues
J. Lejeune
- OC-39 Combination of X-ray absorption spectroscopy and X-ray diffraction under high pressure using nano-polycrystalline-diamond anvils
J.P. Itié
- OC-40 AlH₃: An example of the use of the infrared spectroscopy to study hydrides under pressure
C. Pépin
- OC-41 Abnormal operando structural behavior of sodium battery material: Influence of dynamic on phase diagram of Na_xFePO₄
F. Boucher
- OC-42 First analyses at the MARS beamline above the exemption limits for radioactive materials: Experimental procedures and preliminary results obtained for irradiated ODS ferritic steel
D. Menut
- IT-12 Structural and magnetic properties of LuFe₂O₄
F. Damay
- OC-43 Low-energy orbital excitations in FeCr₂S₄ using resonant inelastic X-ray scattering
S. Brignolo
- OC-44 Structure of the Cd-Tb approximant to the quasicrystal
D. Liu
- OC-45 In-situ tracking of AuCu nanoparticle structure at low pressure of reactant
A. Wilson
- OC-46 The effect of temperature and pressure on an active pharmaceutical ingredient: L-tyrosine ethyl ester
B. Nicolai

Contribution from the Synchrotron Radiation to the Electronic and Structural Description of Prussian Blue Analogues*

J. Lejeune

School of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, United Kingdom

* Results obtained within Prof. A. Bleuzen's group, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Laboratoire de Chimie Inorganique, Université Paris-Sud, 91400 Orsay, France

ABSTRACT

Prussian Blue Analogues (PBAs) constitute a versatile family of isostructural coordination polymers built on the $M-N\equiv C-M'$ pattern, where M and M' are transition metal ions (Figure 1a).¹ Varying the nature of the M and M' cations, the stoichiometry of the network, or the nature and the amount of interstitial alkaline cations may lead to a large variety of interesting properties for numerous applications (catalysis, data storage, batteries...).

Although the bimetallic network of PBAs is periodic, their structure is partly disordered due to the presence of randomly distributed interstitial alkaline cations, constitutive vacancies in $\{M'(CN)_6\}$ entities, and small distortions of the lattice. While an averaged picture of PBAs may be sufficient to successfully account for certain of their properties,^{2,3} a detailed, local description of their structure (Figure 1b) is often needed to understand some of their most exciting properties.^{4,5}

Based on the A_xCoFe series of electronically switchable PBAs, built on the $Co-N\equiv C-Fe$ pattern, we will demonstrate the relevance of the synchrotron radiation-based infra-red (SR-IR) and X-ray absorption (XAS) spectroscopies as such local probes of the challenging electronic structure of PBAs.^{5,6}

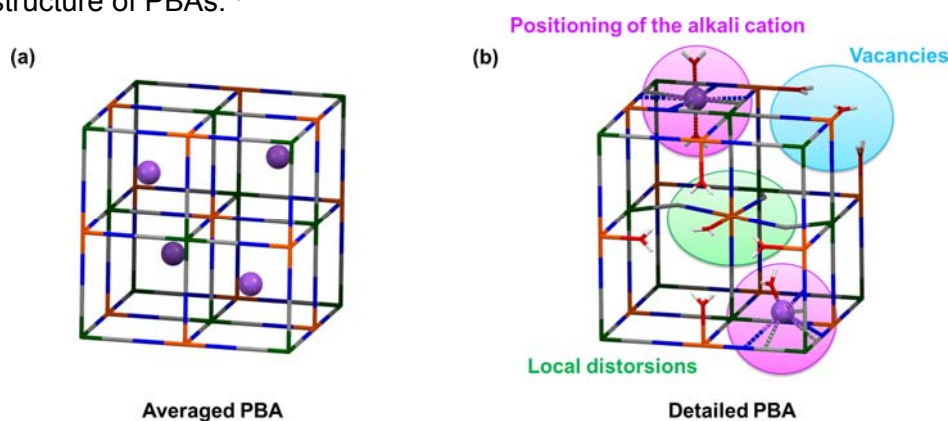


Figure 1 – Schematic comparison of (a) averaged and (b) detailed structures of PBAs. Colours: M (orange), M' (green), C (gray), N (blue), O (red), H (white), alkali (purple).

REFERENCES

1. A. Ludi and H. U. Güdel, "Structural chemistry of polynuclear transition metal cyanides", in *Structure and bonding*, vol.14, Springer Berlin Heidelberg, 1973, pp. 1-21.
2. E. Ruiz, A. Rodríguez-Forteza, S. Alvarez and M. Verdaguer, *Chem. Eur. J.* **11**, 2135-2144 (2005).
3. S. Cobo, R. Fernández, L. Salmon, G. Molnár and A. Bousseksou, *Eur. J. Inorg. Chem.* **11**, 1549-1555 (2007).
4. S.-I. Ohkoshi, H. Tokoro, T. Matsuda, H. Takahashi, H. Irie and K. Hashimoto, *Angew. Chem. Int. Ed.* **46**, 3238-3241 (2007).
5. J. Lejeune, J.-D. Cafun, G. Fornasier, J.-B. Brubach, G. Creff, P. Roy and A. Bleuzen, *Eur. J. Inorg. Chem.*, 3980-3983 (2012).
6. J.-D. Cafun, J. Lejeune, F. Baudelet, P. Dumas, J.-P. Itié and A. Bleuzen, *Angew. Chem. Int. Ed.* **51**, 9146-9148 (2012).

Combination of X-ray Absorption Spectroscopy and X-ray Diffraction under High Pressure using Nano-polycrystalline-diamond Anvils

J.P. Itié, F. Baudalet, E. Fonda, C. Mocuta, L. Nataf and D. Thiaudière

Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin BP48, 91192 Gif sur Yvette Cedex

A. Polian

Institut de Minéralogie et Physique des Milieux Condensés - CNRS UMR 7590, Université P. et M. Curie - Paris 6, Case 115, 4 Place Jussieu, 75252 Paris Cedex 05

ABSTRACT

Thanks to nano-polycrystalline-diamond (NPD) anvils^[1], high pressure X-ray absorption spectroscopy (XAS) at high energy is now accessible (no glitches in the spectra due to the single crystal diffraction of the anvils). Moreover, the high energy makes easier the combination of XAS with X-ray diffraction (XRD). In this presentation we will show three experiments performed respectively on DIFFABS, ODE and SAMBA beamlines of SOLEIL. The two first experiments were done at the Nb K edge on KNbO₃ and the last one at the Sn and I K edges for SnI₄.

1) KNbO₃: this ferroelectric perovskite exhibits under pressure a phase transition from a tetragonal to a cubic structure. In the cubic phase, previous XAS experiments up to 15 GPa^[2] and XRD up to 22 GPa^[3] have shown that the Nb atom was still off center. Using the NPD anvils, pressure up to 57 GPa has been obtained. We observe by XRD a succession of structures (tetragonal-cubic-tetragonal). At the highest pressure measured in the cubic phase, we see clearly by XAS that the Nb atom is at the center of the oxygen octahedron. In the tetragonal phase a modification of the XAS is observed. When pressure is released, the initial phase is recovered.

2) SnI₄: It is a molecular crystal where Sn is at the center of I₄ tetrahedron. Under pressure it becomes metallic and amorphous. This was observed by XRD, resistivity measurements and Mössbauer spectroscopy^[4]. A previous XAS experiment was also performed at the Sn and I K edge up to 22 GPa^[5]. But no combined XRD - XAS experiments were performed. By combining these two techniques on the same sample in the same pressure conditions, we show that there is an intermediate phase between the crystalline cubic ordered phase and the amorphous one. Our results are in good agreement with the model proposed by Pasternak et al^[4], with the creation of chains of linked SnI₄ tetrahedra.

REFERENCES

- 1) T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, H. Sumiya, Nature **421**, 599 (2003); K. Matsumoto, H. Maruyama, N. Ishimatsu, N. Kawamura, M. Mizumaki, T. Irifune, H. Sumiya, J Phys. Soc. Jpn. **80**, 023709 (2011); N. Ishimatsu, K. Matsumoto, H. Maruyama, N. Kawamura, M. Mizumaki, H. Sumiya, T. Irifune, J. Synchr. Rad. **19**, 768 (2012)
- 2) A.I. Frenkel, F.M. Wang, S. Kelly, R. Ingalls, D. Haskel, E.A. Stern and Y. Yacoby, Phys Rev B **56**, 108639 (1997)
- 3) J.P. Itié, A. Polian, S. Ravy and M. Hanfland unpublished
- 4) M P Pasternak and R D Taylor 1988 Phys. Rev. B **37** 8130
- 5) F Wang and R Ingalls 1996 High Pressure Science and Technology ed W A Trzeciakowski (Singapore:World Scientific) p 289

AlH₃: An Example of the use of the Infrared Spectroscopy to Study Hydrides under Pressure

C. Pépin, P. Dumas and P. Loubeyre

*Département de Physique Théorique et Appliquée, CEA/DAM, F-91680 Bruyères-le-Châtel, France
Synchrotron SOLEIL, BP48, F-91192, Gif-sur-Yvette, France*

ABSTRACT

Aluminum hydride (AlH₃) is an important hydride due to its very large hydrogen content of 10.1 wt. % which makes it a very promising hydrogen and energy storage material. AlH₃ could also be seen as an archetype of the intriguing effects predicted in metallic hydrides at high pressure, such as high T_c superconductivity or the existence of nontraditional stoichiometries. Recently, the prediction and observation of the metallization of this compound at 110 GPa [1,2] has launched a series of high pressure studies[3,4]. However, a clear understanding of the evolution of AlH₃ under pressure is still lacking: What is the sequence of structural changes? Does an intermediate ionic hydride exist between the covalent low pressure and metallic high pressure phases? Is the AlH₃ stoichiometry the most stable at high pressure? Why no superconductivity could be measured above 4K in the metallic phase?

We will present a systematic study of the behavior of alpha-AlH₃ under pressure by means of spectroscopy (Raman scattering up to 60GPa, Infrared absorption up to 115GPa) and of X-Ray diffraction up to 120GPa. Changes in stoichiometry have also been investigated up to 90GPa by laser heating of Al in hydrogen. The essential results are the following:

X-Ray diffraction has been realized at ESRF on beamlines ID9 and ID27 on a single crystal pressurized in neon or hydrogen. Two structural transitions are occurring at 64 GPa and 105GPa. The unsolved intermediate phase (hp1) was found to be monoclinic of space group P21/c similarly to that observed by Besedin et al. [4] on AlD₃. We therefore propose a slightly revised equation of state in the pressure range 0-115GPa.

The pressure shift of four Raman modes, as predicted by the factor-group analysis of alpha-AlH₃, could be followed up to 60GPa where the first structural transition occurs. Unlike precedent results we did not observe any abrupt decrease in intensity at 30GPa nor a discontinuity in the pressure evolution up to 60GPa in agreement with our diffraction results.

Infrared absorption measurements were performed for the first time up to 115GPa, using the synchrotron IR beamline SMIS at SOLEIL. Between 0 and 60GPa, four of the six predicted IR-modes have been monitored. Above 60GPa, AlH₃ undergoes a covalent to ionic bonding transition and at 110GPa a ionic to metallic transition. Our measurements show that metallization is not due to a progressive gap closure under pressure but clearly results from the phase transition.

Infrared measurements also allowed us to provide the first experimental evidence of a new type of low-energy plasmon recently predicted to appear under pressure and to induce anomalous optical properties [5].

Changes in stoichiometry were studied by laser heating samples of aluminum and alane in a hydrogen pressure medium and comparing them with samples of alane laser heated without hydrogen. Results showed that between 30 and 90GPa AlH₃ remains the most stable stoichiometry.

REFERENCES

- [1] Goncharenko et al. Phys. Rev. Lett. 100, 045504
- [2] Pickard et al. Phys. Rev. B 76, 144114
- [3] Vajeeston et al. Chem Mater. 20, 5997
- [4] Besedin et al. Phys. Rev. B 84, 104111
- [5] Gurtabay et al. Phys. Rev. B 86, 085106

Abnormal *Operando* Structural Behavior of Sodium Battery Material: Influence of Dynamic on Phase Diagram of Na_xFePO_4

J. Gaubicher,^{1,2} F. Boucher,^{1,2} P. Moreau,¹ M. Cuisinier,^{1,2}
P. Soudan,^{1,2} E. Elkaim,³ and D. Guyomard^{1,2}

¹Institut des Matériaux Jean Rouxel, UMR 6502, CNRS - Université de Nantes, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes cedex France

²Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France

³Synchrotron SOLEIL, 91190 St Aubin, France

ABSTRACT

Na-ion batteries (NIB) are considered as an attractive alternative to Li-ion batteries (LIB) as they could potentially be much less expensive, safer, and environmentally friendlier. Enlightened by the rich experience concerning compounds used in LIB, new materials for positive electrodes of NIB have been developed with structural type based on layered oxides or polyanions. Following this idea, the NaFePO_4 compound has been synthesized and fully characterized by our group.¹ It presents an olivine structural type very close to the parent compound LiFePO_4 . The Na_xFePO_4 phase diagram is however significantly different from the Li_xFePO_4 one with the existence of a stable intermediate composition $\text{Na}_{2/3}\text{FePO}_4$.¹⁻⁴ The Na_xFePO_4 behavior during cycling is also dissimilar with a bi-phasic domain up to $x = 2/3$ but a single-phase one above.^{3,4} In order to further investigate this system, X-Ray diffraction experiments have been done during the cycling.

This study conveys striking findings regarding the *operando* structural behavior of the Na/FePO_4 system during a charge and discharge cycle. From Rietveld refinements of synchrotron *operando* X-Ray diffraction data (CRYSTAL beam line at SOLEIL), it appears that the active material presents large, non-stoichiometric domains while undergoing structural phase transformation. The corresponding extended limits of solubility are characterized by continuous variations in the metrics that mirror the entry of Na occupancy values into thermodynamically forbidden regions.⁵

A major consequence of this smoothed phase transformation is a significant decrease in the lattice volume mismatch, which could well compensate for the less efficient Na-based systems with respect to SEI and adverse effect of cation size in comparison to Li batteries. Comparison of the lattice volume mismatch on charge and discharge revealed an explanation for the asymmetry of the electrochemical curve.

In the near future, we anticipate the elucidation of further noteworthy examples regarding the influence of dynamics on the structural behavior of positive and negative electrode materials of the Na battery. The influence of cycling rate is currently being investigated.

REFERENCES

- (1) Moreau, P.; Guyomard, D.; Gaubicher, J.; Boucher, F. *Chem Mater* **2010**, *22*, 4126–4128.
- (2) Casas-Cabanas, M.; Roddatis, V. V.; Saurel, D.; Kubiak, P.; Carretero-Gonzalez, J.; Palomares, V.; Serras, P.; Rojo, T. *J Mater Chem* **2012**, *22*, 17421–17423.
- (3) Lu, J.; Chung, S. C.; Nishimura, S.; Oyama, G.; Yamada, A. *Chemistry of Materials* **2013**, *25*, 4557–4565.
- (4) Moreau, P.; Cuisinier, M.; Turpin, B.; Gaubicher, J.; Boucher, F.; Guyomard, D. In *7th International Symposium on Inorganic Phosphate Materials (ISIPM7)*; 2011.
- (5) Gaubicher, J.; Boucher, F.; Moreau, P.; Cuisinier, M.; Soudan, P.; Elkaim, E.; Guyomard, D. *Electrochem Commun* **2013**, doi: 10.1016/j.elecom.2013.11.017.

First Analyses at the MARS Beamline above the Exemption Limits for Radioactive Materials: Experimental Procedures and Preliminary Results Obtained for Irradiated ODS Ferritic Steel

D. Menut^{a*}, J.-L. Béchade^a, N. Jonquères^b, D. Leterme^c, B. Sitaud^d,
O. Touchard^e, B. Marchesi^f, C. Gallé^g, B. Debski^c, S. Lauglé^h,
T. Vandenberghe^a, A. Peltier^h, R. Lauberton^b, D. Dubutⁱ, S. Cammelli^d,
I. Monnet^j, J. Ribis^a, Y. de Carlan^a

^a CEA, DEN, Service de Recherches Métallurgiques Appliquées, 91191 Gif-sur-Yvette, France

^b CEA, DEN, Service d'Etudes Mécaniques et Thermiques, 91191 Gif-sur-Yvette, France

^c CEA, DEN, Service de Soutien aux Projets, à la Sécurité et à la Sureté, 91191 Gif-sur-Yvette, France

^d Synchrotron SOLEIL, Ligne de lumière MARS, L'Orme des Merisiers, BP 48,
91192 Gif-sur-Yvette, France

^e CEA, DSM, Section d'Expertises en Radioprotection et de Dosimétrie, 91191 Gif-sur-Yvette, France

^f CEA, DEN, Section d'Assainissement et de Prestations Nucléaires, 91191 Gif-sur-Yvette, France

^g CEA, DEN, Projet RSTB/Métaux et Alliages sous SOLicitation, 91191 Gif-sur-Yvette, France

^h CEA, DSM, Section de Radioprotection des Laboratoires, 91191 Gif-sur-Yvette, France

ⁱ CEA, DEN, Service d'Etude des Matériaux Irradiés, 91191 Gif-sur-Yvette, France

^j CIMAP-ENSICAEN, UMR 6252, 6 Bd Maréchal Juin, 14050 Caen, France

ABSTRACT

The development at CEA of new ferritic/martensitic ODS materials for the cladding of GENIV, Sodium Fast Reactors, and fusion reactor is a key issue [1]. These alloys contain a very high density ($>10^{24} \text{ m}^{-3}$) of Y-Ti-O nanosized particles, responsible of the excellent behavior at high temperature, and favoring the trapping of He in the case of fusion reactor. However, their exact nature is not yet well understood. They appear to range from coherent solute enriched clusters with complex shell structures as found by APT, to near stoichiometric complex oxides, such as Y_2TiO_5 and $\text{Y}_2\text{Ti}_2\text{O}_7$, as found from SANS and TEM analyses. Nevertheless, for these nano-oxides, the main point is to remain stable under irradiation up to high fluence and high temperature.

Here, we focus on the results recently obtained at the MARS beamline during the first experiment above the exemption limits for radioactive materials, thanks to the agreement of the French Safety Authority (ASN). Two experimental techniques, XRD and XAFS at the Y-K edge, have been performed on ODS ferritic steel cladding coming from a subassembly irradiated between 1984 and 1987 in the french sodium fast reactor Phenix. Four locations along the fuel pin were investigated, with a reference for the non-irradiated state [3]. These results, combined with previous TEM analysis, give a new insight into the atomic configuration on the Y-Ti-O nanoclusters [3].

This presentation will also describe the procedures, methods and experimental conditions required to perform these analyses on radioactive samples at SOLEIL. Details will be given about safety constraints for radioactive samples (transportation, control,...), and more specifically on the sample holder designed for these experiments.

REFERENCES

1. P. Dubuisson, *et al.*, J. Nucl. Mater. 428, issues 1-3, 6-12 (2012).
2. A. De Bremaecker, *et al.*, J. Nucl. Mater. 428, 13-30 (2012).
3. I. Monnet, *et al.*, J. Nucl. Mater. 335, 311-321 (2004).

Structural and Magnetic Properties of LuFe₂O₄

F. Damay¹, J. Bourgeois^{1,2}, M. Hervieu², M. Poienar³,
G. André¹, S. Petit¹, J. Robert¹, E. Elkaïm⁴, A. Maignan²,
J. Rouquette³, and C. Martin²

¹Laboratoire Léon Brillouin, CEA-CNRS UMR 12, 91191 GIF-SUR-YVETTE CEDEX, France

²Laboratoire CRISMAT, CNRS UMR 6508, 6 bvd Maréchal Juin, 14050 CAEN CEDEX, France

³Institut Charles Gerhardt, UMR CNRS 5253, Université Montpellier II, Place Eugène Bataillon, cc1503, 34095 MONTPELLIER CEDEX 5, France

⁴Synchrotron Soleil, Saint-Aubin BP 48, 91192 GIF-SUR-YVETTE CEDEX, France

ABSTRACT

The crystal structure and magnetic properties of a polycrystalline sample of multiferroic LuFe₂O₄ [1] have been investigated by means of synchrotron X-ray diffraction, magnetization measurements and neutron scattering, between 1.5 and 350 K [2]. Charge ordering of the Fe²⁺ and Fe³⁺ species occurs simultaneously with a monoclinic distortion of the rhombohedral cell around 330 K, distortion which increases as temperature decreases, though no symmetry lowering is observed down to 10 K. Magnetic Bragg peaks appear below T_N = 240 K, and can be indexed using two propagation vectors, corresponding to either a ferromagnetic or an antiferromagnetic stacking of the iron bilayers. The magnetic arrangement in the *ab* plane follows a 1:2 pattern, which obeys the charge ordering one observed in transmission electron microscopy [3], [4]. The corresponding modeling of the neutron diffraction data shows an additional level of magnetic near-degeneracy, at the level of the bilayer itself.

In-situ high pressure diffraction experiments show that a new form of LuFe₂O₄ is stabilized above 12 GPa, and that this polymorph can be recovered at ambient pressure. Synchrotron X-ray diffraction and XANES studies both agree on an increase in the iron coordination in the [Fe₂O₄] bilayers, resulting from a major reconstruction of the latter under applied pressure.

REFERENCES

- [1] N. Ikeda et al., Nature (London) 436, 1136 (2005)
- [2] J. Bourgeois et al., Phys. Rev. B 86, 024413 (2012)
- [3] J. Bourgeois et al., Phys. Rev. B 85, 064102 (2012)
- [4] M. Hervieu et al., Solid State Sci 23, 26 (2013)

Low-energy Orbital Excitations in FeCr_2S_4 using Resonant Inelastic X-ray Scattering

S. Brignolo^{1,2}, S.G. Chiuzbăian^{1,2}, J.-M. Mariot¹, C.F. Hague¹,
N. Jaouen², A. Nicolaou², F.M.F. de Groot³, and H. Zhou⁴

¹ *Laboratoire de Chimie Physique - Matière et Rayonnement, UPMC (Université. Paris 6) et CNRS (UMR 7614), 11 rue Pierre et Marie Curie, F-75005 Paris, France*

² *Synchrotron SOLEIL, F-91192 Gif Sur Yvette, France*

³ *Department of Chemistry, Group of Inorganic Chemistry and Catalysis, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands*

⁴ *National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310-3706, USA*

ABSTRACT

The main tools used to detect low-energy excitations in complex materials are Raman spectroscopy and neutron inelastic scattering. Here we will present the first resonant inelastic x-ray scattering (RIXS) measurements on a chromium chalcospinel featuring both giant magneto-optical response and colossal magnetoresistance to illustrate the unique advantages of the technique, namely access to excitations over a broad energy region recorded independently for each transition metal component.

Excitations are identified by confrontation with Tanabe-Sugano diagrams and RIXS multiplet calculations.

The results shed light on the origin of the magneto-optical properties in FeCr_2S_4 .

Structure of the Cd-Tb Approximant to the Quasicrystal

D. Liu¹, T. Yamada², C. Gomez³, H. Takakura⁴,
R. Tamura⁵, G. Beutier¹, M. de Boissieu¹

1- SIMAP, Université de Grenoble, CNRS, BP 75 38402 St Martin d'Hères Cedex

2- IMRAM, Tohoku University, Sendai Japan

3 Uppsala University, Sweden

4. Hokkaido University, Sapporo, Japan

5. Tokyo University of science, Tokyo, Japan

ABSTRACT

The Cd₆Tb periodic approximant belongs to one of a large family of isostructural Cd₆M (M=Ca, Sr, Y, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds with cubic symmetry (edge length 1.5 nm), which are periodic approximant to the quasicrystal. Its structure can be described as a bcc cubic packing of the so-called Tsai-type icosahedral cluster, which has been shown to be the building blocks of the stable binary quasicrystals Cd_{5.7}Yb (1,2). Similarly to the Zn₆Sc this phase undergoes a structural phase transition towards a monoclinic phase below 190K (3-4).

We will present a detailed structural analysis carried out on the crystal diffractometer. Full data collection has been carried out above and below the phase transition. Diffuse scattering above T_c, together with the structure of the low temperature have been analyzed. The low T phase is similar to the one of the Zn₆Sc approximant, with an ordered tetrahedron, which strongly distorts the surrounding icosahedral shells (5-6).

REFERENCES

- 1 . Tsai A P, Guo J Q, Abe E, Takakura H and Sato T J 2000 Nature **408** 537.
- 2 . Takakura H, Gomez C P, Yamamoto A, de Boissieu M and Tsai A P 2007 Nature Materials **6** 58.
- 3 . R. Tamura, Y. Muro, T. Hiroto, K. Nishimoto, and T. Takabatake Phys Rev B, 2010, 220201(R)
- 4 . Tamura R, Nishimoto K, Takeuchi S, et al 2005 Phys. Rev. B **71** 092203.
- 5 . Ishimasa T, Kasano Y, Tachibana A, Kashimoto S and Osaka K 2007 Phil. Mag. **87** 2887.
- 6- T. Yamada, H. Euchner, C. P. Gómez, H. Takakura, R. Tamura and M. de Boissieu J. Phys.: Condens. Matter, **25**, 205405, (2013).

In-situ Tracking of AuCu Nanoparticle Structure at Low Pressure of Reactant

A. Wilson^{1,2}, Y. Garreau³, G. Prévot¹, A. Vlad², R. Bernard¹,
A. Coati², Y. Borensztein¹, B. Croset¹, N. Witkowski¹,
A. Naitabdi⁴, H. Cruguel¹

1 Institut des Nanosciences de Paris, UPMC, CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, France

2 Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 91192 GIF-sur-YVETTE CEDEX

3 Matériaux et Phénomènes Quantiques, 10 rue Alice Domon et Léonie Duquet, 75013 Paris

4 LCPMR, UPMC, 11 rue Pierre et Marie Curie, 75005 Paris

ABSTRACT

Specific properties for applications in electronics, optics, magnetism or catalysis can be achieved using nanomaterials based on nanoparticles (NPs). The development and characterization of the bimetallic NPs and the understanding of their physical and chemical properties are thus prerequisites to technological applications in such fields. Among them, catalysis pays a special attention to the bimetallic NPs. Meanwhile, Au NPs have become a paradigm of size effects on the catalytic properties. Au-based bimetallic NPs are thus able to highlight the synergy between two metals for catalytic reactions. For example, Au-Cu/silica NPs display a better activity for CO oxidation than pure Au or Cu ones and a better selectivity for preferential oxidation (PROX) [1]. However, the synergies between the two metals and the substrate are not clearly understood.

Using Grazing incidence X-ray diffraction (GIXD), X-ray photoelectron spectrometry (XPS) and scanning tunneling microscopy (STM), we have studied the synthesis of Au-Cu NPs of controlled size, composition and distribution on rutile TiO₂(110) under UHV, and their evolution under moderate pressure of CO and O₂ (below 10⁻⁵ mbar).

We show that for a specific preparation procedure, alloyed NPs with a narrow distribution of composition can be obtained. In the presence of oxygen (P_{O₂}=10⁻⁷ mbar), STM experiments show that Cu NPs of size smaller than 1 nm are unstable [2] but that a small amount of Au (<10%) is enough to ensure their stability. However, both GIXD and XPS measurements show that the nanoalloys are strongly modify during O₂ exposure: Cu segregate at the NPs surface and the lattice constant of the NPs increases, reflecting the Au enrichment in the core of the NPs. The core-shell configuration obtained is stable at room temperature, even under CO exposure, but annealing above 200°C allows the system to release oxygen and let the Cu diffuse back in the core of the NPs.

REFERENCES

[1] X. Liu et al., J. Catal., 278-288 (2011)

[2] J. Zhou et al., J. Phys. Chem. B 107, 6664-6667 (2003)

The Effect of Temperature and Pressure on an Active Pharmaceutical Ingredient: L-tyrosine Ethyl Ester

B. Nicolai and I.B. Rietveld

Université Paris Descartes - Faculté de pharmacie
4 avenue de l'Observatoire 75006 Paris

ABSTRACT

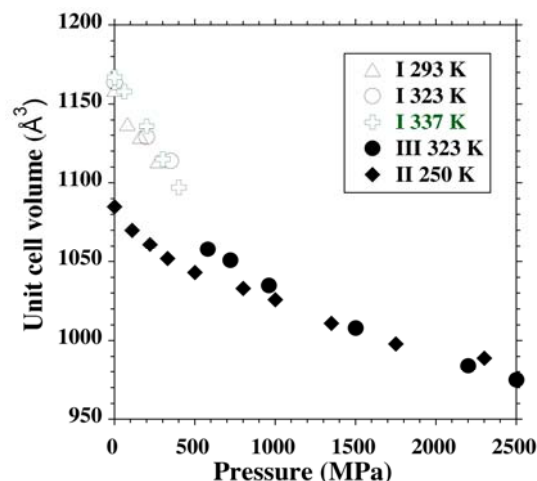
Polymorphism is important in the field of solid-state behavior of drug molecules. Consequently, the investigation of the relative stability of polymorphs of active pharmaceutical ingredients (API) is important and is achieved by our group by constructing pressure-temperature phase diagrams, obtained by X-ray diffraction and differential scanning calorimetry [1-2]. In these phase diagrams, the slope of the solid-solid transition is represented by the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta v} \quad (1)$$

Here dP/dT is the slope of the equilibrium in the pressure-temperature phase diagram, ΔH is the transition enthalpy, T the observed temperature of transition, and Δv the change in specific volume associated with the transition. By incorporating pressure in the analysis it becomes possible to fully describe the phase behavior of crystalline active pharmaceutical compounds and to explain and avoid transformations in drug products during processing and storage. However very few data exists on the effects of pressure on the specific volume of drug molecules, necessary for the Clapeyron equation.

L-tyrosine ethyl ester (LTEE), a carboxylic ester that is a prodrug for the amino acid L-tyrosine, exhibits polymorphism under ordinary pressure [3-4]. Consequently, we measured the diffraction patterns, that gives the volume change, of the two already known crystalline forms under pressure and temperature with Psiché. This allows to map the specific volume v of these two forms as a function of pressure and temperature (see figure).

And surprisingly, a new form appears (III) at a relatively low pressure (around 0.5GPa at room temperature). This new form has been characterized (space group $P2_12_12_1$) and followed at different pressures and temperatures. It appears that this new form is unstable at ambient pressure.



REFERENCES

1. R. Céolin, I.B. Rietveld I.B. (2010) *J. Therm. Anal. Calorim.* **102**, 357–360 (2010)
2. M. Barrio, E. Maccaroni, I. B. Rietveld, L. Malpezzi, N. Masciocchi, R. Céolin, J-Li. Tamarit, *J. Pharm. Sci.* 101(3) 1073-1078 (2012)
3. I. B. Rietveld, M. Barrio, J-Li Tamarit, B. Nicolai, J. van de Streek, N. Mahé, R. Céolin, B. Do *J. Pharm. Sci.* **100**(11), 4774-4782 (2011)
4. B. Nicolai, N. Mahé, R. Céolin, I.B. Rietveld, M. Barrio, J-Li.Tamarit *Structural Chemistry* **22**: 649-659 (2011)

POSTERS SESSION

List of Student Posters

- PO-BH-01** Antioxidant Mn-SOD mimics: Studies in cells
A.S. Bernard
- PO-BH-02** A bimodal cell penetrating peptide for epidermal targeting
S. Clède
- PO-BH-03** Structural study of TrmK a tRNA methyltransferase
C. Dégut
- PO-BH-04** The periplasmic binding protein AccA from agrobacterium tumefaciens
A. El Sahli
- PO-BH-05** Structural study of a human telomeric complex
G. Gaullier
- PO-BH-06** SUFU is a phosphoprotein more stable in presence of Zn
S. Makamté
- PO-BH-07** Evaluating the trapping properties of intestinal bacteria and mucus towards the TiO₂ food additive
J. Radziwill-Bienkowska
- PO-BH-08** DUV microscopy used to localize novel nanosensitizers developed for the hadrontherapy
D. Salado
- PO-BH-09** Structural and functional studies of the heme-hemopexin acquisition system Hxu from Haemophilus influenzae
S. Zambolin
- PO-CP-10** In situ SAXS and UV-Vis monitoring of ZnO/ZnS mixed structures formation using sol-gel process
E. Berbel Manaia
- PO-CP-11** Behaviour of pertechnetate in concentrated acidic media under alpha-irradiation: Technetium sulfate and triflate complexes revealed by X-ray absorption spectroscopy and first principles calculations
I. Denden
- PO-CP-12** Controlling nanoparticles dispersion in ionic liquids by tuning the pH
C. Guibert
- PO-CP-13** Structural study of proteins C3 and C3b by time resolved hydroxyl radical footprinting
A. Mlynarczyk
- PO-CP-14** High resolution FTIR spectroscopy of glycolaldehyde: Towards its remote sensing detection in biomass fires
E. Neeman
- PO-CP-15** Self assembly of mesoporous materials. Kinetics of material formation followed by in-situ SAXS measurements
J. Schmitt
- PO-CP-16** Influence of counterions on hectorite swelling properties monitored by NAP-XPS
H. Tissot
- PO-CP-17** Investigation of oil uptake in fried foodstuffs using Synchrotron radiation
J.M. Vauvre

- PO-CH-18** Trace elemental imaging of rare earth elements discriminates tissues at microscale in flat fossils
P. Gueriau
- PO-DM-19** Understanding large amplitude internal motions - Laboratory search for vibrational excited spectra of oxadisulfane (HSOH) and singly substituted ¹³C dimethyl ether
P. Kutzer
- PO-EM-20** Magnon to electro-active excitation transmutation in the ErMnO₃ multiferroic
L. Chaix
- PO-EM-21** Interface electronic structure of SrRuO₃/BaTiO₃/SrRuO₃ capacitor
S. Gonzalez
- PO-EM-22** Graphene lattice parameter on Ir(111) Vs temperature: Strain, commensurability and defects
F. Jean
- PO-EM-23** Sulfur adsorption on Pd(111) and thiol self assembled layer formation
J. Jia
- PO-EM-24** Resonant soft X-ray scattering on artificial spin ice
J. Perron
- PO-EM-25** XMCD at Fe L_{2,3} edges of two precursors for photomagnetic molecular Prussian Blue analogues: Observation of a large orbital magnetic moment
F. Sadaf
- PO-MM-26** The HAXPES study of full high-k/metal gate stacks deposited on Ge
I. Kalpyris
- PO-MM-27** Plasticity of gold microcrystals investigated by coherent X-ray diffraction
S. Langlais
- PO-MM-28** In-situ GIWAXS and GISAXS measurements during AgCo nanoparticle growth
A. Lemoine
- PO-MM-29** Structure of the Cd-Tb approximant to the quasicrystal
D. Liu
- PO-MM-30** Probing the quantum thermal fluctuations of nuclei at the Si K edge
R. Nemausat
- PO-MM-31** Ferromagnetic nanowires embedded in CeO₂
A. Novikova
- PO-MM-32** TiAlN films around cubic/hexagonal transition studied by DAFS and XAFS
Y. Pinot
- PO-MM-33** Complementarity of inelastic background and high resolution core-level analysis in HAXPES
P. Risterucci
- PO-MM-34** Monitoring the UHV-CVD growth of Si/Ge nanowires by in situ X-ray scattering
T. Zhou
- PO-MM-35** PyRod: Visualization, analysis and simulation of surface diffraction data acquired with 2D detectors
T. Zhou

Antioxidant Mn-SOD Mimics: Studies in Cells

A.S. Bernard,^{a,b,c} N. Delsuc,^{a,b,c} J. Masliah,^{b,c,d} M. Guille Collignon,^{a,b,d}
F. Lemaître,^{a,b,d} C. Amatore,^{a,b,d} N. Trcera,^e C. Policar^{a,b,c}

(a) Ecole Normale Supérieure, Département de chimie, 24, rue Lhomond, 75005 Paris, France,
anne-sophie.bernard@ens.fr

(b) Université Pierre et Marie Curie Paris 6, 4, Place Jussieu, 75005 Paris, France

(c) CNRS, UMR7203, France

(d) CNRS, UMR8640, France

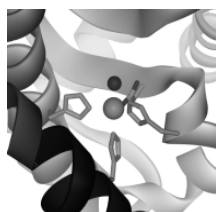
(e) Synchrotron SOLEIL Saint-Aubin, 91192, Gif-sur-Yvette Cedex France

ABSTRACT

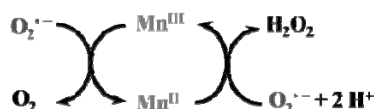
In aerobic organisms, dioxygen is used for cellular respiration through oxidoreduction pathways. They generate production of reactive oxygen species (ROS) including toxic superoxide ion O_2^- (mainly produced in the mitochondrion). Therefore, organisms have developed natural enzymatic defenses among which superoxide dismutase (SOD).^{1, 2} These metalloproteins act as the first line of defense by catalyzing superoxide dismutation into dioxygen and hydrogen peroxide. In some pathological situations, antioxidant defenses can be overwhelmed by the flow of ROS. SOD-mimics are small complexes that reproduce the activity of superoxide dismutases,³ and they have been shown to display an efficient cellular anti-oxidative stress activity.^{2, 4, 5} We designed biomimetic Mn complexes such as $[Mn(enPI_2)]PF_6$ (see figure below), whose coordination sphere is inspired from the MnSOD active site and that show *intrinsic* antioxidant activity against O_2^- .⁶

A first study in activated macrophages will be presented. Macrophages constitute a relevant model to challenge antioxidant activity in a cellular context as they produce ROS fluxes. Activated macrophages were used to test a Mn-complex, which was shown to efficiently reduces the flow of O_2^- .⁷

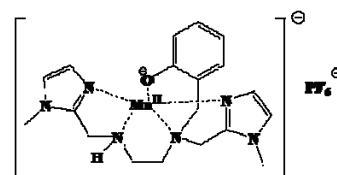
In addition, recent results concerning the anti-inflammatory activity in an alternate cellular model will also be described. The quantification of the Mn-complex was performed using EPR on cell lysates. Its location was investigated using micro-X-fluorescence on the LUCIA and 2-ID-D beamline at SOLEIL and APS synchrotrons.



MnSOD active site



superoxide dismutation



$[Mn(enPI_2)]PF_6$ complexe

Acknowledgements: ENS is gratefully acknowledged for ASB.'s thesis fellowship and ANR for financial support, SOLEIL-synchrotron committees for beamtime.

REFERENCES

1. J. M. McCord and M. A. Edeas, *Biomedecine & Pharmacotherapy*, 2005, **59**, 139-142.
2. I. Batinic-Haberle, S. Reboucas Julio and I. Spasojevic, *Antioxydants and redox signaling*, 2010, **13**, 877-918.
3. O. Iranzo, *Bioorganic Chemistry*, 2011, **39**, 73-87.
4. D. Salvemini, C. Muscoli, D. P. Riley and S. Cuzzocrea, *Pulmonary Pharmacology and Therapeutics*, 2002, **15**, 439-447.
5. J. B. Aitken, E. L. Shearer, N. M. Giles, B. Lai, S. Vogt, J. S. Reboucas, I. Batinic-Haberle, P. A. Lay and G. I. Giles, *Inorg Chem.*, 2013, **52**.
6. F. Cisnetti, A. S. Lefevre, R. Guillot, F. Lambert, G. Blain, E. Anxolabéhère-Mallart and C. Policar, *Eur. J. Inorg. Chem.*, 2007, 4472-4480.
7. A.-S. Bernard, C. Giroud, H. Y. V. Ching, A. Meunier, V. Ambike, C. Amatore, M. Guille Collignon, F. Lemaître and C. Policar, *Dalton Trans.*, 2012, **41**, 6399-6403.

A Bimodal Cell Penetrating Peptide for Epidermal Targeting

S. Clède,^{a,b,c} C. Laugel,^d N. Delsuc,^{a,b,c} F. Lambert,^{a,b,c}
C. Sandt,^e A. Baillet-Guffroy,^d C. Policar^{a,b,c}

(a) Ecole Normale Supérieure, Département de chimie, 24 rue Lhomond, 75005 Paris, France,

(b) Sorbonne Universités, UPMC-Paris 6, 4 Place Jussieu, 75005 Paris,

(c) Laboratoire des Biomolécules, CNRS, UMR7203

(d) Groupe de Chimie Analytique, Faculté de Pharmacie, Université Paris-Sud, 5 rue Jean-Baptiste Clément, 92290 Chatenay-Malabry, France,

(e) SMIS Synchrotron SOLEIL Saint-Aubin, 91192, Gif-sur-Yvette Cedex France.

ABSTRACT

Vibrational excitation in the infrared (IR) is attractive for chemical-imaging¹ as it induces no photo-bleaching and it can be used to probe a local environment without resorting an exogenous marker, relying on the specific absorption of biomolecules. However fluorescence shows a better spatial resolution (<100 nm whereas it is >μm in the mid-IR). Thus probes detectable by several techniques open up the opportunity for cross-correlative studies. We showed that metal-carbonyl compounds (M-CO) can be mapped inside cells using their IR-signature.^{2,3} Interestingly (L)M-CO bearing specific ligands (L) are luminescent.⁴ We envisioned and demonstrated that such compounds based on a single (L)M-CO core could be used as bimodal IR and luminescent probes. We have named them **SCoMPIs** for **Single Core Multimodal Probe for Imaging**.^{5,6}

Cell penetrating peptides (CPPs) are widely used to overcome the cell-membrane weak permeability and to deliver biologically active cargoes.⁷ Application of CPPs in the topical and transdermal delivery systems has recently aroused attention in cosmeceutical and pharmaceutical fields.⁸

We have thus developed a SCoMPI-CPP derivative, called **1**, detectable both by IR and luminescence and exhibiting good permeation properties.

After a 6-hour percutaneous penetration experiment,⁹ **1** was found mainly distributed in the *stratum corneum* (SC), and not detected in the deeper layers of the epidermis. After a 24-hour exposure, **1** was found in the whole epidermis, from the SC to the *stratum basale*, and was not detected in the dermis, deeper than the dermo-epidermal junction. Both IR and luminescent spectroscopies were consistent, showing **1** at the same location (Fig. 1). These preliminary results are very promising, highlighting that SCoMPI-CPP derivatives can be seen as bimodal entities for epidermal targeting.

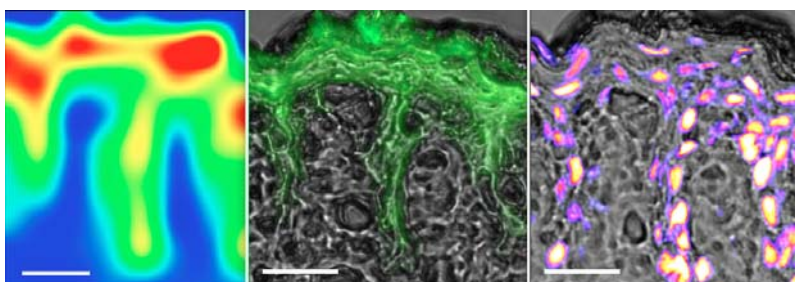


Figure 1. Skin slice after a 24-h exposure to a $2 \cdot 10^{-2}$ M solution of **1** in water. **Left:** mapping of the integral of the absorbance of the A₁-band ($2040\text{-}2000\text{ cm}^{-1}$). **Middle:** bright field image merged with the luminescence signal of **1**. **Right:** bright field image merged with the staining of nuclei by DAPI that shows the limits of the epidermis. Scale bar 20 μm.

REFERENCES

1. P. Dumas, N. Jamin, J. L. Teillaud, L. M. Miller and B. Beccard, *Faraday Discuss.*, 2004, **126**, 289-302; discussion 303-211.
2. C. Policar, J. B. Waern, M. A. Plamont, S. Clède, C. Mayet, R. Prazeres, J.-M. Ortega, A. Vessières and A. Dazzi, *Angew. Chem. Int. Ed.*, 2011, **50**, 860-864.
3. S. Clède, F. Lambert, C. Sandt, Z. Gueroui, N. Delsuc, P. Dumas, A. Vessières and C. Policar, *Biotechnol. Adv.*, 2013, **31**, 393-395.
4. M. Bartholoma, J. Valliant, K. P. Maresca, J. Babich and J. Zubieta, *Chem. Commun.*, 2009, 493-512.
5. S. Clède, F. Lambert, C. Sandt, Z. Gueroui, M. Refregiers, M.-A. Plamont, P. Dumas, A. Vessières and C. Policar, *Chem. Commun.*, 2012, **48**, 7729-7731.
6. S. Clède, F. Lambert, C. Sandt, S. Kascakova, M. Unger, E. Harté, M.-A. Plamont, R. Saint-Fort, A. Deniset-Besseau, Z. Gueroui, C. Hirschmugl, S. Lecomte, A. Dazzi, A. Vessières and C. Policar, *Analyst*, 2013, **138**, 5627-5638.
7. A. Joliot and A. Prochiantz, *Nat. Cell Biol.*, 2004, **6**, 189-196.
8. S. A. Nasrollahi, C. Taghibiglou, E. Azizi and E. S. Farhoud, *Chem. Biol. Drug Des.*, 2012, **80**, 639-646.
9. E. Jungman, C. Laugel, D.N. Rutledge, P. Dumas, and A. Baillet-Guffroy, *Int. J. Pharm.*, 2013, **441**, 628-635.

Structural Study of TrmK a tRNA Methyltransferase

C. Dégut¹, J. Caillet³, F. Brachet¹, M. Roovers²,
L. Droogmans⁴, V. Larue¹, C. Tisé¹

1 Laboratoire de cristallographie et RMN Biologiques UMR 8015 CNRS/ Université Paris Descartes

2 Institut de recherches microbiologiques Jean-Marie Wiame, B-1070 Bruxelles, Belgique

3 Institut de Biologie physico-Chimique, CNRS UPR9073, Paris

*4 Laboratoire de microbiologie, Institut de recherches microbiologiques Jean-Marie Wiame,
B-1070 Bruxelles, Belgique*

ABSTRACT

Nucleotides are often post transcriptionally modified. These chemical modification takes place on the sugar or on the base. tRNA are the most modified RNA, and for now 92 different chemical modification are described for this RNA family (see <http://biochem.ncsu.edu/RNAmods>).

Among these modifications, methylation are the most frequent. They are performed by methyltransferase, using the universal methyl donor : the s-adenosyl-methione (SAM), that give the methyl to the target chemical group.

TrmK is the enzyme that catalyses the methylation of the adenine in position 22 from tRNA^{ser} and tRNA^{tyr}. This protein is member of the COG2384 (Clusters of orthologous groups). Proteins of this COG are well conserved in many procaryote and did not exist in eucaryote, and they are founded in many pathogenic bacteria.

We solved the cristallographic structure of this protein. The protein can be divided in two structural subdomain, the N-ter one is a Rossman fold domain typical in protein that use nucleotide derivative as co-factors, the C-term one is a coiled-coil domain that could be responsible for the fixation and recognition of the targeted tRNA. Both domain form a large concave surface mainly positively charged that can grab the tRNA and bring the adenine 22 to the catalytic pocket.

The Periplasmic Binding Protein AccA from *Agrobacterium tumefaciens*

A. El Sahili¹, D. Faure², S. Morera¹

1-LEBS UPR 3082, CNRS, Avenue de la Terrasse, Gif Sur Yvette, 91198

2-ISV UPR 2355, CNRS, Avenue de la Terrasse, Gif Sur Yvette, 91198

ABSTRACT

Agrobacterium tumefaciens is a soil bacterium that is pathogenic for several plants causing the crown gall disease, which is characterized by tumour formation at the infection site. The infection mechanism is well known and composed of 4 steps:

- 1- The wound on the plant activates *A. tumefaciens*' virulence plasmid.
- 2- T-DNA, a piece of the pTi is transferred to the plant's cell and integrated to its genome.
- 3- The plant secretes hormones, triggering the tumour formation, tumours which are colonized by *A. tumefaciens*. The plant also secretes opines including agrocinopine used as energy source by the bacterium.
- 4- Agrocinopine also activates the quorum sensing mechanisms in *A. tumefaciens* leading to the propagation of the pTi to non-virulent bacteria¹.

Agrocinopine is imported in the bacteria by the Acc system². Acc is composed of an ABC transporter and a periplasmic binding protein namely AccA which recognizes agrocinopine. Genetic studies³ have shown that AccA is also responsible for the import of Agrocin 84, a lethal toxin, produced by the bacteria *A. radiobacter* K84.

The subject of my thesis is to understand the interaction specificity of the PBP AccA with agrocinopine and agrocin 84, combining structural and biochemical studies. We determined the first 3D structure of a PBP in complex with its opine ligand and in complex with the toxin Agrocin 84 allowing us to identify the interactions with each ligand. Using microcalorimetry and structural analysis, we characterized the Acca specificity towards ligands leading to their cytoplasm import by the specific Acc ABC transporter.

REFERENCES

1. Beck von Bodman, S., Hayman, G. T. & Farrand, S. K. Opine catabolism and conjugal transfer of the nopaline Ti plasmid pTiC58 are coordinately regulated by a single repressor. *Proceedings of the National Academy of Sciences of the United States of America* 89, 643–7 (1992).
2. Kim, H. & Farrand, S. K. Characterization of the acc operon from the nopaline-type Ti plasmid pTiC58, which encodes utilization of agrocinopines A and B and susceptibility to agrocin 84. *Characterization of the acc Operon from the Nopaline-Type Ti Plasmid pTiC58, Which Encodes*. *Journal of bacteriology* 179, 7559 (1997).
3. Vicedo, B., Peñalver, R., Asins, M. J. & López, M. M. Biological Control of *Agrobacterium tumefaciens*, Colonization, and pAgK84 Transfer with *Agrobacterium radiobacter* K84 and the Tra Mutant Strain K1026. *Applied and environmental microbiology* 59, 309–15 (1993).

Structural Study of a Human Telomeric Complex

G. Gaullier

*CEA Saclay / iBiTecS / SB2SM / Laboratoire de Biologie Structurale et Radiobiologie,
CNRS UMR 8221, Université Paris Sud, Gif-sur-Yvette, France*

ABSTRACT

Telomeres are nucleoproteic complexes that cap the ends of eukaryotic linear chromosomes. They are essential to maintain genome integrity and their dysfunctions are associated with cancer and ageing pathologies. Telomeric proteins repress DNA double-strand breaks repair machinery, thus preventing telomere fusions, and also control telomere replication and length through regulation of the telomerase enzyme.

In human, telomeric DNA is bound by a complex called shelterin that comprises six proteins: TRF1 and TRF2 (telomeric repeat binding factor 1 and 2), Rap1, TIN2, TPP1 and POT1. We focus on TRF2 and Rap1 because they are the main factors involved in telomere protection.

TRF2 is able to modify DNA topology, promoting strand-invasion of the double-stranded region of telomeric DNA by the single-stranded 3'-overhang and thus allowing formation of a lasso-like structure called t-loop. This loop hides DNA terminus and could explain telomere protection at the molecular level.

Rap1 is widely conserved in eukaryotes and is constitutively associated to TRF2 in vertebrates, in which it modulates TRF2 topology activity.

To understand telomere protection mechanisms at a molecular level, knowledge of the structural basis of TRF2 and Rap1 functions is of top importance. But the only structural data available to date are the 3D structures of isolated domains of both proteins, which are not sufficient to describe the architecture of the full-length complex and to understand how it performs its functions.

Our working hypothesis is that the flexibility of these proteins confers to their assembly a plasticity that is essential to perform its functions. So our goal is to fill the lack of structural data on the full-length complex and describe its architecture. To do so, we are conducting an integrative structural biology approach, combining x-ray crystallography to study extended isolated domains or complexes between isolated domains, SAXS to study full-length proteins and the full-length protein complex, and electron microscopy to study the full-length complex with DNA.

SUFU is a Phosphoprotein more Stable in Presence Of Zn

S. Makamté, V. Biou

*Laboratoire de biologie physico-chimique des protéines membranaire, UMR 7099 CNRS
univ Paris Diderot P7, 13 Rue Pierre et Marie Curie 75005 ,Paris – France*

ABSTRACT

The HH 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. The HH pathway leads to the expression of some genes *via* the activation of its transcription factor, 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, SUFU. Previous studies showed that SUFU shows several isoforms that can be explained by phosphorylation by PKA, CKI and Fused kinases. , The structure of the Nterminal domain of SUFU was solved. Recently, the structure of the entire protein was published in the PDB ; this structure confirms that SUFU has two domains as shown by Small-angle X-ray scattering (SAXS). However, the biochemistry and structural studies of SUFU were not successful. The evidence of its phosphorylation by these kinases is not established.

During the last year, I studied SUFU phosphorylation and stability. I established, by using phosphorylation essays and radiography, that SUFU is phosphorylated by the PKA and Fused kinases. I also established that SUFU is more homogeneous in presence of Zn by using Differential scanning calorimetry (DSC) and circular dichroism (CD). Finally, I optimized the purification of SUFU expressed with Zn with in order to crystallize it and solve its 3D structure.

REFERENCES

1. Nusslein-Volhard, C., and Wieschaus, E. (1980). Mutations affecting segment number and polarity in *Drosophila*. *Nature* 287, 795-801.
2. Dussillol-Godar, F., Brissard-Zahraoui, J., Limbourg-Bouchon, B., Boucher, D., Fouix, S., Lamour- Isnard, C., Plessis, A., and Busson, D. (2006). Modulation of the Suppressor of fused protein regulates the Hedgehog signaling pathway in *Drosophila* embryo and imaginal discs. *Dev Biol* 291, 53-66.
3. Ingham, P.W., and McMahon, A.P. (2001). Hedgehog signaling in animal development: paradigms and principles. *Genes Dev.* 15, 3059-3087.
4. Amy L. Cherry, Csaba Finta, Mikael Karlström, Qianren Jin, Thomas Schwend, Juan Astorga- Wells, Roman A. Zubarev, Mark Del Campo, Angela R. Criswell, Daniele de Sanctis, Luca Jovine and Rune Toftgard. Structural basis of SUFU–GLI interaction in human Hedgehog signalling regulation. *Acta Cryst.* (2013). D69, 2563–2579.

#

Evaluating the Trapping Properties of Intestinal Bacteria and Mucus Towards the TiO₂ Food Additive

J. Radziwill-Bienkowska^{1,2,3}, S. Bettini⁴, B. Cinquin⁵, F. Jamme⁵,
V. Robert^{2,3}, E. Gaultier⁴, C. Cartier⁴, C. Cherbuy^{2,3}, F. Rul^{2,3},
M. Réfrégiers⁵, E. Houdeau⁴, M. Thomas^{2,3}, M. Mercier-Bonin^{2,3}

¹ Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Warsaw, Poland.

² INRA, UMR 1319 MICALIS, AgroParisTech, Domaine de Vilvert, Jouy-en-Josas, 78350, France.

³ AgroParisTech, UMR 1319 MICALIS, Jouy-en-Josas, F-78350, France.

⁴ INRA, UMR1331 Toxalim, INRA/INPT/UPS, Toulouse, France.

⁵ Synchrotron SOLEIL, Gif-sur-Yvette, France.

ABSTRACT

In the gastrointestinal tract, the microbiota and the mucus layer represent the first two front line defenders that act in concert against potentially harmful food components and additives [1]. TiO₂ has a long-standing use as a food additive and is also increasingly considered as an alternative for food packaging applications [2]. However, possible hazards of TiO₂ elements for humans, especially in their nanoparticle form, are under debate, surely depending on their localization and their "bio-reactivity" within the gut. To date, only few information is available on the trapping potential of the intestinal bacteria towards TiO₂, depending on their physiological, physico-chemical and structural properties, notably in terms of cell wall architecture (Gram⁺/Gram⁻). Likewise, the capture ability of the mucus barrier is ignored.

In this framework, our objective was to achieve a complete picture of the TiO₂ distribution inside the bacterial cells and the mucus network. To this end, the imaging branch of the DISCO beamline was used. Two types of TiO₂ particles were investigated: Aeroxide P25 (provided by ANSES and the OECD sponsorship program as a reference sample of TiO₂) and E171 (commercial food additive). Different metrological forms, including micron-sized, submicron-sized and nano-sized TiO₂, were characterized by combining Transmission Electron Microscopy and Dynamic Light Scattering. The intracellular localization and distribution of TiO₂ were mapped for commensal bacteria representative of the dominant intestinal phyla (*Bacteroidetes* and *Firmicutes*). Alimentary bacteria, especially lactic acid bacteria, were also considered, due to their putative beneficial effects on human health. In parallel, the trapping properties of mucus towards TiO₂ were assessed by using the HT29-MTX muco-secreting intestinal cell line [3].

In conclusion, this study will clearly give new insights for defining the benefit/risk balance of food products that are enriched in TiO₂.

REFERENCES

1. J.P. Ouwerkerk, W.M. de Vos and C. Belzer, *Best Pract. Res. Clin. Gastroenterol.* **27**, 25-38 (2013).
2. B. Yu, K.M. Leung, Q. Guo, W.M. Lau and J. Yang, *Nanotechnology* **22**, 115603 (2011).
3. T. Lesuffleur, N. Porchet, J.P. Aubert, D. Swallow, J.R. Gum, Y.S. Kim, F.X. Real and A. Zweibaum, *J. Cell Sci.* **106**, 771-783 (1993).

DUV Microscopy used to Localize Novel Nanosensitizers Developed for the Hadrontherapy

D. Salado, S. Li, L. Stefancikova, E. Porcel and S. Lacombe

Institute des Sciences Moléculaires d'Orsay (UMR 8214) Bât 351, Université Paris Sud 11, CNRS, 91405, Orsay Cedex, France.

ABSTRACT

The group of S. Lacombe develops nanoparticles (NPs) in the perspective of improving the effects of hadrontherapy (irradiation of tumours by fast ions), a technique superior to the conventional radiotherapies (X-rays and γ -rays). Our work aims at developing new high-Z atom based nano-drugs and studying their amplification effect when medical ion beams are used. A multi-scale approach, from the biomolecules to the cellular scale, was used to prove that platinum^[1, 2], gold and lanthanide based nanoparticles are efficient radio-nanosensitizers. These experiments opened the perspectives of theragnostic, which strongly improve the performances of hadrontherapy. We explained the effects of NPs as due to early stage mechanisms of electronic activation and emission, which take place at molecular level and produce a nanoscale dose amplification. In order to better understand the role of these molecular scale processes in living cells, it is necessary to characterize the uptake and localization of the nanoparticles in the cells (human tumour cells).

In this perspective, we use complementary techniques of microscopy. The added value of DUV microscopy stems from its broad excitation window (down to 200 nm), which allows follow up the localization of NPs FREE of fluorescent label. This is of fundamental interest since fluorescent labelling, which may influence the NPs uptake, is the major limitation of other conventional microscopy techniques.

REFERENCES

- [1] Porcel, E.; Li, S.; Usami, N.; Remita, H.; Furusawa, Y.; Kobayashi, K.; Le Sech, C.; Lacombe, S., Nano-Sensitization under gamma rays and fast ion radiation. *Journal of Physics* 2012, Vol. 373.
[2] Porcel, E.; Liehn, S.; Remita, H.; Usami, N.; Kobayashi, K.; Furusawa, Y.; Le Sech, C.; Lacombe, S., Platinum nanoparticles: a promising material for future cancer therapy? *Nanotechnology* 2010, 21, 7pp. (Highlight 2010)

Structural and Functional Studies of the Heme-hemopexin Acquisition System Hxu from *Haemophilus Influenzae*

S. Zambolin, P. Delepelaire

UMR 7099, Institut de Biologie Physico-Chimique, 13 rue Pierre et Marie Curie, 75005 Paris

ABSTRACT

Haemophilus influenzae is a Gram-negative bacterium whose unique host is human. Being heme auxotroph, it displays at the cell surface several heme acquisition systems among which the Hemopexin utilization system (Hxu). Hemopexin is a 50 kDa serum glycoprotein which binds heme with one of the highest known affinities ($K_d < 1\text{pM}$) and is involved in heme recycling. It consists of two similar domains which trap heme with a bis-histidyl linking.

The Hxu system is made up of three proteins encoded by the same operon: the receptor HxuC, and the two proteins HxuB and A which constitute a two partner secretion system (Tps). Previous studies [1] showed that HxuA makes high affinity stoichiometric complexes with hemopexin or heme-hemopexin and that heme is released from hemopexin after the interaction with HxuA and becomes available for the receptor HxuC.

The purpose of my work was to purify, obtain crystals and solve the structure of HxuA.

We managed to have crystals at the following conditions: 0.2 M Magnesium chloride, 0.1 M HEPES pH 7.5, 30% PEG 400. Until now several data sets, the best of which at a 1.6 Å resolution, have been collected. Since HxuA hasn't enough percentage of sequence similarity with other proteins of known structure, we couldn't use the molecular replacement method; for this reason we tried to prepare some heavy-atom derivatives. We were able to detect signals from europium atoms after soaking our crystals in a solution with Eu-DPA (NatX-ray). We obtained phases with the SIRAS method and we are now completing the refinement steps.

$$\frac{d[F_1]}{d\alpha_1} = S \sin \alpha_1 \cos \alpha_2, \quad \frac{d[F_1]}{d\alpha_2} = S \sin \alpha_2 \cos \alpha_1$$

REFERENCES

1. C. Fournier, A. Smith, P. Delepelaire, *Mol Microbiol*, **80**,133-148 (2011).

In Situ SAXS and UV-Vis Monitoring of ZnO/ZnS Mixed Structures Formation using Sol-gel Process

E. Berbel Manaia^{1,5}, R. C. K. Kaminski², B. L. Caetano³, C. V. Santilli³,
S. H. Pulcinelli³, F. Meneau⁴, S. Blanchandin⁵, V. Briois⁵,
C. Bourgaux⁶, L. A. Chiavacci¹

¹*Faculty of Pharmaceutical Sciences, UNESP, Araraquara-Jaú Km 1 road,
14801-902, Araraquara, Brazil*

²*Federal University of Sergipe, Campus Itabaiana, Vereador Olimpio Grande Av.,s/n –
Itabaiana, Brazil*

³*Chemistry Institute, UNESP, 55, Prof. Francisco Degni street, Araraquara, Brazil*

⁴*Brazilian Synchrotron Light Laboratory, PO Box 6192, 13083-970, Campinas, Brazil*

⁵*Synchrotron SOLEIL, L'Orme des Merisiers, BP48, Saint Aubin, 91192 Gif-sur Yvette, France*

⁶*Faculté de Pharmacie - Université Paris-Sud, 5, rue Jean-Baptiste Clément,
92296 Châtenay-Malabry CEDEX, France*

ABSTRACT

ZnO nanoparticles are currently attracting great interest due to their luminescent properties¹. In comparison with organic dyes, “Quantum dots” (QDs) have unique optical properties with broad absorption spectra, narrow symmetric emission peak, high fluorescence quantum yield and resistance to photobleaching. ZnO QDs are promising for bioimaging due to their good biocompatibility. However, the photoluminescence of ZnO QDs is not fully understood. Indeed, it has two components. One is the typical UV exciton emission, the other is defect-based visible emission².

ZnO QDs have been previously synthesized using the sol-gel method. Their nucleation and growth were followed by time-resolved small-angle X-ray scattering (SAXS) and X-ray absorption fine structure (XAFS) measurements coupled with UV-Vis absorption³. The aim of the present study was to obtain core-shell ZnO/ZnS QDs to modulate their luminescent properties. ZnO colloidal suspensions were prepared by hydrolysis and condensation at 40°C of a precursor solution (Zn₄OAc₆ ethanolic solution) upon mixing with LiOH ethanolic solution. An ethanolic solution of thioacetamide (TAA) was then added to the ZnO colloidal suspension to supply sulfur ions to form ZnS. This synthesis was performed at 60°C. Different concentrations of TAA were used in the sulfidation process to investigate the influence of TAA on the formation of ZnO/ZnS mixed structures. The structural properties of the obtained nanoparticles were investigated by SAXS, X-ray diffraction at wide angles and electronic microscopy and their UV-Vis absorption spectra were recorded. The luminescent properties of nanoparticles were shown to depend on TAA concentration. The concentration of TAA promoting the formation of core/shell ZnO/ZnS QDs rather than separated nanoparticles has been determined.

REFERENCES

1. Xiong, H.-M. *Advanced Materials* **25**, 5329-5335 (2013).
2. Nam, W. H.; Lim, Y. S.; Seo, W. S.; Cho, H. K.; Lee, J. Y. *J Nanopart Res* **13**, 5825–5831 (2011).
3. Caetano, B. L.; Santilli, C. V.; Meneau, F.; Briois, V. r.; Pulcinelli, S. H. *The Journal of Physical Chemistry C* **115**, 4404-4412 (2011).

Behaviour of Pertechnetate in Concentrated Acidic Media under Alpha-irradiation: Technetium Sulfate and Triflate Complexes Revealed by X-ray Absorption Spectroscopy and First Principles Calculations

I. Denden¹, J. Roques², F. Poineau³, P. L. Solari⁴,
M. Schlegel⁵, M. Fattahi¹

¹ SUBATECH Laboratory, UMR 6457, 4 rue Alfred Kastler, La Chantrerie BP 20722
44307 Nantes cedex 3, France.

² IPN Orsay UMR 8608, Université Paris Sud, Bâtiment 100, 91406 Orsay Cedex, France

³ Department of Chemistry, University of Nevada Las Vegas, Las Vegas, NV, 89154, USA.

⁴ Synchrotron SOLEIL. L'Orme des Merisiers, Saint-Aubin - BP 48,
F-91192 Gif-sur-Yvette Cedex, France.

⁵ CEA, DEN, DPC/SEARS/, F-91191 Gif-sur-Yvette, France.

ABSTRACT

This project focuses on the fundamental study of technetium speciation in highly acidic medium. The behaviour of technetium in HTFMS was investigated first in the presence of α irradiation. Technetium overall structures were performed using XAS spectroscopy. XAFS measurements were performed on the MARS beamline of the SOLEIL synchrotron. The results indicate the formation of a cyclic dimer of Tc(IV) complexed to triflate ligands and formulated as $\text{Tc}_2\text{O}_2(\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_4$. This compound is linearized to $\text{Tc}^{\text{IV}}\text{-O-Tc}^{\text{IV}}$ with the increase of HTFMS concentration. At high concentration of HTFMS +98% (11.15 M), the protonated species $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ which is formed in the absence of external ionizing radiations, is reduced to the (V) oxidation state under α irradiation. Structural characterization by EXAFS spectroscopy and DFT calculations suggests the formation of monomer species of Tc(V)-triflate complexes where $[\text{OTc}(\text{F}_3\text{CSO}_3)_2(\text{H}_2\text{O})_2]^+$ and $[\text{OTc}(\text{F}_3\text{CSO}_3)_2(\text{OH})_2]^-$ compounds were proposed.

α -radiolysis experiments of Tc(VII) were performed in order to compare the radiolytic behaviour of Tc(VII) in both comparable media HTFMS and H_2SO_4 ($C_{\text{H}_2\text{SO}_4} \geq 12$ M). XANES studies show that radiolytic reduction of Tc(VII) leads to the formation of Tc(V)/Tc(VII) mixture in H_2SO_4 13 M and Tc(V) in 18 M of H_2SO_4 . The analysis of EXAFS spectra is consistent with the formation of $[\text{TcO}(\text{HSO}_4)_3(\text{H}_2\text{O})_2]$ and $[\text{TcO}(\text{HSO}_4)_3(\text{H}_2\text{O})(\text{OH})]$ monomer complexes in H_2SO_4 13 M and $[\text{Tc}(\text{HSO}_4)_3(\text{SO}_4)(\text{H}_2\text{O})]$ and $[\text{Tc}(\text{HSO}_4)_3(\text{SO}_4)(\text{OH})]^-$ species at 18 M of H_2SO_4 .

Controlling Nanoparticles Dispersion in Ionic Liquids by Tuning the pH

C. Guibert^a, F. Cousin^b, F. Meneau^c, V. Dupuis^a, J. Fresnais^a, V. Peyre^a

^a *Laboratoire Physico-Chimie des Electrolytes, Colloïdes et Sciences Analytiques (PECSA)
UMR 7195 Université Pierre & Marie Curie – CC 51, 4, place Jussieu,
75252 PARIS Cedex 5 – France*

^b *Laboratoire Léon Brillouin, UMR 12, CEA Saclay, 91191 Gif-sur-Yvette Cedex – France*

^c *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette Cedex – France*

ABSTRACT

Ionic liquids (ILs) are nowadays of uttermost interest to develop new materials. Among them, dispersions of nanoparticles (NPs) in ILs are promising combinations, e.g. for catalyst and batteries, but remain a challenging task since the electrostatic stabilisation often occurring in molecular liquids is likely to differ in ILs. Hence, keeping NPs dispersed in an IL arises ticklish problems of colloidal stability.

On the one hand, we used ethylammonium nitrate (EAN), a well characterised IL that shares many similarities with water; in particular, it is a protic IL.

On the other hand, magnetic NPs give way to numerous promising applications such as magnetic hyperthermia or catalysis. Synergetic behaviours could occur by combining those two components. In our work, we demonstrated that poly(acrylic acid) (PAA) coated maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs give stable dispersions in salted aqueous solutions as well as in EAN. In water, this coating displays an interesting response with the pH leading to reversible flocculation/redispersion of the coated NPs [1]. It is due to the protonation/deprotonation of the acidic groups of the polymer (figure 1) and it has been fully characterised with the help of SAXS experiments on SWING beamline at the SOLEIL synchrotron.

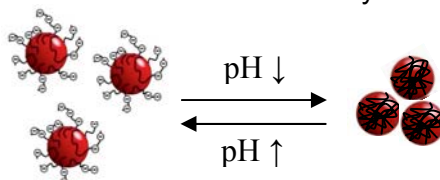


Fig. 1. Reversible mechanism of flocculation/redispersion of PAA coated NPs

Surprisingly, this interesting and reversible transition is preserved in EAN. SAXS experiments shed light upon the mechanisms responsible both for colloidal stability and for this reversible flocculation in EAN (figure 2). These results give a brand new insight on the use of pH for tuning the dispersion state of NPs in protic ILs and an interesting example of similarities between EAN and water.

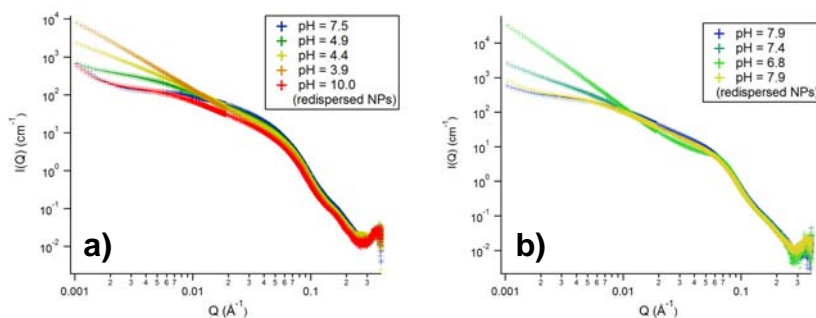


Fig. 2 Spectra of PAA2k coated 6nm maghemite NPs for different pH a) in water, b) in EAN.

REFERENCES

1. J. Fresnais, M. Yan, J. Courtois, T. Bostelmann, A. Bee, J.F. Berret, *J Colloid Interface Sc.*, **395**, 24-30 (2013)

Structural Study of Proteins C3 and C3b by Time Resolved Hydroxyl Radical Footprinting

A. Młynarczyk¹, F. Gonnet¹, I. Salard¹, S. Pin², J.P. Renault²,
A. Giuliani³, P. Mercere³, R. Daniel¹

1. CNRS UMR 8587, LAMBE, Université Evry-Val-d'Essonne, 91025 Evry France

2. CEA, IRAMIS, Laboratoire de Radiolyse and CNRS, URA 331, Laboratoire Claude Fréjacques,
F-91191 Gif-sur-Yvette Cedex, France

3. Synchrotron SOLEIL, L'Orme des Merisiers, 91192 Gif sur Yvette Cedex, France.

ABSTRACT

The complement system is the major component of innate immunity. The central complement protein, C3, and its activated opsonin fragment, C3b, play a major role in all three pathways of complement activation, and are crucial for an efficient immune response. Inappropriate activation and regulation of complement may lead to several autoimmune diseases; thus knowing the structure of C3/C3b will allow us to understand complement activity.

Hydroxyl radical protein footprinting followed by high-resolution mass spectrometry is an emerging method for identifying the dynamics of ligand dependent conformational changes, mapping interfaces and evaluating protein structure. Hydroxyl radicals (OH°), generated from Fenton's reagent, radiolysis or photolysis of water, provide high resolution structural information as they have solvent properties similar to water. We have evaluated two light sources to obtain OH° by radiolysis: linear accelerator ALIENOR (CEA Saclay) delivering high-energy X-rays, and synchrotron beamline Metrology (Synchrotron SOLEIL, Gif sur Yvette). Hydroxyl radicals react with solvent-accessible side chains of proteins, leading to mass shifts useful to study the accessibility of that site. Identification of modified peptides and evaluation of mass increases in the millisecond timescale by liquid chromatography coupled with mass spectrometry allow tracking of the regions implicated in conformational changes during protein complex formation.

Hydroxyl radical footprinting is an alternative to conventional bio-structural methods such as X-ray crystallography, hydrogen-deuterium exchange or electron microscopy, which do not allow the study of dynamic conformational changes. Furthermore, it is a robust and powerful technique for identification of protein interfaces and rearrangements, regardless of protein size.

High Resolution FTIR Spectroscopy of Glycolaldehyde: Towards its Remote Sensing Detection in Biomass Fires

E. Neeman,^a T. R. Huet,^a A. Perrin,^b J. Vander Auwera,^c O. Pirali^{d,e}

^a PhLAM, UMR8523 CNRS – Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France

^b LISA, UMR7583 CNRS – Université Paris 7 & 12, 94010 Créteil Cedex, France

^c SCQP – Université Libre de Bruxelles, 50 Av. F Roosevelt, 1050 Bruxelles, Belgique

^d ISMO, UMR8214 CNRS – Université Paris-Sud, Bât. 210, 91405 Orsay Cedex, France

^e AILES Beamline, SOLEIL, L'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France

ABSTRACT

Cis-glycolaldehyde (HCOCH₂OH) has been detected in biomass fires, by mass spectrometry and low resolution FTIR spectroscopy (Burling et al, 2011). Remote sensing measurements of this species are not yet possible, as its spectroscopy is not precisely known. Indeed, the IR absorption spectrum of gas phase cis-glycolaldehyde has only been recorded at low resolution (Michelsen et al, 1969). This spectroscopic characterization of the species was confirmed by subsequent photolysis experiments (Niki et al 1981).

The main purpose of the present work is to build a database of cis-glycolaldehyde line positions and intensities in the IR range, between 700 and 1300 cm⁻¹. Such a database will ensure that precise quantification of cis-glycolaldehyde can be made when retrieved from atmospheric spectra. It will also make it possible to distinguish the signature of cis-glycolaldehyde from those of other C₂H₄O₂ isomers (namely acetic acid) and of several other Volatile Organics Compounds absorbing in the same region [e.g. formaldehyde, formic acid (Vander Auwera et al 2007; Perrin and Vander Auwera 2007)].

The spectra have been recorded in a multipass cell coupled to the high resolution FTIR spectrometer of the AILES beamline, using the synchrotron radiation. Two strong fundamental bands have been considered: the O=C–C bend and the C–C stretch observed near 751.5 and 860.5 cm⁻¹, respectively. Preliminary results of the analysis will be presented.

This project is part of the GDRI HiResMIR (CNRS-INSU). Support from the *Laboratoire d'Excellence CaPPA* (Chemical and Physical Properties of the Atmosphere) through contract ANR-10-LABX-0005 of the *Programme d'Investissements d'Avenir* is acknowledged.

REFERENCES

- Burling I. R., Yokelson R. J., Akagi S. K. et al: Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States, *Atmos. Chem. Phys.* 11, 12197–12216, 2011.
- Michelsen H. and Klabeo P.: Spectroscopic Studies of Glycolaldehyde, *J. Mol. Struct.* 4, 293-302, 1969.
- Niki H., Maker P. D., Savage C. M. et al: An FTIR study of mechanisms for the HO radical initiated oxidation of C₂H₄ in the presence of NO: detection of glycolaldehyde, *Chem. Phys. Lett.* 80, 499-503, 1981.
- Vander Auwera J., Didriche K., Perrin A., Keller F.: Absolute line intensities for formic acid and dissociation constant of the dimer, *J. Chem. Phys.* 126, 124311/1-9, 2007.
- Perrin A. and Vander Auwera J.: An improved database for the 9 μm region of the formic acid spectrum, *J. Quant. Spectrosc. Radiat. Transfer* 108, 363–370, 2007.

Self Assembly of Mesoporous Materials. Kinetics of Material Formation Followed by In-situ SAXS Measurements

J. Schmitt, M. Impéror

Laboratoire de Physique des Solides, UMR 8502, Université Paris Sud

ABSTRACT

Mesoporous silica materials, with a porosity controlled by use of a surfactant, are systems extensively studied those past 15 years. They are obtained in solution by self-assembly process between surfactant micelles and silica oligomers. In our group, we study the cooperative mechanisms allowing to a hybrid organic/inorganic mesophase to form.

Among those materials, one of the most commonly studied is the SBA-15 (surfactant: P123, and silica precursor: TEOS). Thanks to Small Angle X-Ray Scattering performed at Soleil synchrotron (SWING beamline), we were able to fully characterize the different stages of SBA-15 material synthesis [1]. Especially - by a complete modelling of the SAXS spectra - we highlighted the presence, prior to the material precipitation, of hybrid cylindrical micelles, containing silica oligomers within their corona.

Also by *in situ* SAXS, we studied to syntheses of two other hybrid materials with two different fluorinated surfactants ($R^F_7(EO)_8$ et $R^F_8(EO)_9$) [2]. We were able to link the qualities of the obtained hybrid material with the shape of the micelles in solution. What is more, by mixing $R^F_8(EO)_9$ and P123, we are able to form materials with a well-defined bimodality.

Moreover, meso-structured material presents itself as a powder of micrometric grains. The shape of the grains can be easily tuned by simply changing the synthesis temperature [3]. By mean of USAXS measurements, we were able to study the formation of the grains.

REFERENCES

[1] Manet S., Schmitt J., Impéror-Clerc M., Zholobenko V., Durand D., Oliveira C., Pedersen J., Gervais C., Baccile N., Babonneau F., Grillo I., Meneau F. and Rochas C., **Kinetics of the Formation of 2D-Hexagonal Silica Nanostructured Materials by Nonionic Block Copolymer Templating in Solution**, *J. Phys. Chem B* (2011), 115, 11330–11344

[2] Schmitt J., Impéror-Clerc M., Michaux F., Blin J.L., Stébé M.J., Pedersen J. and Meneau F., **Formation of Nanostructured Silica Materials Templated with Nonionic Fluorinated Surfactant Followed by in Situ SAXS**, *Langmuir* (2013), 29, 2007–2023

[3] Moulin R., Schmitt J., Lecchi A., Degrouard J. and Impéror-Clerc M., **Morphologies of mesoporous SBA-15 particles explained by the competition between interfacial and bending energies**, *Soft Matter* (2013), DOI :10.1039/c3sm52108g

[4] Kjellman T., Asahina S., Schmitt J., Impéror-Clerc M., Terasaki O. and Alfredsson V., **Direct observation of plugs and intrawall pores in SBA-15 using low voltage high resolution SEM and the influence of solvent properties on plug-formation**, *Chemistry of Materials* (2013), 25 (20), 4105–4112

Influence of Counterions on Hectorite Swelling Properties Monitored by NAP-XPS

H. Tissot^{1,2}, G. Olivieri², A. Naitabdi^{1,2}, F. Bournel^{1,2}, J.-J. Gallet^{1,2},
R. Benbalagh¹, F. Rochet^{1,2}, F. Sirotti², V. Marry³, E. Dubois³

¹*Laboratoire de Chimie Physique Matière et Rayonnement (UMR 7614),
Université Pierre et Marie Curie – CNRS, Paris, France*

²*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Gif sur Yvette, France*

³*Laboratoire Liquides Ioniques et Interfaces Chargées, Université P. et M. Curie, Paris, France*

ABSTRACT

Natural clays are key materials in ecological engineering, from the geological storage of long half-time radioactive waste [1] to CO₂ sequestration [2]. With respect to these issues, it is crucial to establish a bridge between the microscopic scale (ionic exchange, ion solvation, ion and matter transport) and the macroscopic scale (swelling, retention capacities). One fundamental question is the hydration of clays, which governs their properties and uses. We are interested here in the initial stages of water adsorption on external surfaces and interlayers of a synthetic hectorite clay which can be considered as a “model clay system” because of its well defined swelling characteristics [3].

NAP-XPS brings a new approach with a surface sensitive technique on the adsorption of water by clays. Counterions core-level are sensitive to the hydration state (change in binding energy) due to a screening effect of the negatively charged clay layers by water molecules. In the case of Na-hectorite a shift of 0.9 eV of the Na 2s binding energy was observed when the relative humidity increased to 60%. Furthermore, varying the electron mean free path through the excitation energy and analysing the O 1s core level [4] reveal the water presence in the clay interlayer. These tools allow us to compare the effect of counterions of different size and charge as Na⁺, Cs⁺ and Sr²⁺; and to understand how the presence of these counterions is affecting the swelling pattern.

REFERENCES

1. M. Bradbury, B. Baeyens, *Technical report, Paul Scherrer Institut* **2003**
2. I. Gaus, *International Journal of Greenhouse gas control* **2010**, 4, 73-89
3. N. Malikova, A. Cadène, E. Dubois, V. Marry, S. Durand-Vidal, P. Turq, J. Breu, S. Longeville, J.M. Zanotti *J. Phys. Chem. C* **2007**, 111, 17603
4. K. Arima, P. Jiang, X. Deng, H. Bluhm, M. Salmeron *J. Phys. Chem. C* **2010**, 114, 14900–14906

Investigation of Oil Uptake in Fried Foodstuffs using Synchrotron Radiation

J.M. Vauvre^(1,2), A. Patsioura⁽¹⁾, R. Kesteloot⁽²⁾, F. Jamme⁽³⁾, O. Vitrac^(1*)

(1) INRA, JRU 1145 Food Process Engineering, Group I2MC

AgroParisTech site de Massy, 1 rue des Olympiades, 91300 Massy, France

(2) Kesteloot conseil, 60 Avenue du Colonel Driant, 59130 Lambersart, France

(3) Synchrotron SOLEIL, Disco beam line, l'orme les Merisiers, 91192 Gif-sur-Yvette, France

ABSTRACT

Fried food products, including French-fries, chips, nuggets... are regularly associated to “junk food”. Consumer preferences for such products originate from their unique crispiness, but their high oil content is definitively a drawback. Imbibition of fried products by oil occurs mainly when they are removed from the frying bath. During this stage, oil capillary pressure exceeds internal pressure and combined with steam condensation trigger oil infiltration. Both connectivity of cells and biphasic oil-air capillary flow play a central role^{1,2}. Previous experiments in micro-computed Xray tomography demonstrated that oil reaches large cavities in par-fried frozen French-fries via a very small number of entry points *ca.* 6 cm⁻². This surprising result was specifically studied at synchrotron SOLEIL via two specific projects using UV (DISCO beamline) and IR (SMIS beamline) radiations. The complementarity between lab-scale experiments and simulations with devoted synchrotron experiments is particularly discussed.

The first project at SOLEIL emphasized the percolation of oil through the two first layers, when the potato parenchyma was first equilibrated with super-heated steam at 120°C (*i.e.* fried without oil) and subsequently exposed to oil at the same temperature. Since air was present during the experiment, the role of trapped air could be elucidated by imaging dynamically the UV fluorescence of cell walls and the fluorescence of dyed oil. A 3D reconstruction at the scale of digitized structures enabled to relate the penetration kinetics of oil and the dynamics of trapped air bubbles within defects smaller than few micrometers. The creation of a bi-phasic counter current was simulated numerically with a capillary model integrating the variations of drag and capillary forces in presence of air bubbles. It was shown that the ratio bubble-to-defect diameters was controlling the delay between the first and second cell layer varying from few tenth seconds up to minutes.

Major constituents of potato parenchyma in the crust (cell walls and glassy molten starch) were found remarkably very good barriers to oil (barriers for hours), while exhibiting a good permeability to steam and air. Numerical simulations demonstrated that such very low permeabilities originate from the high fluctuations of pore diameters from nanometers to micrometers. Conversely, deep oil infiltration observed in industrial French-fries was associated to a zip-like opening of junctions in cells injured during the freezing step. A general methodology to detect the accumulation of mechanical constraints between the rubber crumb and the glassy crust during frying was devised at SOLEIL. At the scale of cell walls, we used 2D FTIR (temperature×wavelength) microspectroscopy in ATR mode to assess the variation of absorption bands with temperature and glass temperature. In temperature and relative humidity conditions, it was shown that the first derivatives of spectra with temperature (T) and glass transition temperature (T_g) were opposed and enabled the identification of the difference T-T_g from the displacements of C-O-C, CH cellulose stretching bands and of COO stretching pectin bands. A new project will be submitted in 2014 to reach a dynamic imaging of T_g map during simulated frying conditions.

REFERENCES

1. Achir, N.; Vitrac, O.; Trystram, G., Heat and mass transfer during frying. In *Advances in Deep-Fat Frying*, Sahin, S.; Sumunu, S. G., Eds. CRC Press: Boca-Raton, 2009; pp 5-32.
2. Achir, N.; Vitrac, O.; Trystram, G. *Food Res. Int.* **2010**, 43, (1), 307-314.

Trace Elemental Imaging of Rare Earth Elements Discriminates Tissues at Microscale in Flat Fossils

P. Gueriau^{1,2}, C. Mocuta³, D.B. Dutheil¹, S.X. Cohen², D. Thiaudière³,
S. Charbonnier¹, G. Clément¹ and L. Bertrand^{2,3}

¹ CR2P, UMR 7207 CNRS, MNHN, UPMC, 57 rue Cuvier, CP 38, F-75005, Paris, France

² IPANEMA CNRS, MCC, USR 3461, BP48 Saint-Aubin, F-91192 Gif-sur-Yvette, France

³ Synchrotron SOLEIL, BP48 Saint-Aubin, F-91192 Gif-sur-Yvette, France

ABSTRACT

The interpretation of flattened fossils remains a major challenge due to compression of their complex anatomies during fossilization, making critical anatomical features invisible or hardly discernible. Key features are often hidden under greatly preserved decay prone tissues, or an unpreparable sedimentary matrix. A method offering access to such anatomical features is of paramount interest to resolve taxonomic affinities and to study fossils after a least possible invasive preparation. Unfortunately, the widely-used X-ray micro-computed tomography, for visualizing hidden or internal structures of a broad range of fossils, is generally inapplicable to flattened specimens, due to the very high differential absorbance in distinct directions. Here we show that synchrotron X-ray fluorescence spectral raster-scanning coupled to spectral decomposition or a much faster Kullback-Leibler divergence based statistical analysis provides microscale visualization of tissues. We imaged exceptionally well-preserved fossils from the Late Cretaceous without needing any prior delicate preparation. The contrasting elemental distributions greatly improved the discrimination of skeletal elements material from both the sedimentary matrix and fossilized soft tissues. Aside content in alkaline earth elements and phosphorus, a critical parameter for tissue discrimination is the distinct amounts of rare earth elements. Local quantification of rare earths may open new avenues for fossil description but also in paleoenvironmental and taphonomical studies.

Understanding Large Amplitude Internal Motions - Laboratory Search for Vibrational Excited Spectra of Oxadisulfane (HSOH) and Singly Substituted ^{13}C Dimethyl Ether

P. Kutzer¹, T.F. Giesen¹, O. Piralli², P. Roy²

¹University of Kassel, Institute of Physics, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

²Société civile Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin – BP 48, F-91192 Gif Sur Yvette Cedex, France

ABSTRACT

Understanding large amplitude internal motions is a prerequisite for sophisticated quantum chemical models and highly accurate laboratory data. Both species Dimethyl ether (DME) and Oxadisulfane are excellent test cases to study internal molecular rotations. Besides both species are also of astrophysical relevance. DME has been found in space in 1974 by Snyder et al and plays an important role in astrochemical processes. The presence of HSOH is postulated in sulfur containing environments of planetary atmospheres and molecular clouds in the ISM.

Both molecules are accidental prolate tops showing very dense spectra in the millimeter and sub millimeter frequency range. DME possesses two internal rotors (CH_3) that can perform large amplitude motions. Oxadisulfane possesses two moieties (OH) and (SH) that can rotate around the (SO) bond.

Standard *ab initio* calculations and fitting programs are not well suited to predict and analyze such species containing one or two internal rotors and showing strong coupling effects. Another open question is the influence of the symmetry properties and their influence on rovibrational spectra. A simple rigid rotor model will not be suitable to describe such molecules, so that interaction terms are strongly needed. To understand such highly dependent internal motions, suitable theoretical models are needed.

Up to now especially for the vibrational excited states of singly ^{13}C substituted species only *ab initio* calculations were available the same is true for HSOH. There have up to this summer been no broadband measurements of pure probes of singly ^{13}C substituted DME.

In summer 2013 we aimed for measurements of oxadisulfane. Therefore we used a completely new designed absorption cell that consisted of parts from Kassel and from SOLEIL. This very challenging RF-plasma experimental setup worked well and we gained an absorption pathway of 4 m. We were also able to record broadband spectra of a pure sample of singly ^{13}C substituted DME. All measurements were done within the spectral region from 50cm^{-1} to 700cm^{-1} at a resolution of 30MHz using the FT-IR spectrometer at the AILES beam-line. The gained spectra have perfect signal to noise ratio and reveal many transitions.

For DME they allow us the assignment of the C-O-C in bending mode as well as of the first torsional excited states ν_{11} and ν_{15} . The band centers of the last two lie roughly at 190cm^{-1} and 240cm^{-1} this corresponds to temperatures of 270K and 340K. This is within the range of lukewarm cores of star forming regions. In the case of Oxadisulfane first analyses of the spectra gives clues about the formation process within the plasma.

The recorded data will help us to identify these species in interstellar medium and thereby help to break through the line confusion of interstellar weeds. The recorded spectra will help to develop improved quantum chemical models and calculations, for a better understanding of large amplitude internal motions.

Magnon to Electro-active Excitation Transmutation in the ErMnO₃ Multiferroic

L. Chaix^{1,2}, S. de Brion², V. Simonet², E. Ressouche³, R. Ballou²,
P. Lejay², S. Petit⁴, A. Cano⁵, L.P. Regnault³, J. Ollivier¹,
J.B Brubach⁶, F. Willaert⁶, P. Roy⁶

¹ Institut Laue-Langevin, 6 rue Jules Horowitz BP 156 38042 Grenoble, FRANCE

² Institut Néel, 25 avenue des Martyrs BP 166 38042 Grenoble cedex 9, FRANCE

³ INAC/SPSMS-MDN, CEA/Grenoble, 17 rue des Martyrs 38054 Grenoble, FRANCE

⁴ CEA, Centre de Saclay, /DSM/IRAMIS/ Laboratoire Léon Brillouin, 91191 Gif-sur-Yvette, France

⁵ European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France

⁶ Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48,

F-91192 Gif-sur-Yvette Cedex, France

ABSTRACT

The recent interest for spintronic and more generally of spins/charges cross controls devices motivates material science research in the field of (i) multiferroicity where magnetic and ferroelectric order parameters coexist, (ii) magneto-electric effect, cross coupling between magnetic and electric degrees of freedom and (iii) magnonics. The dynamical magneto-electric effect has been investigated so far in the form of electric-charge dressing of magnons called electromagnons, as observed recently in some multiferroics [1,2,3].

The low energy dynamical properties of the multiferroic hexagonal perovskite ErMnO₃ have been studied using FIR and THz spectroscopies and inelastic neutron scattering, with and without polarization analysis. These complementary spectroscopic tools have allowed us to ascribe the various observed excitations either to magnons induced by the Mn magnetic ordering, to crystal field transitions of the rare earth ions or to phonons. A main antiferromagnetic order for the Mn³⁺ ions takes place below $T_N \approx 80\text{K}$. A complex phase diagram (magnetic field / temperature) is induced at low temperature with several transitions and spin reorientations due to the Mn-Er coupling. The dynamical spectra were obtained by measuring the THz transmission at the AILES beamline of the Synchrotron SOLEIL within a cryogenic environment. The wide-range energy [10cm^{-1} to 200cm^{-1}] combined with the natural polarization (98%) of the THz radiation allowed us measuring magnetic and structural excitations with different selection rules implying all possible geometries for the THz electric and magnetic field as regards to the crystal **c**-axis: **h//c e \perp c**, **h \perp c e//c** and **h \perp c e \perp c**.

Two intense absorption signals were detected at 6K for **h//c e \perp c** and **h \perp c e//c** around 18.5 cm^{-1} and 45 cm^{-1} respectively. Both absorptions disappear above T_N . For **h \perp c e \perp c**, no particular absorption was detected in this energy range. From comparison with inelastic neutron scattering and spin wave calculations, we assign the first signal to a standard magnon (**M**) whereas the signal at 45 cm^{-1} (**h \perp c e//c**) is attributed to an electromagnon (**EM**).

The cross coupling between Mn and Er might explain the electrical dipolar behaviour of the non conventional **EM** excitation observed in the THz and FIR experiments with a hybridization between the Er crystal field and the Mn magnetic moment [5].

REFERENCES

1. A. Pimenov, A. A. Mukhin, V. Y. Ivanov, *et al.*, Nature Physics 2 (2006) 97.
2. D. Senff, P. Link, K. Hradil, A. Hiess, L.P. Regnault, *et al.*, Phys. Rev. Lett. 98, 137206 (2007).
3. S. Petit, F. Moussa, M. Hennion, *et al.*, Phys. Rev. Lett. 99, 266604 (2007) ; S. Pailhès, X. Fabrèges, L. P. Regnault, L. Pinsard-Godart, I. Mirebeau, F. Moussa, M. Hennion, and S. Petit, Phys. Rev. B 79, 134409 (2009).
5. L. Chaix *et al.*, in preparation.

Interface Electronic Structure of SrRuO₃/BaTiO₃/SrRuO₃ Capacitor

S. Gonzalez, J. Rault, T. Maroutian, G. Angus, D. Cooper, N. Barrett

¹DSM/IRAMIS/SPEC, CEA Saclay, 91191 Gif-sur-Yvette, France

²Synchrotron-SOLEIL, BP 48, Saint-Aubin, F91192 Gif sur Yvette CEDEX, France

³Institut d'électronique fondamentale, Bât. 220, Université Paris-Sud, 91405 Orsay Cedex, France

⁴CEA, LETI, Minatec Campus, F-38054 Grenoble Cedex 09, France

ABSTRACT

The defining property of a Ferroelectric (FE) material is a spontaneous macroscopic polarization which can be reversed under an applied electric field. This has attracted wide interest, the perspective of strain engineering films for FE-based electronics [1]. Switching the polarization of such films requires a metallic contact, raising fundamental issues on the behavior of the interface between the FE layer and the electrode.

Metallic oxide electrode screening can be very different from that of a noble metal such as platinum. High quality epitaxial growth reduces the interface defect concentration. In spite of lower free charge carrier concentration and mobility, ionic relaxation at the electrode/ferroelectric interface provides an additional screening mechanism of the depolarizing field [2].

We have used hard X-ray photoemission spectroscopy (HAXPES) to probe the buried SrRuO₃/BaTiO₃ interface in a SrRuO₃/BaTiO₃/SrRuO₃ capacitor with varying thicknesses of the top SrRuO₃ electrode.

We directly measure the polarization dependent band alignment thanks to a sample design allowing in-situ biasing. We observe a polarization-induced shift in the electron barrier heights of 0.40 eV when polarization switches. This shift is smaller than those measured with other metallic electrodes [3,4] and is related to the additional screening provided by ionic displacement of the SRO ions as observed by HRTEM.

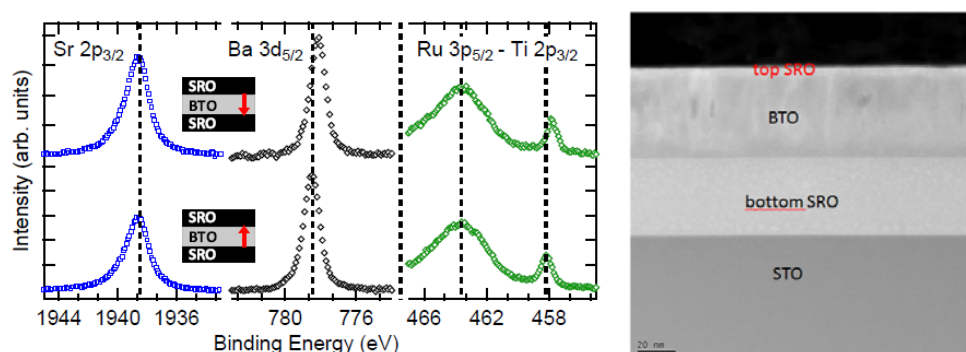


Figure: (left) Sr 2p, Ba 3d and Ru 3p/Ti 2p core level spectra for opposite polarization states. (right) HRTEM cross-section of the complete capacitor structure with a 5 nm SrRuO₃ top electrode.

REFERENCES

- [1] X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom, C. B. Eom, A. Tofterup, K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, and Y. B. Chen, *Science* 306, 1005 (2004).
- [2] A. K. Tagantsev and G. Gerra, *Journal of Applied Physics* 100, 051607 (2006).
- [3] F. Chen and A. Klein, *Physical Review B* 86, 094105 (2012).
- [4] J. E. Rault, G. Angus, T. Maroutian, V. Pillard, P. Lecoq, G. Niu, B. Vilquin, M. G. Silly, A. Bendounan, F. Sirotti, and N. Barrett, *Physical Review B* 87, 155146 (2013).

Graphene Lattice Parameter on Ir(111) Vs Temperature: Strain, Commensurability and Defects

F. Jean,¹ N. Blanc,¹ T. Zhou,² R. Felici,³ J. Coraux,¹ G. Renaud²

¹ Institut Néel (CNRS), Grenoble, France

² CEA INAC, Grenoble, France

³ European Synchrotron Radiation Facility, Grenoble, France

ABSTRACT

The exceptional properties of graphene can be modified and hopefully tailored by strains [1]. The origins of strain in epitaxial graphene are diverse : tendency to commensurability with the substrate, defects, and mismatch of thermal expansion coefficients. Isolated graphene was predicted to have a negative thermal expansion coefficient below room temperature [2]. This could account for recent observations made on exfoliated graphene on SiO₂ [3]. Whether this effect should be expected also in epitaxial graphene remains unknown.

We prepared high quality graphene on Ir(111) by chemical vapor deposition [4]. The structural properties of the system were investigated in situ, in the ultra-high vacuum chamber where the samples were prepared, as a function of sample temperature, by surface X-ray diffraction using synchrotron light. At variance with the expectation for free-standing graphene, epitaxial graphene on Ir has a positive thermal expansion coefficient between 10 and 300 K that matches the behavior of iridium (see Figure linked). Despite the very high graphene stiffness, its weak but non-zero interaction with Ir is sufficient to strain it. Moreover, different commensurate states between the graphene and the substrate are observed during and after the growth as a function of temperature.

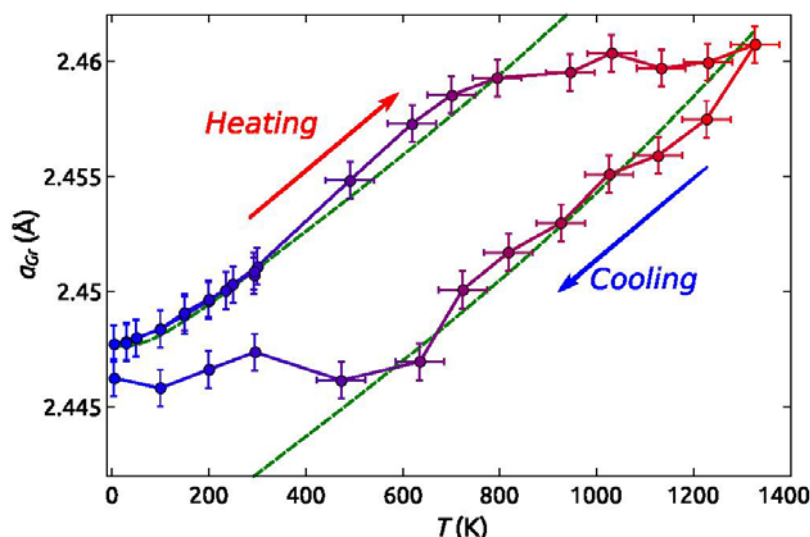


Figure 1 : Evolution of the graphene lattice parameter a_{Gr} as a function of the temperature T (blue and red circles). The dashed green curves are the evolution of the bulk Ir lattice parameter with temperature reported as a guide for the eyes to match the evolution of the graphene lattice parameter. The arrows mark the thermal history of the sample.

REFERENCES

- [1] N. Levy et al, Science, **329**, 544 (2010).
- [2] K. V. Zakharchenko et al., Phys. Rev. Lett. **102**, 046808 (2009).
- [3] D. Yoon et al., Nano Lett. **11**, 3227 (2011)
- [4] J. Coraux et al., Nano Lett. **8**, 565 (2008).

Sulfur Adsorption on Pd(111) and Thiol Self Assembled Layer Formation

J. Jia^{1,2}, A. Bendounan³, L. Pasquali^{4,5}, K. Chaouchi³,
F. Sirotti³ and V.A. Esaulov^{*1,2}

¹ *Université-Paris Sud, Institut des Sciences Moléculaires d'Orsay, Orsay.*

² *CNRS, UMR 8214, Institut des Sciences Moléculaires d'Orsay, Orsay.
Bâtiment 351, Université Paris Sud, 91405 Orsay, France.*

³ *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48,
F-91192 Gif-sur-Yvette Cedex, France*

⁴ *CNR-IOM, s.s.14, km 163.5 in Area Science Park, 34012 Trieste, Italy*

⁵ *Dipartimento di Ingegneria 'Enzo Ferrari', Università di Modena e Reggio Emilia,
Via Vignolese 905, 41125 Modena, Italy*

ABSTRACT

The absorption of S on Pd(111) was studied using high resolution X-ray photoemission spectroscopy at TEMPO beam line in Soleil. The sample was prepared by immersing a pristine Pd(111) crystal into an aqueous solution of Na₂S. The photoemissions results show that the immersion leads to S adsorption and appearance of a multi-structured S(2p) related peak centered at about 163 eV. Formation of Pd-S bonds induces large binding-energy shifts to higher binding energy in the core levels of Pd(3d). After annealing to a temperature of about 450 degree, the S(2p) peak changes dramatically in form and is mainly composed of only one component with a very small structure at lower binding energy. The Pd_3d peak changes into a main peak and lower lying shoulder. The main peak lies close to the binding energy before annealing. The other one at a lower binding energy must be due to Pd bulk atoms. A LEED study shows the appearance of a clear pattern attributable to formation of a ($\sqrt{7} \times \sqrt{7}$) R19.1° surface layer. This is a mixed top-surface which consists of both S and Pd atoms. Some measurements of absorption of C12 alkanethiol molecules on mixed S and Pd reconstructed surface was also performed in order to compare with thiol molecules on Pd(111) surface.

Resonant Soft X-ray Scattering on Artificial Spin Ice

J. Perron^{1, 2, 3}, L. Anghinolfi^{2, 3}, B. Tudu¹, N. Jaouen⁴, J.M. Tonnerre^{5, 6},
F. Nolting³, J. Lüning¹, L.J. Heyderman^{2, 3}

(1) *Laboratoire de Chimie-Physique – Matière et Rayonnement (UMR 7614 UPMC/CNRS),
Université Pierre et Marie Curie, 75231 Paris Cedex 05, France*

(2) *Laboratory for Mesoscopic Systems, ETH Zürich, 8093 Zürich, Switzerland*

(3) *Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

(4) *Synchrotron SOLEIL, 91192 Gif-sur-Yvette, France*

(5) *Université Grenoble Alpes, Institut Néel, 38042 Grenoble, France*

(6) *CNRS, Institut Néel, 38042 Grenoble, France*

ABSTRACT

Artificial spin ice systems are arrays of dipolar coupled nanomagnets arranged on the sites of kagome or square lattices [1, 2]. At the vertices where the nanomagnets meet, geometrical frustration prevents all dipolar interactions being satisfied simultaneously. These systems are usually studied with real space microscopy techniques such as Lorentz microscopy or photoelectron emission microscopy [3, 4]. Scattering techniques can provide complementary information on magnetic correlations over larger areas and potentially shorter timescales.

In the present work carried out at the SEXTANTS beamline of Synchrotron SOLEIL, the use of a CCD detector allowed us to measure an extended portion of the reciprocal space at once. By applying a magnetic field and flipping the circular helicity of the x-ray beam, variations in the intensity of the Bragg peaks were obtained via the x-ray magnetic circular dichroism effect. Our analysis of these data demonstrates that information about the organisation of the magnetic moments in artificial spin ice arrays can be deduced from reciprocal space measurements.

We observe pure magnetic Bragg peaks in artificial square ice, which is related to the establishment of a long range antiferromagnetic ground state ordering in the as-grown state [5]. Applying a magnetic field annihilates this ordering and evolution of the scattering pattern is compared with numerical simulations based on the kinematical approach. On calculating the full x-ray scattering pattern, we have been able to reproduce correctly the main features as well as to estimate the number of reversed nanomagnets in the artificial spin ice array [6].

The presented work is the first step of an on-going project, which aims at studying magnetic correlations and their dynamics in artificial spin ice.

REFERENCES

1. R.F. Wang *et al.*, *Nature* **439**, 303-306 (2006).
2. L.J. Heyderman and R.L. Stamps, *J.Phys.: Condens.Matter.* **25**, 363201 (2013).
3. C. Phatak *et al.*, *Phys. Rev. B* **83**, 174431 (2011).
4. A. Farhan *et al.*, *Phys. Rev. Lett.* **111**, 057204 (2013).
5. J.P. Morgan, A. Stein, S. Langridge and C.H. Marrows, *Nat. Phys.* **7**, 75-79 (2011).
6. J. Perron *et al.*, submitted to *Phys. Rev. B*.

XMCD at Fe L_{2,3} Edges of two Precursors for Photomagnetic Molecular Prussian Blue Analogues: Observation of a Large Orbital Magnetic Moment

F. Sadaf¹, D. Mitcov^{2,3}, M.-A. Arrio¹, A. Juhin¹, O. Bunau¹, V. Schuler¹,
C. Mathonière², R. Clérac³, E. Otero⁴, P. Ohresser⁴,
C. Cartier dit Moulin⁵, P. Sainctavit^{1,4}

[1] IMPMC, CNRS UMR 7590, UPMC, France

[2] ICMCB, CNRS UPR 9048, France

[3] CRPP, CNRS UPR 8641, France

[4] Synchrotron SOLEIL, Saint-Aubin, France

[5] IPCM, CNRS UMR 7201, UPMC France

ABSTRACT

Photomagnetism in CoFe prussian blue analogues is a complex phenomenon. In order to develop molecular nanomagnets with desired photomagnetic properties, the electronic and magnetic properties of the corresponding precursors, which are the building blocks of molecular magnets, must be investigated. In this talk, we present our results obtained on two Fe bearing precursors (see figure1) of two photomagnetic FeCo Prussian Blue analogues that have either a cube shape or square shape. We have performed X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at Fe L_{2,3} edges, on the DEIMOS beamline at SOLEIL, that make available the wealth of information about the spin and orbit magnetic moments. The detailed interpretation of the XAS and XMCD data was achieved using Ligand Field Multiplet calculations. For both precursors, Fe^{III} ions were found to possess a large orbital magnetic moment 1.24μ_B which is significantly higher than the value of the spin magnetic moment 0.98μ_B. The exceptionally large orbital magnetic moment is crucial in the coupling of the iron magnetic properties with the crystal structure. It certainly plays a major role in driving the thermo-induced charge transfer phase transition that is observed in the associated PBA.



Figure1: Structure of the [(pzTp)Fe^{III}(CN)₃] (left) and [(Tp*)Fe^{III}(CN)₃] (right) precursors. The iron atoms are in red, carbon atoms are in black and the nitrogen ones are in blue. Hydrogen atoms are not shown here.

REFERENCES

1. D. Li, S. Parkin, G.Wang, G.Yee, and S.Holmes, "Synthesis and spectroscopic and magnetic characterization of tris(3,5-dimethylpyrazol-1-yl) borate iron tricyanide building blocks, a cluster, and a one-dimensional chain of squares," INORGANIC CHEMISTRY, vol.45, pp.1951--1959, March 6, 2006.
2. D. Li, R. Clérac, O. Rubeau, E. Harte, C. Mathonière, R. Le Bris, and S.M. Holmes, "Magnetic and optical bistability driven by thermally and photoinduced intramolecular electron transfer in a molecular cobalt-iron Prussian blue analogue," JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 130, pp.252--258, JAN 9,2008.
3. D.Li, R.Clérac, S.Parkin, G.Wang, G.Yee, and S.Holmes, "An S=2 Cyanide-Bridged Trinuclear Fe^{III}₂ Ni^{II} Single Molecule Magnet", INORGANIC CHEMISTRY, vol.45, pp.5251--5253, March 6, 2006

The HAXPES Study of Full High-k/Metal Gate Stacks Deposited on Ge

I. Kalpyris^{a,b,c}, T. Conard^a, C. Fleischmann^a, C. Adelman^a, S. Sioncke^a,
J.-P. Rueff^c, J.M. Ablett^c, W. Vandervorst^{a,b}

a) imec, Kapeldreef 75, B-3001 Leuven, Belgium

b) IKS-Dept Physics, KU Leuven, Celestijnenlaan 200D, Leuven, B-3001, Belgium

c) Soleil Synchrotron, L'Orme des Merisiers Saint Aubin - BP 48 91 192 Gif sur Yvette CEDEX

ABSTRACT

The introduction of Ge in CMOS devices beyond the 14 nm technology node, requires effective passivation of the Ge gate stack. Besides the interface passivation, a highly scaled gate stack is needed for the next generation of CMOS devices. Scaling of the gate stack can be achieved by several means, for instance by changing process conditions. In this work, we investigate the influence of both the high-k stack and the metal gate on the properties of the GeO_xS_y interfacial passivation layer by Hard X-ray Photoelectron Spectroscopy (HAXPES). The thickness of the interfacial oxide layer depends on various parameter such as temperature treatments or the chemistry of the metal gate deposited on top of the high-K layer. Controlling the interfacial layer is critical to achieve high electrical performances. In many cases a scavenging effect of this layer can be observed during several of these processes that results in reduction of the interfacial film thickness. A correct analysis of this interfacial layer is thus of prime importance and photoemission is an interesting tool for this purpose. This is, however, metrological very challenging as the thickness of a typical gate stack exceeds the information depth of regular XPS analysis. Using high energy x-rays should allow to circumvent the problem by increasing the photoelectron mean free path in the materials

In this work, we investigated the possibilities of the buried interface between the high-k layer and the Ge substrate using HAXPES. For the purpose of this study we considered three high-k stacks (Al₂O₃, HfO₂ and an Al₂O₃/HfO₂ bi-layer) and two metal gates (TiN and TiW). Samples have been measured both after atomic layer deposition and after forming gas anneal, to investigate the effect of a thermal treatment on the interfacial properties. The measurements were carried out using high energy x-rays (6 keV) in GALAXIES beamline at SOLEIL Synchrotron. To disentangle the impact of the particular metal gate, comparison is made to a high-k stack sample without metal gate. To validate the results, HAXPES results were compared with partial sputtering results in a conventional XPS system.

Plasticity of Gold Microcrystals Investigated by Coherent X-ray Diffraction

S. Langlais¹, M. Dupraz¹, G. Beutier¹, F. Berenguer²,
S. Ravy² and M. Verdier¹

¹ SIMaP, CNRS, Grenoble-INP & UJF, BP 75, 38402 Saint-Martin d'Hères cedex, France

² Synchrotron Soleil, L'Orme des merisiers, Saint-Aubin BP 48, Gif-sur-Yvette cedex, France

ABSTRACT

The peculiar mechanical behaviour of small crystals (below the micron), in contrast to their bulk counterpart, has been the focused of intensive research recently. The proposed models, based on so-called 'dislocation starvation', still need to be challenged experimentally.

Coherent X-ray Diffraction (CXD) is an attractive non-destructive technique to address this question because of its sensitivity to crystal defects [1]. By using a microfocused beam, one has the opportunity to observe the defects in a single crystal of sub-micron size.

Here we report of a study of gold sub-micron crystals prepared in various defect states. The crystals were obtained by solid-state dewetting on a sapphire substrate and mechanically loaded in our laboratory by applying a controlled force with a diamond pyramidal tip. Several similar crystals were loaded with various chosen forces in order to obtain various states of plasticity. They were individually measured with a coherent microfocused beam at beamline Cristal of synchrotron Soleil. The fine structure of their 222 Bragg reflection was measured in 3 dimensions.

Unloaded crystals show a 'clean' diffraction pattern which can be modelled by considering the substrate-induced strain in a Finite-Element Model [2]. Loaded samples show a more complex diffraction pattern, due to the multiple crystal faults. A plasticity model can be included in the FEM to understand the main diffraction features [3], while statistical analysis of the speckle pattern could lead to a statistical interpretation of the number of defects. Attempts of phase-retrieval, to retrieve a real space image of the defects, are under way [4].

Such experiment is a first necessary step toward CXD measurements with *in situ* loading at Soleil, such as already implemented in other facilities [5]. With this respect, our beamtime was the opportunity to implement fast mapping of the sample in Bragg geometry and to characterise the recent microfocusing optics of the beamline.

REFERENCES

1. V.L.R. Jacques *et al*, Phys. Rev. Lett. **106**, 065502 (2011).
2. G. Beutier *et al*, Thin Solid Films **530**, 120 (2013).
3. H. Proudhon *et al*, C. R. Physique **11**, 293 (2010).
4. Y. Takahashi *et al*, Phys. Rev. B **87**, 121201(R) (2013).
5. G. Beutier *et al*, J. Physics: Conf. Series **425** 132003 (2013).

In-situ GIWAXS and GISAXS Measurements During AgCo Nanoparticle Growth

A. Lemoine^{1,2*}, P. Andreazza¹, Y. Garreau^{2,3}, C. Andreazza-Vignolle¹,
Z. Kataya¹, A. Coati²

*1 Centre de Recherche sur la Matière Divisée, Université d'Orléans, CNRS,
1b rue de la Férollerie, 45071 Orléans*

2 Synchrotron Soleil, L'Orme de Merisiers, Saint Aubin, 91192 Gif-sur-Yvette

*3 Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Diderot-Paris 7, CNRS, 10 rue
Alice Domon et Léonie Duquet, 75205 Paris*

** asseline.lemoine@cnr-orleans.fr ; asseline.lemoine@synchrotron-soleil.fr*

ABSTRACT

AgCo nanoalloys are studied for their promising magnetic and plasmonic properties, which are governed by size, morphology, structure, and composition effects, but also by the mixing state. Specially, cobalt and silver present a complete immiscibility gap in bulk at room temperature. Owing to the energetic parameters of this system (surface energy, mixing energy), and lattice parameter mismatch between Co and Ag, theoretical studies reveal a strong segregation even at reduced scale. According to nanoparticle (NP) size, and composition, the segregation may be partial (core-shell), or total as Janus-like particles [1,2]. To understand AgCo NP structure and chemical configuration, growth mechanisms need to be studied.

The purpose of our experimental work is to investigate thermodynamic phenomenon influence, relative to kinetic parameter role, on the structural and morphological evolution during AgCo NP growth. The study focuses on NPs smaller than 5nm, prepared by UHV evaporation\condensation on an amorphous substrate. In-situ characterizations are performed thanks to Grazing Incidence Wide and Small Angle X-rays Scattering methods [3] (GIWAXS and GISAXS) on the SixS beam line (SOLEIL synchrotron).

Firstly, bi-metallic NP formation by sequential deposition (Ag then Co) is examined. GISAXS measurements permit to identify nucleation steps, and morphological changes, while GIWAXS gives access to the structural atomic arrangement evolution. A comparison with AgCo NP growth, prepared by a co-deposition mode (Ag and Co simultaneously), reveals that thermodynamic mechanisms overcome on kinetic parameters at these NP sizes, and govern the nanoalloy final structure for similar concentrations and amount of matter. Secondly, a study of Co oxidation influence reveals significant structural and chemical configuration changes. A simple annealing above 300°C permits Co atoms deoxidation [4]. Finally, Anomalous X-rays Scattering [5,6] measurements realized at the Co K-edge, which provide selective information about Co atoms environment, exhibit a strong phase separation between Co and Ag.

REFERENCES

1. I. Parsina, F. Baletto, J. Phys. Chem. C 114, 1504-15011 (2010).
2. R. Ferrando, A. Fortunelli, G. Rossi, Phys. Rev. B 72, 085449 (2005).
3. P. Andreazza in « Nanoalloys: Synthesis, Structure and Properties », Eds D. Alloyeau et al. , p69 (2012) Springer-Verlag, London
4. Z. Kataya, Thèse de Doctorat de l'Université d'Orléans (2013)
5. P. Andreazza, H. Khelifane, O. Lyon, C. Andreazza-Vignolle, A. Ramos, and M. Samah, Eur. Phys. J., 218, 231-244 (2012)
6. T. U. Schüllli, et al., Phys. Rev. B, 71, 035326 (2005)

Structure of the Cd-Tb Approximant to the Quasicrystal

D. Liu⁽¹⁾, T. Yamada⁽²⁾, C. Gomez⁽³⁾, H. Takakura⁽⁴⁾,
R. Tamura⁽⁵⁾, G. Beutier⁽¹⁾, M. de Boissieu⁽¹⁾

1- SIMAP, Université de Grenoble, CNRS, BP 75 38402 St Martin d'Hères Cedex

2- IMRAM, Tohoku University, Sendai Japan

3 Uppsala University, Sweden

4. Hokkaido University, Sapporo, Japan

5. Tokyo University of science, Tokyo, Japan

ABSTRACT

The Cd₆Tb periodic approximant belongs to one of a large family of isostructural Cd₆M (M=Ca, Sr, Y, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds with cubic symmetry (edge length 1.5 nm), which are periodic approximant to the quasicrystal. Its structure can be described as a bcc cubic packing of the so-called Tsai-type icosahedral cluster, which has been shown to be the building blocks of the stable binary quasicrystals Cd_{5.7}Yb (1,2). Similarly to the Zn₆Sc this phase undergoes a structural phase transition towards a monoclinic phase below 190K (3-4).

We will present a detailed structural analysis carried out on the crystal diffractometer. Full data collection has been carried out above and below the phase transition. Diffuse scattering above T_c, together with the structure of the low temperature have been analyzed. The low T phase is similar to the one of the Zn₆Sc approximant, with an ordered tetrahedron, which strongly distorts the surrounding icosahedral shells (5-6).

REFERENCES

- 1 . Tsai A P, Guo J Q, Abe E, Takakura H and Sato T J 2000 Nature **408** 537.
- 2 . Takakura H, Gomez C P, Yamamoto A, de Boissieu M and Tsai A P 2007 Nature Materials **6** 58.
- 3 . R. Tamura, Y. Muro, T. Hiroto, K. Nishimoto, and T. Takabatake Phys Rev B, 2010, 220201(R)
- 4 . Tamura R, Nishimoto K, Takeuchi S, et al 2005 Phys. Rev. B **71** 092203.
- 5 . Ishimasa T, Kasano Y, Tachibana A, Kashimoto S and Osaka K 2007 Phil. Mag. **87** 2887.
- 6- T. Yamada, H. Euchner, C. P. Gómez, H. Takakura, R. Tamura and M. de Boissieu J. Phys.: Condens. Matter, **25**, 205405, (2013).

Probing the Quantum Thermal Fluctuations of Nuclei at the Si K Edge

R. Nemausat,¹ D. Cabaret,¹ Ch. Gervais,² A. Bordage,³
Ch. Brouder,¹ N. Trcera⁴

¹ IMPMC, UPMC, UMR 7590, case 115, 4 place Jussieu, 75005 Paris

² LCMCP, UPMC, UMR 7574, Collège de France, 11 place Marcelin Berthelot, 75005 Paris

³ Institut Néel, UPR 2940, 25 rue des Martyrs, BP 166, 38000 Grenoble

⁴ Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint-Aubin

ABSTRACT

X-ray Absorption Near Edge Spectroscopy (XANES) is a powerful tool to probe the electronic environment of nuclei because the edge structure provides lots of physical information. In many minerals and oxides a pre-edge structure exists at the K-edge of low Z cations in XANES and its origin is still misunderstood. We think that pre-edge features must be described precisely so it can supply other information about materials studied.

In the case of Al K edge [1] it was shown that electronic transitions occurring in the pre-edge involve the 3s empty states of the Al absorbing atom. These $1s \rightarrow 3s$ transitions are supposed to be forbidden in the electric dipole approximation. XANES calculations performed at the equilibrium atom positions do not correctly reproduce the pre-edge structure and it has been shown that the intensity of the pre-edge depends on the temperature [1], and on the site geometry [2]. These are clues about the influence of atoms motion and/or vibrations on the pre-edge structure.

In the present work we study stishovite and α -quartz, two polymorphs of SiO_2 , where the Si atoms are octahedrally and tetrahedrally coordinated to oxygen, respectively. The XANES spectra of these two compounds were measured at the Si K edge for different temperatures (20°C - 500°C) with the aim to relate the pre-edge structure to the structural and vibrational properties of the materials. In the same time, Density Functional Theory (DFT) calculations in a pseudo-potential plane-wave framework are performed to reproduce experimental results [3,4]. Calculations were performed using both equilibrium positions and within a pseudo-dynamic scheme.

We observed that the pre-edge structure is affected by temperature. In the case of stishovite, the pre-edge peak increases with temperature, while the white line decreases. Moreover, both are shifted towards lower energies. In the case of α -quartz, the pre-edge peak slightly emerges, while the white line decreases but the energy shifts are not obvious. These different behaviours seem to be induced to the different symmetries in the neighbouring environment of the absorbing atom.

This work provides both experimental and theoretical evidence of the impact of vibrations on the Si K pre-edge structures for SiO_2 polymorphs.

REFERENCES

1. D. Manuel, D. Cabaret, C. Brouder, Ph. Sainctavit, A. Bordage, N. Trcera, *Phys. Rev. B*, **85**, 224108 (2012). Highlights SOLEIL 108 (2012).
2. D. Cabaret, Ch. Brouder. *J. Phys.: Conf. Series*, **190**, 012003 (2009).
3. C. Gougoussis, M. Calandra, A.P. Seitsonen and F. Mauri, *Phys. Rev. B* **80**, 075102 (2009).
4. P. Giannozzi *et al*, *J. Phys.: Condens. Matter* **21** 395502 (2009).

Ferromagnetic Nanowires Embedded in CeO₂

A. Novikova^{1,*}, E. Fonda¹, Y. Zheng², Y. Dumont³, F. Vidal²

¹ SYNCHROTRON SOLEIL, L'Orme des Merisiers Saint Aubin, Gif-sur-Yvette 91192 France

² INSP, CNRS UMR 7588, UPMC Université Paris 06, 4 Place Jussieu, 75005 Paris, France

³ GEMaC, CNRS-UVSQ, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

* anastasiia.novikova@synchrotron-soleil.fr

ABSTRACT

Magnetic nanowires are promising for high density data recording [1] and very interesting from the theoretical point of view because of their large form anisotropy and small lateral size (from several to several tens of nanometers). Several approaches to their fabrication are possible [2, 3]. This work is dedicated to the characterization of ferromagnetic nanowires fabricated by pulsed laser deposition [4]. Nanowires form spontaneously within cerium oxide thin films during growth from CoO and CeO₂ oxides. The nanowires grow perpendicular to the substrate surface with a diameter of 1-5 nm and they have an easy magnetization axis parallel to their geometrical axis (Fig. 1).

We analyze the nanowires using X-rays absorption spectroscopy (XAS) and magnetometry. XAS is carried out *ex situ* at ambient pressure and temperature as well as *in situ* during thermal treatments (under high vacuum or at low pressure of oxygen) on samples doped with cobalt with proportion varying from 5 to 30%. Recent studies were dedicated to consequent oxidation-reduction treatments in order to investigate the cobalt crystalline state reversibility within the samples. These studies show that the state may be reversible under certain temperature, oxygen pressure and oxidation duration (Fig. 2). This approach gives us an idea on the stability of the nanowires structure as well as on their growth mechanism.

By means of XANES we demonstrate that nanowires contain cobalt mostly in metallic (hcp) or in oxide form and determine the proportion of Co in the matrix. The Co fcc phase has been detected too and confirmed by HRTEM. Alloying with Ni stabilizes the Co fcc phase [5].

We acknowledge financial support from the ANR (ANR-2011-BS04-007).

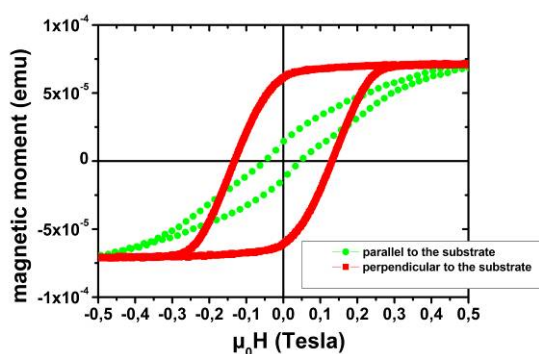


Fig. 1 : Hysteresis curves for magnetic field applied parallel (green) and perpendicular (red) to the film plane

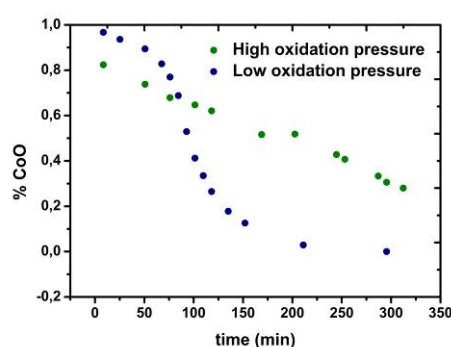


Fig. 2 : Evolution of the CoO ratio during reduction in samples which underwent different oxidation treatments

REFERENCES

- [1] M. Hernandez-Vélez, Thin Solid Films **495**, 51-63 (2006).
- [2] T. Thurn-Albrech et al., Science **290**, 2126 (2000).
- [3] K. Shantha Shankar, A.K. Raychaudhuri, Materials Science and Engineering C **25** (2005).
- [4] F. Vidal, Y. Zheng, J. Milano, D. Demaille, P. Schio, E. Fonda, B. Vodungbo, Applied Physics Letters **95**, 152510 (2009).
- [5] F. J. Bonilla et al. ACS Nano **7** (5), 4022–4029 (2013)

TiAlN Films around Cubic/Hexagonal Transition Studied by DAFS and XAFS

Y.Pinot^a, M.-J. Pac^a, M.-H. Tuilier^a, C.Rousselot^b, D.Thiaudière^c

^a *Université de Haute Alsace, LPMT- PPMR (EA 4365), 61 rue Albert Camus, 68093 Mulhouse cedex, France.*

^b *Université de Franche-Comté, FEMTO-ST (UMR 6174 CNRS), 4 place Tharradin, 25211 Montbéliard cedex, France.*

^c *Synchrotron Soleil, Saint Aubin, F-91192 Gif sur Yvette, France.*

ABSTRACT

Nano-structured metallic nitride films are generally used as protective coatings in different machining applications [1]. $Ti_{1-x}Al_xN$ ($0 \leq x \leq 1$) is considered as a model system, where TiN (fcc) and AlN (hcp) do not mix over the whole composition range due to their low miscibility. However, the physical vapour deposition (PVD) allows achieving metastable phases of $Ti_{1-x}Al_xN$, where Al atoms are partially substituting for Ti in fcc lattice [2]. $Ti_{1-x}Al_xN$ coatings exhibit high hardness and oxidation resistance for the maximum Al substituted to Ti in fcc lattice (about $x=0.6$) [3]. The proportion of grain boundaries and the limit solubility play a major role on the mechanical properties and resistance to wear of the coatings. Several techniques are employed to investigate two sets of $Ti_{1-x}Al_xN$ thin films deposited by magnetron reactive sputtering from two types of metallic targets onto Si (100). By combining the selectivity on the lattice symmetry of X-ray diffraction (XRD) and the local approach of X-ray absorption fine structure (XAFS) [4, 5], diffraction anomalous fine structure spectroscopy (DAFS) [6, 7] allows a separate investigation of crystalline domains regardless of less-ordered area. X-ray absorption near-edge structure (XANES) and Diffraction anomalous near edge structure (DANES) are ideally suitable to provide insight into local environment of atoms present within complex films like ternary nitride coatings. Therefore, the coordination of Al and Ti in $Ti_{1-x}Al_xN$ nitrides is either tetrahedral (hexagonal-like) or octahedral (cubic-like) and determines the shape of pre-edge. For Al-rich films close to $x=0.6$, the difference observed between DANES of hcp [002] and XANES proves that a significant part of Ti atoms are located in nanocrystallites with cubic symmetry outside of the hcp crystallized columns. For Ti-rich films close to $x=0.5$, the pre-edge peak has roughly the same shape for XANES and DANES indicating that Ti atoms in crystallized domains and grain boundaries are all in octahedral cubic local order. By combining those local probes, it becomes possible to know how the tetrahedral and octahedral sites are shared between crystallized domains and grain boundaries, depending on the composition.

REFERENCES

1. A. Horling, L. Hultman, M. Oden, J. Sjolen, L. Karlsson, *Surf. Coat. Technol.* **191**, 384-392 (2005).
2. H.W. Hugosson, H. Högberg, M. Algren, M. Rodmar, T.I. Selinder, *J. Appl. Phys.* **93**, 4505-4511 (2003).
3. A. Kimura, M. Kawate, H. Hasegawa, T. Suzuki, *Surf. Coat. Technol.* **169-170**, 367-370 (2003).
4. R. Gago, A. Redondo-Cubero, J.L. Endrino, I. Jiménez, N. Shevchenko, *J. Appl. Phys.* **105**, 113521 (2009).
5. M.-H. Tuilier, M.-J. Pac, G. Covarel, C. Rousselot, L. Khouchaf, *Surf. Coat. Technol.* **201**, 4536-4541 (2007).
6. M. G. Proietti, H. Renevier, J. L. Hodeau, J. Garcia, J. F. Bézar and P. Wolfers, *Phys. Rev. B* **59**, 5479 (1999).
7. M.-H. Tuilier, M.-J. Pac, D.V. Anokhin, D.A. Ivanov, C. Rousselot, D. Thiaudière, *Thin Solid Film* **526**, 269-273 (2012).

Complementarity of Inelastic Background and High Resolution Core-level Analysis in HAXPES

P. Risterucci¹⁻³⁻⁴, O. Renault¹, E. Martinez¹, D. Bertrand¹,
D. Ceolin², J.-P. Rueff², S. Tougaard³, G. Grenet⁴

¹ CEA, LETI, MINATEC Campus, 17 rue des Martyrs, 38054 GRENOBLE Cedex 9, France.

² Synchrotron SOLEIL - L'Orme des Merisiers Saint-Aubin - BP 48- 91192 Gif-sur-Yvette, France.

³ Dept. of Physics, Chemistry & Pharmacy, University of Southern Denmark,
DK-5230 Odense M, Denmark.

⁴ Institut des nanotechnologies de Lyon (INL), UMR CNRS 5270, Ecole Centrale de Lyon,
36 avenue Guy de Collongue 69 134 Ecully Cedex.

ABSTRACT

Non destructive analysis of interfaces is of prime importance to study elemental intermixing in nanoelectronic devices at depths usually around 30nm. We have recently extended the probing depth of HArD X-ray Photoelectron Spectroscopy (HAXPES) above 50 nm [¹] with the use of inelastic background analysis. Here we present the complementarity of this approach with the usual core-level analysis.

Samples processed for this study are based on an Al_{0.25}Ga_{0.75}N/GaN (24/1000 nm) epitaxial stack and a Ti/Al (15/10 nm) metal layers. Then, samples were annealed in a Rapid Thermal Annealing (RTA) system under N₂ atmosphere. The annealings were respectively: no annealing, 600°C for 300s, 600°C for 300s then 800°C for 60s and 600°C for 300s then 900°C for 60s.

We show results of two different photoemission experiments both carried out at GALAXIES beamline [²] with photon energy of 8 keV. The first experiment is to measure high resolution spectra of Al 1s and Ti 1s (inset of Fig. 1), performed with an overall resolution of 0.35 eV. In this experiment, the chemical environment of the element in

the first few nanometers (estimated to be 15.9 nm) is unraveled. We find three major components corresponding to a metallic state (labeled A), oxide state (labeled B) and two alloy states (labeled C and D) with changing relative intensity depending on the annealing process. However this classic method is unreliable for determining depth profile of inhomogeneous samples; therefore a second experiment, performed with an optimized photon flux is used for inelastic background analysis based on Tougaard's method [³]. This method allows to obtain elemental depth distribution over a larger probing depth (estimated to be 42 nm). The results show that Ti is located from 17 to 31 nm below the surface for the as deposited sample and diffusion is quantitatively determined for each annealing process; toward the surface and up to 40 nm toward the substrate.

We show the complementarity of core level and inelastic background analysis, unraveling the chemical state and the depth distribution of a specific element giving an overall description of the technological sample up to 40 nm below the surface.

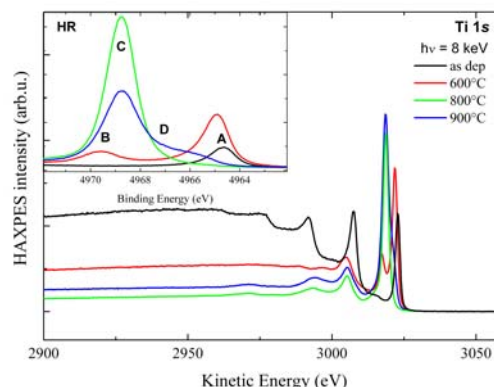


Figure 1: Ti 1s spectra measured at 8 keV. The inset shows high resolution spectra of Ti1s with their attributions.

REFERENCES

1. P. Risterucci, O. Renault, B. Dettlefs, E. Martinez, J. Zegenhagen, G. Grenet, S. Tougaard, Surf Interface Anal. accepted (2014)
2. D. Céolin, J. M. Ablett, D. Prieur, T. Moreno, J. P. Rueff, T. Marchenko, L. Journal, R. Guillemin, B. Pilette, T. Marin and M. Simon, Journal of Electron Spectroscopy and Related Phenomena **190, Part B**, 188-192 (2013).
3. S. Tougaard, Journal of Electron Spectroscopy and Related Phenomena **178–179**, 128-153 (2010).

Monitoring the UHV-CVD Growth of Si/Ge Nanowires by *in situ* X-ray Scattering

T. Zhou¹, V. Cantelli¹, O. Ulrich¹, O. Geaymond², N. Blanc²
and G. Renaud¹

¹ CEA-Grenoble, INAC/SP2M/NRS, 17 rue des Martyrs, 38054 Grenoble Cedex 9

² Institut Néel, CNRS/UJF UPR2940 25 rue des Martyrs BP 166 38042 Grenoble Cedex 9

ABSTRACT

The *in situ* growth of Nanostructures on Surfaces/Interfaces (INS) end station of the BM32 French CRG beamline (ESRF) has been used for years to analyze the structural properties of nanoparticles *in situ*, during their MBE (Molecular Beam Epitaxy) growth, combining grazing incidence x-ray diffraction (GIXD) and grazing incidence small angle x-ray scattering (GISAXS)[1]. A UHV-CVD injection system has been added recently to allow investigation of the VLS and the VSS growth processes of Si and Ge NWs[2].

Results on the growth of Si NWs on Si(111) (fig. 1) will first be presented. The Si NWs sidewalls are decorated with dodecagonal sawtooth faceting, as shown by the intense scattering streaks observed in reciprocal space. The NW length (hence their growth velocity) as well as their size distribution are probed *in situ* with different X-ray techniques.

Recent attempts on the heteroepitaxial growth of SiGe coreshell (radial) and rootstem (axial) NWs will then be presented. The strong overgrowth of Ge on Si NWs causes substantial changes to their original sidewall morphology while in the reverse scenario well-ordered faceted signals are observed coming from the Bragg peaks of both materials (fig. 2). With *in situ* anomalous scattering techniques, we were able to probe the stress relaxation during the very early stage of heteroepitaxial growth, i.e. when materials close to the heterojunction were being deposited. Preliminary results of these measurements will also be presented.

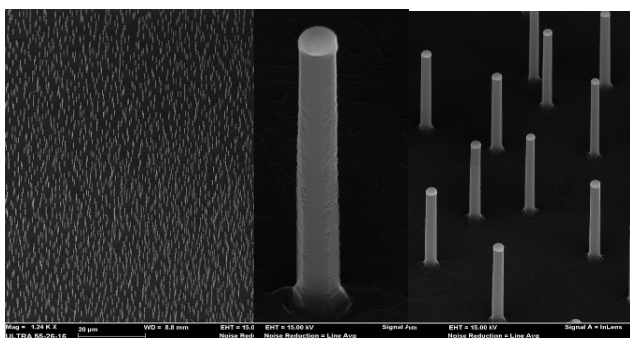


Figure 1 : Typical Si NWs growth on the BM32/INS chamber using disilane and Au catalysts.

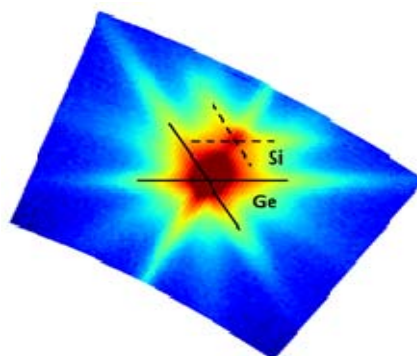


Figure 2 : Reciprocal Space Map around a Ge Bragg peak after Si overgrowth reveals sidewall faceting of both the Ge core and the Si shell.

REFERENCES

- [1] G. Renaud, R. Lazzari, F. Leroy Surf. Sci. Rep. 64, 255-380 (2009); T. Zhou, G. Renaud, C. Revenant, J. Issartel, T.U. Schüllli, R. Felici and A. Malachias, Phys. Rev. B 83, 195426 (2011); T.U. Schüllli, R. Daudin, G. Renaud, A. Vaysset, O. Geaymond and A. Pasturel, Nature 464, 1174 (2010).
[2] V. Cantelli, O. Geaymond, O. Ulrich, T. Zhou, N. Blanc and G. Renaud, "The In situ growth of Nanostructures on Surfaces (INS) end station of the ESRF IF-BM32 beamline: a combined UHV-CVD and MBE reactor for in situ x-ray scattering investigations of growing nanoparticles; especially semiconductor nanowires", submitted.

PyRod: Visualization, Analysis and Simulation of Surface Diffraction Data acquired with 2D Detectors

T. Zhou¹

¹ CEA-Grenoble, INAC/SP2M/NRS, 17 rue des Martyrs, 38054 Grenoble Cedex 9

ABSTRACT

PyRod is a python based software developed on the BM32 (French CRG) beamline at the ESRF, for the visualization, analysis and simulation of surface diffraction data acquired with 2D detectors. (i) The visualization mode offers an easy access to the comprehensive view of the 3D volume spanned by the 2D detector during a scan, as well as support for quick ROI integration and reciprocal space mapping. (ii) The analysis mode adopts some advanced ways of data integration [1], allowing data acquisition time to be reduced by an estimated factor of 20-50 compared to point detectors. (iii) The simulation mode works in a similar way as ROD [2], but comes with a more user-friendly graphical interface. It also accepts functions for the description of atomic positions in the unit cell, thus allowing reduction of the total number of fitting parameters when necessary. The project is still under development with ongoing efforts to add GISAXS support and live display of data. TZ wants to thank Odile Robach, Gilles Renaud for useful discussion and Nils Blanc, Fabien Jean for beta testing.

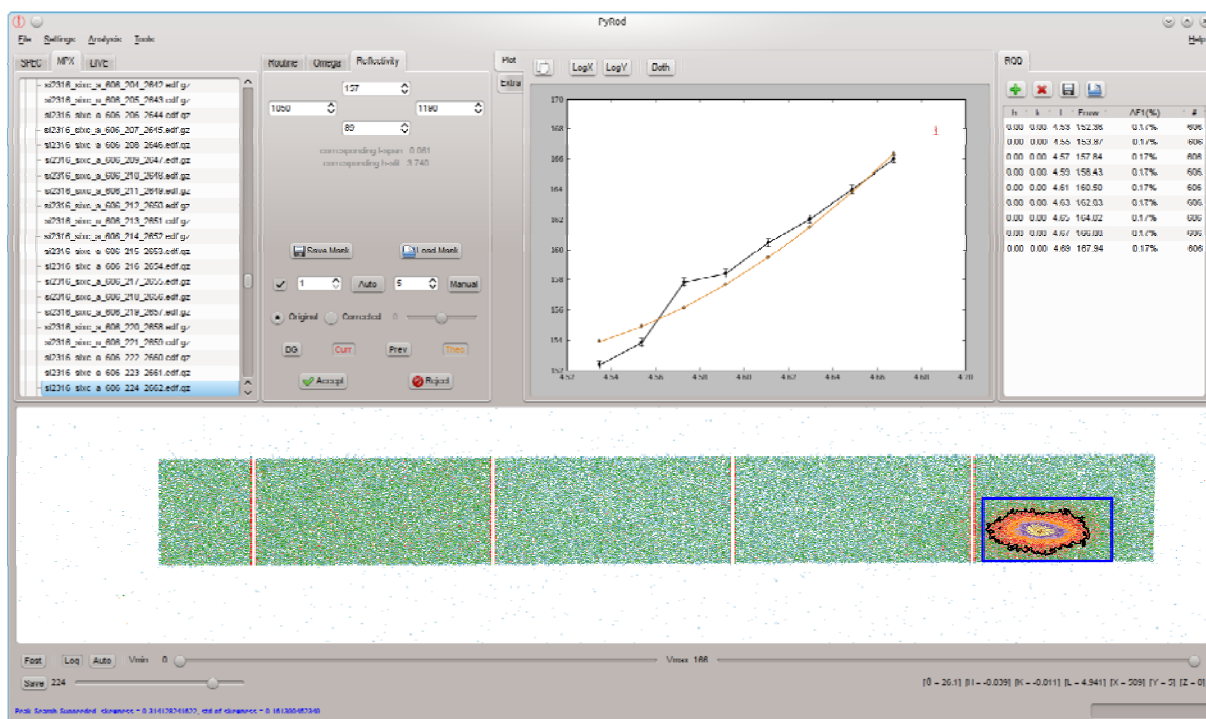


Figure 1 : A quick glance of the interface under analysis mode. Bottom panel: raw data displayed in fake color scale with the 2D peak signal found (black contour) by the peak search algorithm. The intensities within the contour are to be integrated, background-subtracted, before applying various correction factors for the calculation of the corresponding structure factor. Top panel: Input/output file selection, configuration, a line plot showing the experimental structure factors (black line, from integrated intensities, analysis mode) along with the calculated values from the model (yellow line, simulation mode).

REFERENCES

- [1] J. Drnec, T. ZHOU, S. Pintea, W. Onderwaater, E. Vlieg, G. Renaud, R. Felici, J. Appl. Cryst. (2013), Accepted.
 [2] E. Vlieg, J. Appl. Cryst. (2000), **33**, 401-405

List of Other Posters

- PO-01** IR spectroscopy of selected terpenes, their oxidation and degradation products: Towards their detection by remote Sensing techniques in biomass fires
J.R. Aviles-Moreno
- PO-02** UV Photodesorption of Interstellar Ices Analogues: New Contributions from the Synchrotron Radiation
M. Bertin
- PO-03** Fission product chemistry on nuclear SIMFUEL (SIMulated FUEL) studied by HERFD-XANES using the emission spectrometer of the MARS beamline.
R. Bès
- PO-04** Micro-structures LIGA pour les lignes de lumière sur Rayonnement Synchrotron
F. Bouamrane
- PO-05** Biophysical studies of the interactions of mannose-based anti-adhesives with the escherichia coli fimbrial adhesin FimH
J. Bouckaert
- PO-06** SF₆: The forbidden band unveiled
V. Boudon
- PO-07** X-ray absorption spectroscopy investigation of ion irradiated pyrochlore Y₂Ti₂O₇
S. Cammelli
- PO-08** Monitoring nanocatalysts by ambient-pressure XPS and high-pressure XAS
S. Carenco
- PO-09** Magnetic property of Dy₂₆Co₇₄ alloy investigated using XMCD and XMLD.
K. Chen
- PO-10** Synchrotron Radiation based methods in the research of the process of epileptogenesis in the electrical kindling rat model
J. Chwiej
- PO-11** Cryo soft X-ray tomography beamline project : TOMIX
B. Cinquin
- PO-12** Photo-induced fragmentation of 5 halo-uracils by Synchrotron Radiation in the region 9-21 eV
R. Cireasa
- PO-13** Coherent X-ray diffraction studies of the brittle-ductile transition in mechanically deformed low-dimensional silicon pillars
A. Davydok
- PO-14** Structure of the icosahedral Zn-Sc quasicrystal
M. de Boissieu
- PO-15** The near-ambient-pressure XPS at SOLEIL, first results
J.J. Gallet

- PO-16** In-situ time-resolved characterization of gold nanoparticles synthesis in a microfluidic device
J.S. Girardon
- PO-17** PSICHE: A new beamline dedicated to X-ray diffraction and tomography at high pressure at synchrotron SOLEIL
N. Guignot
- PO-18** Effect of the boron concentration on the electronic band structure of the metallic diamond
H. Guyot
- PO-19** k-dependence of the spin polarisation in Mn₅Ge₃/Ge(111) thin films
K. Hricovini
- PO-20** Status and development of imaging at PSICHE
A. King
- PO-21** Advanced characterization of materials for the electrochemical energy storage: Collaborative work between the RS2E and SOLEIL.
C. La Fontaine
- PO-22** Molecular single photon double K-shell ionization and related processes
P. Lablanquie
- PO-23** Accurate theoretical spectroscopic properties of molecular species of astrophysical and atmospherical interest
R. Linguerri
- PO-24** Evolution of Co Nanoparticles Oxidation State under Water Pressure Followed by NAP-XPS
A.-S. Mamede
- PO-25** High resolution investigation of the V₃ Band of trifluorimethyl iodide (CF₃I) at Synchrotron SOLEIL
L. Manceron
- PO-26** A new low temperature long-path cell for MID-IR TO THz spectroscopy
L. Manceron
- PO-27** A new high spectroscopic resolution momentum microscope
C. Mathieu
- PO-28** Étalonnage en rendement absolu d'une photodiode avec un radiomètre cryogénique à substitution électrique
Y. Ménesguen
- PO-29** Métrologie des coefficients d'atténuation massique
Y. Ménesguen
- PO-30** Crystal structure of the Hsp90-Sti1 complex and mechanism of client proteins recognition
P. Meyer
- PO-31** ARPES measurements of hydrogenated graphene layers grown on SiC using CVD
A. Michon
- PO-32** Sweet block copolymer nanoparticles
E. Minatti
- PO-33** Vibrationally resolved C 1s photoionization cross section of CF₄
M. Patanen

- PO-34** pH responsive peptide nanotubes: An atomic view of the pH-induced conformational switch that governs the assemblies
M. Paternostre
- PO-35** Study of nanocrystalline Mg-TM complex hydrides used as negative electrodes of Li-ion batteries by in-situ XAS (TM=Fe, Co, Ni)
V. Paul-Boncour
- PO-36** Structural and magnetic properties of $\text{YFe}_2(\text{H,D})_{4.2}$ and $\text{Y}_{0.5}\text{Tb}_{0.5}\text{Fe}_2\text{D}_{4.2}$ under high pressure
V. Paul-Boncour
- PO-37** X-ray absorption spectroscopy during evolution of the Pd_2Ga -phase used in methanol synthesis
H. W. Pereira de Carvalho
- PO-38** Core-hole-clock spectroscopies in the tender X-ray domain
M.N. Piancastelli
- PO-39** Silicene on silver reconsidered: Evidence of a Ag(110) reconstruction induced by Si growth.
G. Prévot
- PO-40** XANES, a probe to follow the reaction of carboplatin and oxaliplatin with Cl^- and sulfur nucleophiles
K. Provost
- PO-41** Mg_6Pd nanoparticles in a porous carbon matrix: EXAFS characterization of native and hydrogenated nanoparticles
K. Provost
- PO-42** Structural basis of myosin V cargo recognition
O. Pylypenko
- PO-43** Small-angle X-ray solution scattering study of the multi-aminoacyl-tRNA synthetase complex reveals an elongated and multi-armed particle
L. Renault
- PO-44** Probing deeper by HAXPES: Inelastic background analysis of layered systems for transistor devices
O. Renault
- PO-45** Synchrotron X-ray footprinting coupled with mass spectrometry for the structural study of large macromolecular complexes
B. Sclavi
- PO-46** Structure and electronic properties of the giant rashba-split BiTeCl and BiTeI semiconductors
O.E. Tereshchenko
- PO-47** Build-in lateral p-n junction on (0001) $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ topological insulators
O.E. Tereshchenko
- PO-48** Towards a better Understanding of atmospheric pressure photoionization using APEX (DISCO) endstation
D. Touboul
- PO-49** ESUO, a Pan-european organization to promote access to Synchrotrons and free electron lasers
M.C. Feiters

IR Spectroscopy of Selected Terpenes, their Oxidation and Degradation Products: Towards their Detection by Remote Sensing Techniques in Biomass Fires

J.-R. Aviles-Moreno,^a T. R. Huet,^a M. Goubet,^a P. Soulard,^b P. Asselin,^b
R. Georges,^c O. Pirali,^{d,e} P. Roy^e

^a PhLAM, UMR8523 CNRS – Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France

^b LADIR, UMR 7075 CNRS – Université Paris 6, 75005, Paris, France

^c IPR, UMR 6251 CNRS – Université Rennes 1, 35042 Rennes Cedex, France

^d ISMO, UMR8214 CNRS – Université Paris-Sud, Bât. 210, 91405 Orsay Cedex, France

^e AILES Beamline, SOLEIL, L'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette, France

ABSTRACT

We have recently demonstrated our ability to characterize in laboratory monoterpenes in the gas phase using 1/ quantum chemical calculations to predict the most stable conformers, 2/ Fourier transform microwave spectroscopy to experimentally identify the most stable conformers, and 3/ FTIR spectroscopy to observe and to identify their fingerprint FIR signature in a long optical path multi-pass cell at ambient temperature, and to determine the associated cross-sections [1-3].

Using the Jet-AILES setup and a long path cell, we have observed the FIR and IR spectrum of a selected series of monoterpenes: R-(+)-Limonene, α -Pinene, β -Pinene and γ -Terpinene and of a few oxidation products. Monoterpenes are hydrocarbons composed of one non-aromatic cycle of 6 carbon atoms bearing CH_2 and CH_3 groups. They are an important class of atmospheric molecules, almost never studied in the gas phase by spectroscopic techniques, mainly because their spectrum is difficult to obtain (semi volatile compounds) and of high complexity to model (several conformers/rotamers and large amplitude motions).

The lifetime of terpenes in the atmosphere is of the order of a few hours. Indeed they react with O_3 , OH, several NO_x , etc ... to give oxidation and degradation products which are forming secondary organic aerosols (SOA). In particular, the very complex "isoprene-OH" reaction mechanism was studied in laboratory and gave as major products formaldehyde (H_2CO), methacrolein ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$), and methyl vinyl ketone ($\text{CH}_2=\text{CHC}(\text{O})\text{CH}_3$). We have observed and characterized the IR spectrum of methacrolein and methyl vinyl ketone.

Support from the *Laboratoire d'Excellence CaPPA* (Chemical and Physical Properties of the Atmosphere) through contract ANR-10-LABX-0005 of the *Programme d'Investissements d'Avenir* is acknowledged.

REFERENCES

- 1 "Terpenes in the gas phase: the Far-IR spectrum of perillaldehyde", T. R. Huet, J.-R. Aviles-Moreno, O. Pirali, M. Tudorie, F. Partal Urena, J. J. Lopez Gonzalez, *Journal of Quantitative Spectroscopy and Radiative Transfer* 113(11), 1261-1265 (2012).
- 2 "Terpenes in the gas phase: the structural conformation of S-(-)-Perillaldehyde investigated by microwave spectroscopy and quantum chemical calculations", Juan Ramon Aviles Moreno, Francisco Partal Urena, Juan Jesus Lopes Gonzalez and Thérèse R. Huet, *Chemical Physics Letters* 473, 17-20 (2009).
- 3 « Conformational relaxation of S-(+)-Carvone and R-(+)-Limonene studied by microwave Fourier transform spectroscopy and quantum chemical calculations » Juan Ramon Aviles Moreno, Thérèse R. Huet, Juan Jesus Lopez Gonzalez, *Structural Chemistry*, DOI 10.1007/s11224-012-0142-8 (2012).

UV Photodesorption of Interstellar Ices Analogues: New Contributions from the Synchrotron Radiation

M. Bertin,¹ E. C. Fayolle,² C. Romanzin,³ K. I. Öberg, X. Michaut,¹
L. Philippe,¹ P. Jeseck,¹ H. Linnartz,² and J.-H. Fillion.¹

¹ UPMC univ Paris 6, Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique (LPMAA), Paris, F-75252, France.

² Leiden Observatory, Sackler Laboratory for Astrophysics, Leiden, NL-2300 RA, The Netherlands.

³ Univ Paris Sud 11, Laboratoire de Chimie Physique (LCP), Orsay, F-91400, France.

⁴ Harvard Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA

ABSTRACT

In the colder parts of the interstellar medium (ISM), the majority of molecules are formed or accrete onto dust grains, forming icy mantles. These molecular ices represent the main reservoir of molecules in these regions, constantly enriching the gas phase *via* desorption processes, and thus strongly influencing its chemistry. Because of the low temperatures ($T \sim 10$ K), non-thermal desorption, *i.e.* desorption triggered by energetic particles (photons, electrons, cosmic rays) impact on the ices, is seen as the major process which explains the observed gas-to-ice balance of small molecules. The VUV photodesorption of several pure molecular ices have been investigated in a number of studies, using broad-band H_2 discharge lamps peaking at 10.2 eV (Lyman- α) (*e.g.* [1-2]). These studies have provided an idea of the photodesorption yields of several pure species as well as empirical constraints on the underlying mechanism, but could not (*i*) take into account the spectral structure of the UV field, that can significantly vary from a region to another, and (*ii*) unveil the molecular mechanism responsible for the molecules desorption.

Using the monochromatized vacuum UV output of the synchrotron SOLEIL - DESIRS beamline, we show that the photodesorption from simple molecular ices, in the 7-14 eV range, is strongly dependent on the photon energy [3-5]. The energy-resolved desorption spectra allowed us to derive the underlying molecular mechanism. The process has been revealed to be an indirect surface mechanism, triggered by the electronic excitation of subsurface molecules, and strongly influenced by the intermolecular interactions in the ice. These interactions being very sensitive on the local environments of the molecules, it is expected that the photodesorption efficiency varies significantly in pure ices or in binary mixed-ices [6].

Recent results on pure CO and N_2 ices photodesorption will be presented. In particular, the roles of the photon energy and of the composition of the ices (pure vs mixed) will be highlighted, together with some astrophysical implications for the gas phase abundances in the cold parts of the ISM [7].

REFERENCES

- [1] K.I. Öberg et al., *Astron. Astrophys.* 496 (2009), 281-293
- [2] G.M. Muñoz Caro et al., *Astron. Astrophys.* 522 (2011), 14
- [3] E.C. Fayolle et al., *Astrophys. J. Lett.* 739 (2011), L36
- [4] M. Bertin et al., *Phys. Chem. Chem. Phys.* 14 (2012), 9929-9935
- [5] E.C. Fayolle et al., *Astron. Astrophys.* 556 (2013), A122
- [6] M. Bertin et al., *Astrophys. J.* (2013) in press

Fission Product Chemistry on Nuclear SIMFUEL (SIMulated FUEL) Studied by HERFD-XANES using the Emission Spectrometer of the MARS Beamline.

R. Bès^{1,2}, E. Geiger¹, P. Martin¹, P.-L. Solari²,
O. Proux³ and J.-L. Hazeman⁴

¹CEA, DEN/DEC/SESC/LLCC, F-13108 Saint Paul Lez Durance, France

²Synchrotron SOLEIL, Ligne de lumière MARS, L'orme des Merisiers, Saint Aubin, BP48,
F-91192 Gif-sur-Yvette Cedex, France

³Observatoire des Sciences de l'Univers de Grenoble, UMS 832 CNRS Université Joseph Fourier,
F-38041 Grenoble Cedex 9, France

⁴Institut Néel, UPR 2940 CNRS, F-38042 Grenoble Cedex 9, France

ABSTRACT

The most challenging research in nuclear energy concerns nuclear fuel and its behavior particularly in case of accident. Nuclear fuel behavior and its interaction with cladding materials strongly depend on the chemistry of fission products during the irradiation process. A good knowledge of fission products chemistry in nominal and accidental conditions is mandatory to understand, model and finally control the release of radioactive materials during severe accident, such as Fukushima one in 2011. In particular, speciation data are key parameters to establish accurate thermodynamics modeling. Such information can be supplied using X-ray Absorption Spectroscopy (XAS). But, due to the very high radioactivity of the sample (>200 Mbq/mg), and the impossibility to isolate the fluorescence line of one element (background interference of radioactivity, Bragg peaks due to the actinide matrix and fluorescence from other nearer Z elements), implementation of this analysis is impossible.

To overcome the former difficulty, the use of simulated UO₂ nuclear fuel, as known as SIMFUEL, is a good alternative. SIMFUEL samples are manufactured by doping a UO₂ powder with 11 different elements (Ba, Ce, La, Mo, Sr, Y, Zr, Rh, Ru, Pd and Nd) in concentration representative to ones reported in irradiated fuel [1]. Extensive characterizations have demonstrated that the microstructure and phase structure obtained are similar to those of irradiated fuel [1].

To overcome the latter difficulty, the XAS experiment can be performed by using a multi-crystal analyser spectrometer such as the one that is present on the MARS beamline. This spectrometer is based on the use of silicon crystals in the Rowland circle geometry which, by diffracting the emitted X-rays, allows simultaneous focusing and energy discrimination with higher resolution than a conventional solid detector.

The comparison between High Energy Fluorescence Detected XANES (HERFD-XANES) and Total Fluorescence Yield XANES (TFY-XANES) shows large benefits of this approach to collect good spectra in diluted radioactive materials. The latest results obtained on virgin and annealed SIMFUEL samples at the Mo [2], Zr and Ru K-edges using the emission spectrometer of the MARS beamline will be discussed.

REFERENCES

1. P.G. Lucuta et al., Journal of Nuclear Materials 178 (1991) 48-60.
2. I. Lorrens et al., to be published in Radiochemica Acta

Micro-structures LIGA pour les Lignes de Lumière sur Rayonnement Synchrotron

F. Bouamrane^{1,2}, P. Mercère², P. Da Silva², A. Delmotte²

¹Unité Mixte de Physique CNRS-THALES et Université Paris-sud 11, Campus de Polytechnique, 1Av. A. Fresnel, 91767 Palaiseau Cedex

²Synchrotron SOLEIL, L'Orme des Merisiers BP 48 Saint-Aubin, 91192 Gif/Yvette Cedex

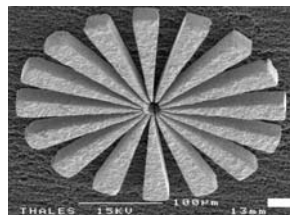
ABSTRACT

Grace au haut degré de cohérence transverse des sources de lumière de 3^{ème} et 4^{ème} génération sur rayonnement Synchrotron, le potentiel d'analyse des matériaux évolue rapidement avec l'émergence de nouvelles techniques d'imagerie. En conséquence un besoin récurrent de micro-structures avec des résolutions micrométriques voire sub-micrométriques apparaît dans le but de mettre en forme le faisceau, caractériser les détecteurs et diagnostiquer le faisceau lui-même et ses optiques et pour réaliser de l'imagerie. Pour répondre à ces exigences de métrologie optique et d'imagerie en rayons X, nous avons utilisé le potentiel du LIGA, technologie de micro-fabrication qui allie précision et haut rapport de forme dans des matériaux fortement absorbant comme l'or.

Dans le cadre de ce projet, nous avons réalisé un ensemble de micro-structures spécifiquement dédiées aux lignes de lumière du Synchrotron SOLEIL. Leurs dimensionnements dépendent des conditions d'éclairement et des résolutions spatiales recherchées sur les échantillons à analyser mais elles auront toutes des structures de dimension micrométrique et des champs millimétriques :

- des structures type "knife-edge" permettant de caractériser des faisceaux de petite dimension à l'aide de structures de diverses géométries mais présentant toutes un bord propre et franc
- des structures "pinholes" composées de trous de 2 à 10 μm définissant une ouverture qui permet la réalisation d'imagerie par diffraction cohérente
- des grilles Hartmann consistant en une matrice de trous de forme et de positionnement précis qui permettent une mesure du front d'onde dans le domaine des rayons X durs.

Pour ce travail nous avons réalisé l'étape de lithographie sur la ligne LIGA I à ANKA, du KIT à Karlsruhe en Allemagne, qui est équipé d'un miroir sélectionnant le domaine d'énergie 2,2-3,3 keV. Nous avons aussi dû développer une technique spécifique de masque auto-supporté.



Mire en or sur substrat de graphite.
Épaisseur de l'or: 25 μm .

Biophysical Studies of the Interactions of Mannose-based Anti-adhesives with the *Escherichia coli* Fimbrial Adhesin FimH

J. Bouckaert

Unité de Glycobiologie Structurale et Fonctionnelle, UMR du CNRS 8576, Université de Lille 1,
59655 Villeneuve d'Ascq, France. Fax +33 (0) 320 43 65 55

julie.bouckaert@univ-lille1.fr *

ABSTRACT

Structure-thermodynamic relationships in protein-carbohydrate interactions provide important decision makers in the design and maturation of bacterial anti-adhesives. Many interactions in our innate defense depend on the specific recognition, of a high enough density of a glycan sequence, to evoke immune reaction. Bacteria hijack glycan receptors that are reminiscent of a physiological state of a mammalian cell that indicates a suitable habitat for the completion of their pathogenic cycle. The interruption of this process is envisioned using anti-adhesives that selectively block bacterial adhesion but do not interfere with the immune system.

The understanding of the biophysical basis of host-pathogen interactions to empower intervention can be studied using purified adhesins and synthetic multivalent inhibitors. We measured affinities and stoichiometries using surface plasmon resonance (SPR), isothermal titration calorimetry (ITC) and dynamic light scattering (DLS). The geometry of a multivalent complex was determined using small angle X-ray scattering (SAXS) and was found to agree with the stoichiometry and molecular size derived from ITC and DLS data respectively (1). Stunningly, a correlation could be found between the dispersion part of interaction energies calculated using quantum chemistry, ITC-derived entropies and crystal structure electron densities of inhibitors bound to FimH (2,3).

REFERENCES

1. J. Bouckaert J, Z. Li, C. Xavier, M. Almant, V. Caveliers, T. Lahoutte, S. D. Weeks, J. Kovensky, S. G. Gouin, *Chemistry, a European Journal* **19** (24):7847-7855 (2013).
2. S. Brument, A. Sivignon, T. I. Dumych, N. Moreau, G. Roos, Y. Guérardel, T. Chalopin, D. Deniaud, R. O. Bilyy, A. Darfeuille-Michaud, J. Bouckaert*, S. G. Gouin* *J. Med. Chem.* **56** (13), 5395–5406 (2013).
3. G. Roos, A. Wellens, M. Touaibia, N. Yamakawa, P. Geerlings, R. Roy, L. Wyns, J. Bouckaert, J. *ACS Med. Chem. Lett.* **4** (11), 1085–1090 (2013).

SF₆: The Forbidden Band Unveiled

V. Boudon^a, L. Manceron^{b,c}, F. Kwabia Tchana^d, M. Loëte^a,
L. Lago^c and P. Roy^c

^a *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS Université de Bourgogne, 9 avenue Alain Savary, B.P. 47870, F-21078 Dijon Cedex, France.*

^b *Laboratoire de Dynamique, Interactions et Réactivité, CNRS UMR 7075, 4 Place Jussieu, F-75252 Paris Cedex, France.*

^c *Ligne AILES – Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France.*

^d *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS UMR 7583, Université Paris-Est Créteil et Université Paris-Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France.*

ABSTRACT

Sulfur hexafluoride is an important molecule for modeling thermophysical and polarizability properties. It is also a potent greenhouse gas of anthropogenic origin, whose concentration in the atmosphere, although very low is increasing rapidly; its global warming power is mostly conferred by its strong infrared absorption in the ν_3 S–F stretching region near 948 cm^{-1} . This heavy species, however, features many hot bands at room temperature (at which only 31% of the molecules lie in the ground vibrational state), especially those originating from the lowest, $\nu_6 = 1$ vibrational state. Unfortunately, the ν_6 band itself (near 347 cm^{-1}), in the first approximation, is both infrared- and Raman-inactive, and no reliable spectroscopic information could be obtained up to now and this has precluded a correct modeling of the hot bands. It has been suggested theoretically and experimentally that this band might be slightly activated through Coriolis interaction with infrared-active fundamentals and appears in high pressure measurements as a very faint, unresolved band^{1,2}. Using a new cryogenic multipass cell with 93 m optical path length and regulated at $163 \pm 2\text{ K}$ temperature, coupled to synchrotron radiation and a high resolution interferometer, the spectrum of the ν_6 far-infrared region has been recorded. Low temperature was used to avoid the presence of hot bands. We are thus able to confirm that the small feature in this region, previously viewed at low-resolution², is indeed ν_6 . The fully resolved spectrum has been analyzed³, thanks to the XTDS software package⁴. The band appears to be activated by faint Coriolis interactions with the strong ν_3 and ν_4 fundamental bands, resulting in the appearance of a small first-order dipole moment term, inducing unusual selection rules. The band center ($\nu_6 = 347.736707(35)\text{ cm}^{-1}$) and rovibrational parameters are now accurately determined for the $\nu_6 = 1$ level. The ν_6 perturbation-induced dipole moment is estimated to be $33 \pm 3\text{ }\mu\text{D}$ and the ν_6 integrated intensity to be $0.0035\text{ km mol}^{-1}$.

REFERENCES

1. W. B. Person and B. J. Krohn, *J. Mol. Spectrosc.* **98**, 229–257 (1983).
2. C. Chappados and G. Birnbaum, *J. Mol. Spectrosc.* **105**, 206–214 (1984).
3. V. Boudon, L. Manceron, F. Kwabia Tchana, M. Loëte, L. Lago and P. Roy, *Phys. Chem. Chem. Phys.* **16**, 1415–1423 (2014).
4. Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov and J.-P. Champion, *J. Mol. Spectrosc.*, **251** 102–113 (2008).

X-ray Absorption Spectroscopy Investigation of Ion Irradiated Pyrochlore $Y_2Ti_2O_7$

S. Cammelli¹, D. Menut², J.L. Bechade², N. Sellami³, G. Sattonnay³

¹Soleil, L'Orme des Merisiers Saint-Aubin - BP 4891192 GIF-sur-YVETTE CEDEX

²CEA, DEN, Service de Recherches Métallurgiques Appliquées, 91191 Gif-sur-Yvette, France

³Univ. Paris Sud , LEMHE - ICMMO bat.410 91405 Orsay cedex

ABSTRACT

Oxide dispersion-strengthened (ODS) steel are candidate for the reactor of forth generation. These steels are composed of ferritic steel strengthened with implanted nano-particles of Y, Ti and O. These particles are expected to be coherent and to be stable under irradiation improving the mechanical properties of the steel. About their composition there is not agreement in the community: particles may assume a pyrochlore structure with the composition of $Y_2Ti_2O_7$ [1,2] or have a size dependent composition based on Y, Ti, O atoms [3] or even be composed of different shells with the presence not negligible of Cr [4]. The pyrochlore structure has been deeply analyzed [5,6,7] because of its magnetic, electric, thermal properties and because is a candidate for the immobilization of of actinide rich waste. This study is focused on the characterization of pyrochlore $Y_2Ti_2O_7$ under ion irradiation in order to understand how irradiation could influence the structure, composition and stability of $Y_2Ti_2O_7$. The analysis has been performed at the MARS beamline in a frame of collaboration with CEA and Paris Sud University.

The irradiation was performed at six different fluences (from 2×10^{11} to 10^{13} ions/cm²) with high energy ions and the results may be summarized as follows.

By X-ray diffraction it has been observed that the oxide becomes more and more amorphous above all after certain fluence ($\sim 10^{12}$ ions/cm²). Similar results have been obtained by linear combination fit of XANES spectra measured at the Ti K edge combining the reference un-irradiated sample with and the most irradiated sample. The XANES spectra of Ti show also a change of the pre-edge features, from the typical three pre-edge peaks to one large peak. The slight shift of the absorption edge to smaller energies confirms a change of the coordination number from Ti^6 to Ti^5 [7]

At the Y K edge it has been possible to evaluate the Y-Y and Y-Ti distances. The Y-Y distance slightly increases with the ion fluence. The most important result at the Y K edge concerns the appearance of anti-site substitution (Y at the place of Ti and *vice versa*) which seems to increase up to involve the $\sim 30\%$ of the atomic sites. Moreover the analysis of spectra of the samples irradiated at the highest fluences show also a split of the second shell of oxygen meaning probably a *local* deformation to a different structure.

REFERENCES

1. M. Ohnuma, J. Suzuki, S. Ohtsuka, S.-W. Kim, T. Kaito, M. Inoue, H. Kitazawa, Acta Materialia, 2009, 5571-5581.
2. M Klimiankou, R Lindau, A Möslang . J. Nucl. Mater 2004, 347-351.
3. M. Brocq, B. Radiguet, S. Poissonnet, F. Cuvilly, P. Pareige, F. Legendre, J. Nucl. Mater 2011, 80-85.
4. V. de Castro, E.A. Marquis, S. Lozano-Perez, R. Pareja, M.L. Jenkins, Acta Materialia, 2011, 3927-3936
5. C. H. Booth, J. S. Gardner, G. H. Kwei, R. H. Heffner, F. Bridges, M. A. Subramanian PRB 62, 2000, 755
6. S.-W. Han, J. S. Gardner, C. H. Booth, PRB 69, 2004, 024416
7. M. L. Sanjuán, C. Guglieri, S. Díaz-Moreno, G. Aquilanti, F. Fuentes, L. Olivi, J. Chaboy PRB 84, 2011, 104207

Monitoring Nanocatalysts by Ambient-pressure XPS and High-pressure XAS

S. Carenc¹, Z. Liu,² J. Guo,² H. Bluhm,³ M. Salmeron¹

¹Materials Sciences Division,

²Advanced Light Source and

³Chemical Sciences Division,

Lawrence Berkeley National Lab, 1 Cyclotron Road, Berkeley, California, USA

ABSTRACT

Because of their infinite complexity, nanomaterials can be tailored for many catalytic applications: they provide a catalog of active and selective catalysts. In particular, it has been shown that multimetallic nanoparticles (alloy, core-shell structure, etc.) present properties that are significantly different than those of the corresponding physical mixtures of metals. This prompted a wide community of experimentalists to design innovative nanostructures and assess their capabilities in environmentally-relevant processes, such as the Fischer-Tropsch Synthesis.

In this latter reaction, carbon monoxide and dihydrogen are reacted on metal nanocatalysts (Fe, Co, Ru...) to produce a range of products including liquids fuels and valuable chemicals. While this process is gaining more and more attention due to limited natural oil and gas supply, its detailed mechanism is still subject to controversy. In the present work, ambient-pressure XPS and soft X-Rays high-pressure XAS have been combined as *in situ* techniques to unveil the nature of the nanocatalysts surface and give indications about the adsorbates and reaction mechanism. Size-controlled cobalt-based nanoparticles (mono and bimetallic) have been shown to dissociate the CO molecule more efficiently with the help of adsorbed hydrogen. Moreover, changes in surface composition under catalytic conditions have been observed and linked to increased selectivity for oxygenated products.

REFERENCES

1. S. Carenc, A. Tuxen, M. Chintapalli, E. Pach, C. Escudero, T. D. Ewers, P. Jiang, F. Borondics, G. Thornton, A. P. Alivisatos, H. Bluhm, J. Guo and M. Salmeron, *J. Phys. Chem. C* **117**, 6259–6266 (2013).
2. A. Tuxen, S. Carenc, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. J. Beberwyck, A. P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher and M. Salmeron, *J. Am. Chem. Soc.* **135**, 2273–2278 (2013).
3. C. Escudero, P. Jiang, E. Pach, F. Borondics, M. W. West, A. Tuxen, M. Chintapalli, S. Carenc, J. Guo and M. Salmeron, *J. Synchrotron Rad.* **20**, 504–508 (2013).

Magnetic Property of Dy₂₆Co₇₄ Alloy Investigated using XMCD and XMLD.

K. Chen

*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48,
91192 GIF-sur-YVETTE CEDEX, France*

ABSTRACT

From theory, the rare earth element of Dy has the strong magnetic moment while Co is the typical ferromagnetic 3d element. The alloy of Dy₂₆Co₇₄ is ferri-magnetic with the magnetic moment of Dy and Co antiparallel coupled with each other. In the presentation, I will show recent XMCD and XMLD results for the Dy₂₆Co₇₄ alloy, which fits perfectly with the theory calculation. Besides, the temperature dependent results show the spin reorientation at about 180K. The magnetic property of DyCo is helpful to understand the perpendicular exchange bias in DyCo/FeGd and the dynamics of magnetism in rare earth-3d alloy.

Synchrotron Radiation based Methods in the Research of the Process of Epileptogenesis in the Electrical Kindling Rat Model

J. Chwiej¹, J. Kutorasinska¹, H. Gabrys¹, K. Janeczko²,
K. Gzielo-Jurek², K. Matusiak¹, P. Dumas³, C. Sandt³,
J. Frederic³, K. Appel⁴ and Z. Setkowicz²

¹AGH University of Science and Technology, Faculty of Physics and Applied Computer Science,
al. Mickiewicza 30, 30-059 Krakow, Poland

²Jagiellonian University, Institute of Zoology, ul. Gronostajowa 9, 30-387 Krakow, Poland

³SOLEIL, L'Orme des Merisiers, 91190 Saint-Aubin, France

⁴Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg Hamburg, Germany

ABSTRACT

Although many different animal models are used in scientific research to study the process of epileptogenesis only two groups are recommended as the most useful for examination of new antiepileptogenic and disease-modifying therapies. These are kindling and post *status epilepticus* models of temporal lobe epilepsy (TLE) [1].

The phenomenon of kindling was for the first time described by Goddard *et al.* in 1969 and it means repeated, usually electrical, stimulation of the brain which initially induces only subclinical afterdischarges but over time, after many repetitions leads to progressive increase in the severity and duration of the seizures [2,3].

Determination of elemental and biochemical anomalies occurring in the hippocampal formation as a result of repetitive electrical stimulation may help to define pathological processes underlying the phenomenon of kindling and leading to spontaneous seizure activity that may also occur in this model of epilepsy.

Two groups of animals were examined in frame of the study. Adult rats subjected to repetitive transauricular electroshocks through a pair of ear-clip electrodes were compared with naive controls.

The topographic and quantitative elemental data obtained using X-ray fluorescence microscopy at the HASYLAB beamline L were compared with the results of biochemical study done using FTIR microspectroscopy at SOLEIL beamline SMIS as well as parameters describing behavior of animals subjected to electroshocks.

ACKNOWLEDGEMENTS

This work was supported by Polish Ministry of Science and Higher Education and Polish National Science Centre grants: 2921/B/T02/2011/40 and 2011/01/B/NZ4/00586.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°312284 and was realized in frame of HASYLAB (I-20110056 EC) and SOLEIL (20100166 and 20120043) experimental grants.

REFERENCES

1. W. Loscher and C. Brandt, *Pharmacol. Rev.* **62**, 668-700 (2010).
2. G.V. Goddard, D.C. McIntyre, C.K. Leech, *Exp. Neurol.* **25**, 295-330 (1969).
3. R.J. Racine, *Electroencephalogr. Clin. Neurophysiol.* **32**, 281-294 (1972).

Cryo Soft X-ray Tomography Beamline Project : TOMIX

B. Cinquin, F. Polack

Synchrotron SOLEIL, L'Orme des Merisiers, F-91190 Gif-sur-Yvette, France

ABSTRACT

Soft X ray microscopy is a modern technique requiring a bright X ray source perfectly suitable in a synchrotron environment. Tuned in the water window energy, the photons are mostly absorbed by the carbon and the water molecules are transparent. Observations of hydrated specimen under X rays are possible without any chemical contrast. Such microscope enables studies of near native state biological objects with a nanometric resolution (50 nm) due to diffractive optics termed Fresnel Zone Plate.

Our team proposes the design of such a beamline housed in Soleil that will support, further advance, and innovate biological and biomedical research. Other beamlines (MISTRAL-CELLS, HZB-TXM, CRYO-TXM, NCXT) offer a similar technique but do not explore all the possibilities offered by the photons in the water window energy. We will discuss our goals and the ways to reach them. Spearheading cryo tomography of single cells, bacteria, even tissue biopsies with such spatial resolution (125 Å³) will give the biological community a powerful tool.

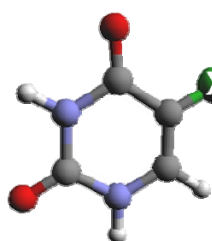
Photo-induced Fragmentation of 5 Halo-Uracils by Synchrotron Radiation in the Region 9-21 eV

R. Cireasa, P. Çarçabal, J.-C. Houver, K. Veyrinas, D. Dowek

*Institut des Sciences Moléculaires d'Orsay, UMR 8214, CNRS,
Université Paris Sud, 91405 Orsay Cedex, France*

ABSTRACT

5-halo-uracils (5XU) are formed by substituting the hydrogen atom at position 5 of the uracil ring with a halogen atom (X=F, Cl, Br, I) and they only differ from the DNA base, thymine, by this halogen atom which replaces the thymine's methyl group. It was found out



X = F, Cl, Br, I
(X= H → Uracil)
(X= CH₃ → Thymine)

that the tumour cells are more sensitive to the lethal effects of the UV, X-ray and γ radiation when their DNA is modified to replace the thymine with such molecules [1]. 5FU is a drug routinely used in combined chemo- and radiotherapy treatments for its radio-sensitising properties [2]. Although these properties are well established, the underlying reaction mechanisms are under debate.

Gas-phase studies of the 5XU irradiation by high-order harmonics (HH) in the energy range 9-27 eV indicate that similar fragmentation mechanisms should be at play as for the irradiation by 100 keV proton beams. The similar mass spectra obtained in these experiments can be explained only by considering that the parent ionisation is followed by a complex dynamics involving among other, proton/hydrogen transfer and sequential reactions [3, 4]. Confirming some of these mechanisms requires performing complementary time- and energy-resolved measurements.

For a better understanding of the fragmentation mechanisms at the molecular level, we propose to investigate the ionisation and the fragmentation of 5FU by synchrotron radiation in the region 9-21 eV by employing the photoelectron-photoion coincidence momentum spectroscopy method [5]. In the first instance, we have performed preliminary measurements in order to obtain information about the molecular parent ion states involved in these processes. Measuring at different photon energies the photoemission spectra of the electrons coincident with the parent ion and with different fragment ions enables us to relate the various peaks to the parent cation states that should contribute to the open fragmentation channels. The fragment ion distributions show that all the fragments bear very little kinetic energy, typically less than 0.5 eV. These results are consistent with those obtained in the fragmentation induced by HH at 15 and 21 eV and indicate that most of the energy is transferred to the fragments as internal energy. The lack of kinetic energy for the light fragments might suggest that they result from secondary dissociation processes of highly excited fragment ions.

REFERENCES

1. T.J. Kinsella, P.P. Dobson, J.B. Mitchell and A.J. Fornace, Jr., *Int. J. Radiat. Oncol. Biol. Phys.* **13**, 733 (1987)
2. O. Pradier, K. Eberlein, E. Weiss, M.C. Jackel, C.F. Hess, *British J. Oncol.* **74**, 368 (2001)
3. J.P. Champeaux, P. Çarçabal, J. Rabier, P. Cafarelli, M. Sence and P. Moretto-Capelle, *Phys. Chem. Chem. Phys.* **12**, 5454 (2010)
4. private communication
5. M. Lebech, J. C. Houver, and D. Dowek, *Rev. Sci. Instrum.* **73**, 1866 (2002)

Coherent X-ray Diffraction Studies of the Brittle-ductile Transition in Mechanically Deformed Low-dimensional Silicon Pillars

A. Davydok¹, T.W. Cornelius¹, Z. Ren¹, F. Mastropietro¹,
M. Texier¹, C. Tromas², L. Thilly², M.-I. Richard^{1, 3}, O. Thomas¹

¹Aix-Marseille University, CNRS, IM2NP (UMR 7334), Marseille (France)

²PPRime institute, Poitiers (France)

³ID01 beamline, ESRF, Grenoble (France)

ABSTRACT

In the recent past, nanostructures attracted enormous attention due to their novel properties not observed for bulk materials originating from size effects. While bulk Si is brittle at room temperature and becomes ductile at elevated temperatures, silicon nanopillars with diameters of less than few hundred nanometers show a ductile behavior [1].

To study this brittle-ductile transition, Si pillars were created from a silicon on insulator (SOI) wafer by electron beam lithography, deformed employing a nano-indenter [2], and subsequently investigated by coherent X-ray diffraction. The SOI layer with a different crystalline orientation than the bulk wafer allows for disentangling the diffraction signals of the pillars and the substrate. Figure 1 (a), (b), and (c) present the diffraction signal of a pristine pillar, the loading-unloading curve, and the diffraction pattern for the mechanically deformed pillar. Compared to the pristine pillar, the diffraction pattern of the deformed one shows a splitting of the Bragg peak and an inclination of size oscillations. During the User Meeting results obtained on pillars with diameters ranging from 100 nm to 2 μm will be presented. In the future, we plan to perform in-situ mechanical tests on Si nanostructures using a newly developed in-situ atomic force microscope [3].

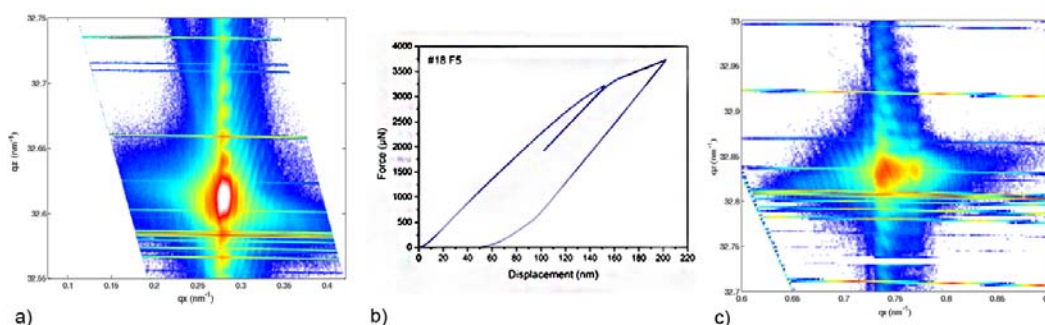


Figure 1. a) reciprocal space map (RSM) recorded from non-deformed pillar at Si(220) reflection; b) loading curve of indentation process; c) RSM at Si(220) of deformed pillar

REFERENCES

1. F. Oestlund, K. Rzepiejewska-Malyska, K. Leifer, L.M. Hale, Y. Tang, R. Ballarini, W. W. Gerberich, J. Michler, *Advanced Functional Materials*, 19, 2439–2444 (2009)
2. M. Texier, A. De Luca, B. Pichaud, M. Jublot, C. Tromas, J-L. Demenet, J. Rabier, *Journal of Physics: Conference Series*, 471, 012013 (2013)
3. Z. Ren, F. Mastropietro, A. Davydok, M.-I. Richard, O. Thomas, M. Dupraz, S. Langlais, M. Verdier, G. Beutier, P. Boesecke, T.U. Schüllli, T.W. Cornelius, in preparation

Structure of the Icosahedral Zn-Sc Quasicrystal

T. Yamada¹, C. Pay Gomez², H. Takakura³, R. Tamura⁴, M. de Boissieu⁵

1- IMRAM, Tohoku University, Sendai Japan

2 Uppsala University, Uppsala Sweden

3. Hokkaido University, Sapporo, Japan

4. Tokyo University of science, Tokyo, Japan

5- SIMAP, Université de Grenoble, CNRS, BP 75 38402 St Martin d'Hères Cedex

ABSTRACT

We will present the atomic structure of the binary Zn-Sc quasicrystals [1]. This quasicrystal belongs to the Cd-Yb 'Tsai' type family [2]. However its chemical composition is significantly different ($Zn_{88}Sc_{12}$ and $Cd_{85}Yb_{15}$) and is mainly deficient in the large Sc atom.

A full data set has been collected on the cristal beam line using 3 different attenuation (1000, 50 and 1) in order to cover the large dynamical range of the diffraction pattern.

The structure has been refined using as starting point the CdYb model [3]. We find that the main differences can be explained (as proposed by A.P. Tsai [4]) by the replacement of a Sc atom by a Zn atom in a single atomic site namely the so-called double Friauf polyhedron.

We also observe that the diffraction pattern is characterized by a large amount of diffuse scattering, which can be interpreted as resulting from phason fluctuations, characteristic of a 3-fold instability.

REFERENCES

1. Canfield P C, Caudle M L, Ho C S, Kreyssig A, Nandi S, Kim M G, Lin X, Kracher A, Dennis K W, McCallum R W and Goldman A I 2010 Phys. Rev. B **81** 020201
2. Tsai A P, Guo J Q, Abe E, Takakura H and Sato T J 2000 Nature **408** 537.
3. Takakura H, Gomez C P, Yamamoto A, de Boissieu M and Tsai A P 2007 Nature Materials **6** 58.
4. Tsai A P 2013 Chem. Soc. Rev **42**[12] 5352-5365

The Near-ambient-pressure XPS at SOLEIL, First Results

J.J. Gallet

Laboratoire de Chimie Physique Matière et Rayonnement (UMR 7614), Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France

ABSTRACT

The recent installation on the TEMPO beamline of a new photoemission apparatus operating in environmental condition up to 25 mbar currently in the commissioning phase open promising perspectives for environmental molecular chemistry as well as catalysis. I will draw a brief description of the NAP-XPS set up and the tools available tools for the preparation and characterization of samples.

In-situ Time-resolved Characterization of Gold Nanoparticles Synthesis in a Microfluidic Device

J.-S. Girardon¹, A. Tougeri¹, E. Fonda², S. Fazzini³ and E. Payen¹

¹ *Unité de Catalyse et de Chimie du Solide, Université Lille 1, 59655 Villeneuve d'Ascq Cedex*

² *Synchrotron SOLEIL (SAMBA), L'Orme de Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette Cedex*

³ *Università agli studi di Bologna, Facoltà di Chimica Industriale, Viale Risorgimento 4, 40136 Bologna*

ABSTRACT

Gold nanoparticles (AuNPs) are highly catalytically active [1, 2]. The molecular mechanisms of Au-NPs formation remain unclear due first to the quantity of material analyzed (~mM), second to the relative short time scale for the nucleation and growth steps and third to the limited accessibility to *in-situ* time-resolved characterization. To overcome those issues and regarding the experimental aspects, Synchrotron radiation related techniques are useful to characterize such rapid NPs formation [3]. In order to access to a direct in situ time-resolved characterization, we build [4] and adapt a micro-fluidic system under continuous flow conditions, whereby we follow, via in situ XANES spectroscopy, the Au-NPS formation from a gold precursor (HAuCl₄) with sodium citrate as reducing and stabilizer agent. We studied the embryonic state NPs formation, geometry modifications of the precursor and ligand substitutions by a micro-fluidic system under continuous flow conditions. The setup is constituted by two glass syringes, a syringe pump, and a tee-mixer for combining the reagents into a 1.5 m × 200 μm internal diameter fused silica capillary as micro-reactor heated using a heating plate. By focusing the X-rays, the reaction was followed by monitoring the gold LIII-edge XAS spectra at different locations along the micro-tube, temperature and flow rates. Thanks to this set up it is possible to convert a "time scale" reaction in a "length scale" reaction. The XAS measurements were performed with synchrotron radiation at the SAMBA beamline at the Soleil Synchrotron. By adjusting the analysis position and the reactant flow rate introduction, it was possible to get information of the evolution of the precursor since the first seconds of reaction. From our measurements and data analysis, the reaction starts with the substitution of the chlorides by OH groups then citrate precursor. Then starts the progressive reduction of this new gold complex. The rate of metallic gold increase from 2% up to 80% in 60 s. As conclusion, we demonstrated that the *in-situ* characterization is possible in such original micro-setup on SAMBA. During the beamtime allocations, important informations concerning the gold transformation and transportation inside the microtube were highlighted. Those informations strengthen our knowledge of physico-chemical phenomena that take place in the microtube during the synthesis of nanoparticles.

REFERENCES

- [1] G. J. Hutchings, *Gold Bull.* 37 (2004) 3
- [2] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* 118 (2006) 8064; *Angew. Chem. Int. Ed.* 45 (2006) 7896
- [4] J. Ftouni, M. Penhoat, A. Addad, E. Payen, C. Rolando, J.S. Girardon, *Nanoscale* 4 (2012) 4450
- [3] J. Polte, T. T. Ahner, F. Delissen, S. Sokolov, F. Emmerling, A. F. Thünemann, R. Kraehnert, *J. Am. Chem. Soc.* 132 (2010) 1296

PSICHE: A New Beamline Dedicated to X-ray Diffraction and Tomography at High Pressure at Synchrotron SOLEIL

N. Guignot, J.-P. Itié, A. King, P. Zerbino, A. Delmotte, T. Moreno

Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin

ABSTRACT

The PSICHE beamline (for "Pressure, Structure and Imaging by Contrast at High Energy") is a new facility opened for high pressure experiments at synchrotron SOLEIL (St-Aubin, France). With its source, optics, detectors and 3 experimental stations, it can handle a large variety of experimental setups. High energy photons are produced with an in-vacuum wiggler. The white beam obtained, with photons energy ranging continuously from 15 to 80 keV (from a 2.75 GeV machine), is used on the first experimental station for energy dispersive X-ray diffraction (EDX) measurements using different pressure cells. The main setup is a 1200 tons load capacity multi-anvil press featuring a (100) DIA compression module with a 15° horizontal aperture, allowing measurements up to 30° in 2theta by rotating the press. Other setups are a Paris-Edinburgh (PE) large volume press and diamond anvil cells (DACs). On the detection side we have a rotating Ge detector, based on the CAESAR design described by Wang et al. (2004) (combination of EDX and angular dispersive X-ray diffraction, ADX). One of the difficulties when building such setups is the rotation mechanism which cannot be physically attached to the rotation axis, potentially leading to large circle of confusions on the horizontal position of this axis. Thanks to translation corrections done at each angle step, the circle of confusion is minimized to 3x6 μm^2 along the 35° travel, making possible measurements on very small objects. Combining EDX and ADX has a lot of advantages and we will present our first results obtained using this setup.

The PSICHE focusing optics and monochromator are also used to focus monochromatic beams (up to 52 keV) on 2 different experimental stations. The first focal point at 31 m gives a beam size of 100x50 μm^2 (HxV) and is useful for low pressure experiments and experiments done with the PE press associated with Soller slits. A PerkinElmer flatpanel detector can be precisely scanned in 3 directions, making ADX measurements at the highest possible resolution on this beamline. This station will also be used for diffraction tomography experiments. The second focal point at 37.6 m is located behind KB mirrors on the third experimental station. 10x10 μm^2 beam sizes (full width) are expected. This station will be used for DAC experiments, with or without our future laser heating setup.

Finally, parallel beams can be produced with sizes up to 15x5 mm² (HxV) for tomography experiments, in pink (filtered white) beam or monochromatic beam. We plan to use rotating anvils presses such as the rotoPEc (J. Philippe et al., 2013) to take full advantage of this beam mode, but it can be opened to other techniques.

The PSICHE beamline is opened for users since July 2013. Some stations are not available yet, and will be opened through 2014 and 2015.

REFERENCES

- X. Dong et al., Ray tracing application in hard x-ray optical development: Soleil first wiggler beamline (PSICHÉ) case" (2011), Proc. SPIE 8141, 814113
 Y. Wang et al., A new technique for angle-dispersive powder diffraction using an energy-dispersive setup and synchrotron radiation (2004), J. Appl. Cryst. (2004). 37, 947–956
 J. Philippe, Y. Le Godec, F. Bergame et M. Morand, Patent INPI 11 62335 (2013)

Effect of the Boron Concentration on the Electronic Band Structure of the Metallic Diamond

H. Guyot^A, A. Nicolaou^B, A. Taleb^B and E. Bustarret^A

A. *Institut Néel, CNRS-UJF, BP 166, 38042 Grenoble Cédex 9, France*
B. *Synchrotron Soleil, Saint-Aubin, BP 48 91192 Gif-sur-Yvette Cédex, France*

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 at the Fermi level, and makes this phase easily measurable by ARPES. The threefold Γ X band structure has been measured and is found to be in good agreement with the rescaled theoretical DFT band structure. The evolution of the band structure around the Γ point is coherent with the calculated band structures predicted by the analytical k.p model. The evolution of the band structure is also analyzed as a function of the boron concentration over a decade in the metallic state: only a very weak dependence on the doping concentration appears experimentally.

k-dependence of the Spin Polarisation in Mn₅Ge₃/Ge(111) Thin Films

W. Ndiaye,¹ J.-M. Mariot,² P. De Padova,³ M. C. Richter,^{1, 4} W. Wang,^{1, 5}
O. Heckmann,^{1, 4} A. Taleb-Ibrahimi,⁶ P. Le Fèvre,⁷ F. Bertran,⁷
C. Cacho,⁸ A. Stroppa,^{9, 10} S. Picozzi,^{9, 10} and K. Hricovini^{1, 4}

¹ LPMS, Université de Cergy-Pontoise, 5 mail Gay-Lussac, 95031 Cergy-Pontoise, France

² LCP-MR, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, 75231 Paris, France

³ CNR, Istituto di Struttura della Materia, via Fosso del Cavaliere, 00133 Roma, Italy

⁴ DSM, IRAMIS, SPCSI, CEA-Saclay, 91191 Gif-sur-Yvette, France

⁵ IPOE, Department of Physics, Tongji University, Shanghai 200092, People's Republic of China

⁶ UR1-CNRS/Synchrotron SOLEIL, Saint-Aubin, B.P. 48, 91192 Gif-sur-Yvette Cedex, France

⁷ Synchrotron SOLEIL, Saint-Aubin, B.P. 48, 91192 Gif-sur-Yvette Cedex, France

⁸ Central Laser Facility, Rutherford Appleton Laboratory, Didcot, Oxon OX11 0QX, United Kingdom

⁹ CNR, Institute for Superconducting and Innovative Materials and Devices, 67100 L'Aquila, Italy

¹⁰ Dipartimento di Fisica, Università degli Studi dell'Aquila, Via Vetoio 10, 67010 Coppito, Italy

ABSTRACT

Mn₅Ge₃(001) thin films grown on Ge(111)-c(2x8) reconstructed surfaces were studied by angle- and spin-resolved photoemission using synchrotron radiation in the 17-40 eV photon energy range. We obtained the ground-state band structure of this system from first-principles full-potential linearized augmented plane-wave calculations. Since the calculation of the photoemission process is still difficult for Mn₅Ge₃, we simulated it using a simple model. In a previous investigation [1] we showed that the angle-resolved photoemission spectra of Mn₅Ge₃ could be satisfactorily reproduced from ground-state band structure calculations within a model based on the free-electron approximation for the final states and with the inclusion of the photohole lifetime effects (Lorentzian broadening), and correlation and *k*-perpendicular broadening effects (Gaussian broadening), the transition matrix element effects being ignored.

The comparison of the measured spin polarisation of the valence band with the simulated spin-polarisation is very good for the studied *k*-points in the Γ MLA plane of the Brillouin zone and achieves a unique validation of the ground state calculations. The contributions of Mn1 and Mn2 *d* states to the spin polarisation of the photoemission spectra can be clearly identified. We confirm as well the prediction by calculations of a negative spin-polarisation in the vicinity of the Fermi level, at variance with recently published results [2].

REFERENCES

1. W. Ndiaye, M. C. Richter, O. Heckmann, P. De Padova, J.-M. Mariot, A. Stroppa, S. Picozzi, W. Wang, A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran, C. Cacho, M. Leandersson, T. Balasubramanian, and K. Hricovini, *Phys.Rev. B* **87**, 165137 (2013).
2. Yu. S. Dedkov, M. Holder, G. Mayer, M. Fonin, and A. B. Preobrajenski, *J. Appl. Phys.* **105**, 073909 (2009).

Status and development of imaging at PSICHE

A. King, N. Guignot, P. Zerbino, A. Delmotte, J.-P. Itié

Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin – BP 48 91192 GIF-sur-YVETTE CEDEX

ABSTRACT

PSICHE is a multi-technique beam line, combining high pressure diffraction experiments with imaging and tomography. The imaging activity will open to expert users in the second half of 2014. This poster presents the current status of imaging at the beam line, the equipment that will be available, and the technical performance that is anticipated. The beam line and the tomography equipment is optimized for in-situ experiments with high beam energies and high speed data acquisition. Examples of possible applications will be described, and perspectives for future experiments combining imaging and diffraction will be shown.

Advanced Characterization of Materials for the Electrochemical Energy Storage: Collaborative Work between the RS2E and SOLEIL.

C. La Fontaine^{1,6}, S. Belin¹, M. T. Caldes^{2,6}, L. Croguennec^{3,6},
C. Masquelier^{4,6}, L. Monconduit^{5,6}, L. Stievano^{5,6} and G. Ouvrard^{2,6}

¹Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin BP 48, 91192 Gif-sur-Yvette cedex (France)

²IMN, UMR 6502, Univ. Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3 (France)

³ICMCB, CNRS UPR 9048, Univ. Bordeaux, 87 avenue Schweitzer, 33608 Pessac (France)

⁴LRCS, UMR 7314, Univ. Picardie Jules Verne, 33 rue St. Leu, 80039 Amiens cedex 9 (France)

⁵ICG-AIME, UMR 5253, Univ. Montpellier 2, place E. Bataillon, 34095 Montpellier cedex 5 (France)

⁶RS2E, FR 3459, 33 rue St. Leu, 80039 Amiens cedex 9 (France)

ABSTRACT

The RS2E (“Réseau pour le Stockage Electrochimique de l’Energie”) is a French research and technology transfer network, launched in 2010 by the French Ministry of Higher Education and Research, devoted to electrochemical energy storage systems: rechargeable batteries, supercapacitors and other alternative technologies. The main scientific goals of this network are to improve the performance, the reliability and the safety of the existing systems as well as to develop new ones.

To achieve such objective, it is mandatory to have a precise understanding of the structures of the materials and of the mechanisms involved during their electrochemical cycling. There is then a great need for advanced characterization methods, which has led to an intensification of the previous collaborative work between SOLEIL and the research laboratories of the RS2E [1,2]. In this line, a BAG proposal is under progress on SAMBA beamline to perform XAS measurements, together with standard proposals on other beamlines (e.g. CRISTAL, LUCIA).

This poster will be the opportunity to present the RS2E, the organization of this collaborative work at SOLEIL and the scientific studies carried out for the characterization of materials dedicated to the electrochemical energy storage.

REFERENCES

1. J. B. Leriche, S. Hamelet, J. Shu, M. Morcrette, C. Masquelier, G. Ouvrard, M. Zerrouki, P. Soudan, S. Belin, E. Elkaïm, and F. Baudalet, *J. Electrochem. Soc.* **157**, A606-A610 (2010)
2. G. Ouvrard, M. Zerrouki, P. Soudan, B. Lestriez, C. Masquelier, M. Morcrette, S. Hamelet, S. Belin, A. M. Flank and F. Baudalet, *J. Power Sources* **229**, 16-21 (2013)

Molecular Single Photon Double K-shell Ionization and Related Processes

F. Penent^{1,2}, M. Nakano^{3,4}, M. Tashiro⁵, T. P. Grozdanov⁶, M. Žitnik⁷, S. Carniato^{1,2}, P. Selles^{1,2}, L. Andric^{1,2}, P. Lablanquie^{1,2}, J. Palaudoux^{1,2}, E. Shigemasa⁵, H. Iwayama⁵, Y. Hikosaka⁸, K. Soejima⁸, I.H. Suzuki³, N. Kouchi⁴ and K. Ito³

¹UPMC, Université Paris 06, LCPMR, 11 rue P. et M. Curie, 75231 Paris Cedex 05, France.

²CNRS, LCPMR (UMR 7614), 11 rue P. et M. Curie, 75231 Paris Cedex 05, France.

³Photon Factory, Institute of Materials Structure Science, Oho, Tsukuba 305-0801, Japan.

⁴Department of Chemistry, Tokyo Institute of Technology, O-okayama, Tokyo 152-8551, Japan

⁵Institute for Molecular Science, Okazaki 444-8585, Japan.

⁶Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia.

⁷Jožef Stefan Institute, P. O. Box 3000, SI-1001 Ljubljana, Slovenia.

⁸Department of Environmental Science, Niigata University, Niigata 950-2181, Japan

ABSTRACT

We have studied single photon double K-shell ionization of small molecules: N₂, CO, C₂H_{2n} (n=1-3), H₂O, C₂H₆, C₄H₅N (pyrrole), C₅H₅N (Pyridine), C₃H₄ (propyne), CH_nCl_{4-n}... and the Auger decay of the resulting double core hole (DCH) molecular ions thanks to multi-electron coincidence spectroscopy using a magnetic bottle time-of-flight spectrometer to detect two photoelectrons in coincidence with the subsequent Auger electrons. After our first observation [1] of single site (K⁻²) double K-shell ionization in N₂ and oxygen compounds followed by the first evidence [2] of two sites (K⁻¹K⁻¹) in C₂H₂, we have observed the same processes in N₂, CO and C₂H_{2n} (n=1-3) series [3]. The relative cross-sections for single-site (K⁻²) and two-site (K⁻¹K⁻¹) double K-shell ionization with respect to single K-shell (K⁻¹) ionization have been measured and reveal the mechanisms of single photon double ionization (shake-off and knock-out). The spectroscopy of two-site (K⁻¹K⁻¹) DCH states in the C₂H_{2n} (n=1-3) series shows important chemical shifts due to a strong dependence with the C-C bond length. In addition, the complete cascade Auger decay following single site (K⁻²) ionization has been obtained [4]. Below K⁻² double ionization threshold simultaneous K-shell ionization/K-shell excitation (K⁻²V) has been observed in C₂H_{2n} (n=1-3) series that reveal NEXAFS type structures due to dipole excitation/monopole ionization in addition to dipole ionization/monopole excitation [5]. These measurement have been extended recently, at SOLEIL on PLEIADES and SEXTANTS beamlines, to many other molecules to see the effect of the bond length in the chemical shift: C-C bond (C₂H₆ and C₃H₄), C-N bond (C₄H₅N and C₅H₅N) and C-Cl bond (CH_nCl_{4-n}) for C(1s)Cl(2p). New and important results have been obtained that will be shown during the user's meeting.

REFERENCES

- [1] P. Lablanquie et al., Phys. Rev. Lett. 106 (2011) 063003
- [2] P. Lablanquie et al. Phys. Rev. Lett. 107 (2011)193004
- [3] M. Nakano et al. Phys. Rev. Lett. 110 (2013) 163001
- [4] M Tashiro et al. J. Chem.Phys 137 (2012) 224306
- [5] M. Nakano et al, Phys. Rev. Lett 111 (2013), 123001

Accurate Theoretical Spectroscopic Properties of Molecular Species of Astrophysical and Atmospheric Interest

R. Lingerri^a, M. Hochlaf^a, J. S. Francisco^b,
C. E. Cotton^b, S. B. Yaghlane^c

^aUniversité Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France

^bDepartment of Chemistry and Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47906

^cLaboratoire de Spectroscopie Atomique, Moléculaire et Applications – LSAMA Université de Tunis, Tunis, Tunisia.

ABSTRACT

We report two examples of application of highly correlated methods for accurate description of the electronic structure of small molecular systems: HSNO and HPS/HSP.

The lowest electronic states of singlet and triplet spin multiplicities of HSNO are investigated by configuration interaction *ab initio* methods and a large basis set [1]. One-dimensional cuts of the potential energy hypersurfaces of these electronic states along the R_{HS} , R_{SN} , θ_{HSN} , θ_{SNO} internal coordinates are calculated. Several avoided crossings and conical intersections are found. Radiative lifetimes and spin-orbit couplings of these electronic states are characterized. Our work reveals a complex dynamics on these excited states, and suggests that multi-step mechanisms will populate the ground state via radiationless processes or will lead to predissociation, or intramolecular isomerization.

For the HPS/HSP molecules and corresponding cations and anions accurate *ab initio* computations of structural and spectroscopic parameters have been performed [2]. For the electronic structure computations, standard and explicitly correlated coupled cluster techniques in conjunction with large basis sets have been adopted. In particular, equilibrium geometries, rotational constants, harmonic vibrational frequencies, adiabatic ionization energies, electron affinities and, for the neutral species, singlet-triplet relative energies are presented. In addition, the full-dimensional potential energy surfaces (PESs) for HPS^x and HSP^x ($x=-1,0,1$) systems have been generated at the standard coupled cluster level with a basis set of augmented quintuple-zeta quality. By applying perturbation theory to the calculated PESs an extended set of spectroscopic constants, including τ , first-order centrifugal distortion and anharmonic vibrational constants has been obtained. Moreover, the potentials have been used in a variational calculation to deduce the whole pattern of vibrational levels up to 4000 cm^{-1} above the minima of the corresponding PESs.

These properties may be probed at the AILS or DESIRS beamlines of the SOLEIL synchrotron.

REFERENCES

- [1] M. Hochlaf, R. Lingerri, J. S. Francisco, *Journal of Chemical Physics*, accepted.
[2] S. B. Yaghlane, C. E. Cotton, J. S. Francisco, R. Lingerri, M. Hochlaf, *Journal of Chemical Physics* **139**, 174313 (2013).

Evolution of Co Nanoparticles Oxidation State under Water Pressure Followed by NAP-XPS

A.-S. Mamede¹, G. Olivieri¹, J.-F. Paul¹, J.-J. Gallet², A. Naitabdi²,
F. Bournel², F. Rochet² and F. Sirotti³

¹ *Unité de Catalyse et de Chimie du Solide, UCCS UMR CNRS 8181, Université Lille1, France*

² *Laboratoire de Chimie Physique Matière et Rayonnement, LCPMR UMR CNRS 7614, Université Pierre et Marie Curie, France*

³ *Synchrotron SOLEIL, St Aubin, France*

ABSTRACT

Cobalt-based catalysts are classically used in Fischer-Tropsch (FT) synthesis (conversion of CO/H₂ mixture into hydrocarbons). The improvement of the activity and selectivity of these catalysts requires a fine description (at the molecular level) of the active phase structure. However the characterization of the active phase can be made difficult by the low amount of metal impregnated on a high surface area oxide support. To overcome this difficulty, one methodology is to mimic the preparation of conventional catalysts by using model catalysts made of active phase deposited on oriented single crystals.

Near Ambient Pressure-XPS gives the opportunity to follow the evolution of catalyst oxidation states under near *in situ* conditions¹. The oxidation of the Co-based catalyst by water produced during the FT reaction has been proposed to favour the particles sintering and the catalyst deactivation. However, this mechanism is still under debate due to the lack of experimental evidence of the Co oxidation by water.

In this study, a model catalyst was first prepared *in situ* by metallic Co evaporation on thermally oxidized Si(111) in the preparation chamber. Then, the evolution of the Co nanoparticles oxidation state was followed in function of the water pressure (from 10⁻² to 5 mbar) at room temperature in the analysis chamber. Finally, the presence of Co²⁺ (as CoO) is detected and its proportion increases with water pressure.

REFERENCES

1. H. Bluhm *et al.*, *J. Phys. Chem. B* 108, 2004, 14340.

High Resolution Investigation of the ν_3 Band of Trifluoromethyl iodide (CF_3I) at Synchrotron SOLEIL

F. Willaert, P. Roy, O. Pirali, L. Manceron,

Synchrotron SOLEIL, AILES, L'Ome des Merisiers, BP 48, 91192 Saint-Aubin, France;

C. Medcraft, D. Appadoo, R. Plathe,

Australian Light Source, Blackburn Road, Monash, Australia;

D. McNaughton,

Monash University, Chemistry Department, Clayton, Australia,

J. Demaison,

Chemical Information Systems, Universität Ulm, D-89069 Ulm, Germany

A. Perrin, F. Kwabia-Tchana,

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR7583 CNRS/ Univ Paris Est Creteil and Univ Paris 7 Diderot, 61 Av du Général de Gaulle, 94010 Créteil, France

ABSTRACT

The high-resolution absorption spectrum of trifluoromethyl iodide (CF_3I), an alternative gas to chlorofluorocarbon but with potential greenhouse effects, has been recorded in the 200-350 cm^{-1} region with the Bruker IFS125HR Fourier transform spectrometer at the AILES Beamline at SOLEIL. This enables a detailed analysis of the ν_3 band of CF_3I .

The lowest vibrational modes of the CF_3I molecule in the far infrared can be recorded at high resolution with Synchrotron sources. Using these spectra, a detailed analysis of the ν_3 band was undertaken. Due to the spectral congestion and the presence of numerous hot bands involving the ν_3 and ν_6 bending fundamentals^{1,2}, spectra have been recorded at 0.001 cm^{-1} resolution at the AILES Beamline facility at SOLEIL either at room temperature using a 150 m optical path length cell or at 163 K using the new LISA-SOLEIL cryogenic cell.⁴ An improved parameter set is proposed for the $\nu_3 = 1$, vibrational state (C-I stretching, at 286 cm^{-1}). Indeed this new calculation accounts for the first time for the Coriolis resonance coupling the $\nu_3 = 1$ energy levels with those from the dark $\nu_6 = 1$ state (I-C-F bending, at $\sim 261.5 \text{ cm}^{-1}$).

The outcome of this work can contribute to a better modelling of the infrared signature of this molecule, considered as a replacement for some chlorine- or bromine-containing gases in industrial applications.

REFERENCE

¹K. Burczyk and H. Bürger, *Spectrochim. Acta*, **A40**, 929-938, (1984).

²S.B. Walters and D.H. Whiffen, *J.C.S. Faraday Trans.*, **279**, 941-949, (1983).

³P. Roy, M. Rouzières, Z. Qi, O. Chubar, *Infrared Phys. Tech.*, **49**, 139-144, (2006).

⁴F. Kwabia Tchana, F. Willaert, X. Landsheere, J.-M. Flaud, L. Lago, M. Chapuis, C. Herbeaux, P. Roy, L. Manceron. *Rev. Sci. Inst.*, **84**, 093101 (2013).

A New Low Temperature Long-path Cell for MID-IR TO THz Spectroscopy

F. Kwabia Tchana, F. Willaert, X. Landsheere, J.-M. Flaud

*LISA, UMR CNRS 7583, Université Paris-Est Créteil and Université Paris-Diderot, 61 Avenue de
Général de Gaulle, 94010 Créteil Cedex, France*

L. Manceron, L. Lago, M. Chapuis, P. Roy, C. Herbaux

*Beamline AILES and Groupe ULTRA HIGH VACUUM Group– Synchrotron SOLEIL, L'Orme des
Merisiers, F-91192 Gif-sur-Yvette, France*

ABSTRACT

We present the details and performances of a new cell, specially designed for accurate spectroscopic measurements in the 80 to 400K temperature range with variable path lengths from 3 to more than 140m, as well as to accommodate the specific requirements of high resolution measurements in the mid- and Far-Infrared on the AILES beamline at SOLEIL. The spectral coverage at these temperatures ranges from the visible to less than 10 cm^{-1} , thanks to the use of diamond windows. The designs of the cryostatic and vacuum set-ups allow vibration-free operation. The equipment provides for temperature homogeneity and pressure control to better than 2 percent over the 100 to 400K and 0.1 to 1000 mbar ranges. Remote-controlled opto-mechanical systems enable in situ readjustments as well as changes of the optical path length within half an hour, in order to optimize measurement time in an open user facility such as SOLEIL. The design and performance of the equipment is presented and illustrated on spectroscopic examples. This new instrument opens up the way for many experiments in the field of high-resolution gas-phase IR spectroscopy, in particular in quantitative spectroscopy for atmospheric applications: measurements of absorption line parameters (absolute intensities and pressure-induced widths) using Fourier transform spectroscopy.

A New High Spectroscopic Resolution Momentum Microscope

C. Mathieu and N. Barrett

DSM/IRAMIS/SPEC, CEA Saclay, 91191 Gif-sur-Yvette, FRANCE

ABSTRACT

The investigation of the electronic properties of materials down to the micron scale is crucial in the view of applications in nanoelectronics. Angle Resolved PhotoEmission Spectroscopy (ARPES) is still the most common technique to probe the band structure of materials. However, spatial resolution is limited by the beam spot, of the order of $\sim 100 \mu\text{m}$, much larger than typical device sizes. An alternative method is photoelectron emission microscopy (PEEM) which has made considerable progress in recent years thanks to instrumental innovation [1,2] and the availability of high brightness VUV and X-ray sources. Recent advances in Energy Filtered PEEM allows to correlate the real space chemical and work function mapping with reciprocal space imaging of the complete band structure of micron scales areas [3,4].

Here we present significant instrumental developments of PEEM optics which allows, for both reciprocal and real space imaging, an energy resolution better than 50 meV. We image, for the first time in PEEM, the spin-orbit splitting of the Au(111) surface state in a $20 \mu\text{m}$ region. These truly microscopic, high resolution band structure results obtained using a focused laboratory He I source are competitive with many current ARPES experiments using synchrotron radiation and constitute an exciting development in the analysis of the band structure on a scale compatible with many electronic applications.

Such an instrument, combined with high intensity synchrotron radiation, should be able to yield the band structure from $1 \mu\text{m}$ sized regions.

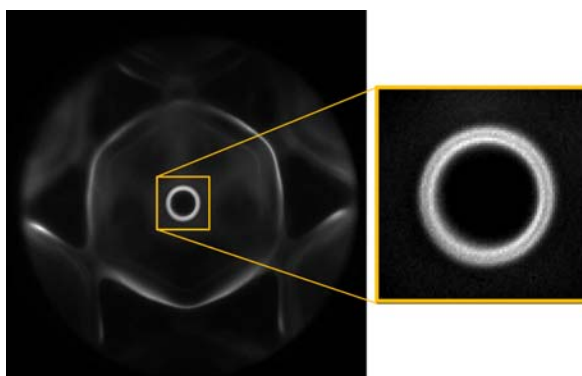


Figure: (left) Fermi surface of Au(111), using He lamp ($h\nu=21.2 \text{ eV}$) at 35 K, with an energy resolution of 50 meV. (right) Zoom around the Γ point, highlighting the Rashba splitting of the surface state.

REFERENCES

1. M. Escher, k. Winkler, O. Renault and N. Barrett, *J. Electron Spectrosc. Relat. Phenom.* **178-179**, 303 (2010).
2. A. Locatelli, E. Bauer, *J. Phys.: Condens. Mat.* **20**, 093002 (2008).
3. C. Mathieu, N. Barrett, J. E. Rault, Y. Y. Mi, B. Zhang, W. A. de Heer, C. Berger, E. H. Conrad and O. Renault, *Phys. Rev. B*, **83**, 235436 (2011).
4. J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C. M. Schneider, G. Geneste, and N. Barrett, *Phys. Rev. Lett.* **111**, 127602 (2013).

Étalonnage en Rendement Absolu d'une Photodiode avec un Radiomètre Cryogénique à Substitution Electrique

Y. Ménesguen¹, B. Boyer¹, M.-C. Lépy¹, G. Lidove²,
M. Rodrigues¹, P. Troussel²

¹CEA, LIST, LNHB, 91191 Gif-sur-Yvette cedex, FRANCE.

²CEA, DAM, DIF, 91297 Arpajon, FRANCE.

ABSTRACT

La caractérisation absolue en rendement des détecteurs permet de connaître la puissance optique incidente sur l'échantillon étudié et s'avère indispensable pour les applications à caractère métrologique et pour des analyses quantitatives précises. L'utilisation d'un radiomètre cryogénique à substitution électrique est une technique largement utilisée par les laboratoires de métrologie nationaux, particulièrement dans le domaine des rayonnements visibles (1,2). La technique est basée sur l'équivalence entre la puissance fournie par le rayonnement photonique et la puissance produite par un courant électrique.

L'application aux rayonnements X a été développée par le CEA/DAM (3) : le bolomètre (BOLUX : BOLomètre pour l'Utilisation dans le domaine des rayons X) utilise un cristal de germanium refroidi à 1,3K comme élément de détection de l'élévation de température consécutive à l'interaction d'un faisceau de photons monochromatiques. La mesure s'effectue en deux temps : le bolomètre est soumis au rayonnement photonique, puis le faisceau est occulté et le bolomètre est chauffé par un courant électrique tel que l'élévation de température soit identique à celle obtenue avec les photons. Les grandeurs électriques peuvent être mesurées de manière absolue et la puissance obtenue peut être déterminée avec des très faibles incertitudes. Le faisceau photonique est ainsi parfaitement caractérisé et peut être envoyé sur un autre détecteur (photodiode) à étalonner.

Le bolomètre BOLUX est donc capable de mesurer une puissance radiante de manière absolue et avec précision. Il a été utilisé pour étalonner en rendement une diode de type AXUV du Laboratoire National Henri Becquerel sur la ligne de Métrologie dans la gamme 4-28 keV. Cette gamme d'énergie dépasse la gamme originelle du bolomètre et des simulations de Monte-Carlo viennent en appui pour quantifier la perte de rendement dû à l'échappement des photons fluorescence au-dessus de l'énergie de liaison K du germanium. Les résultats ont été comparés avec les valeurs de rendement fournies par le constructeur pour une diode de la même gamme et montrent un très bon accord avec les mesures.

L'expérience a de plus montré que la sensibilité maximale obtenue à une température de 1,3K n'est pas nécessaire quand la puissance est supérieure au μW et qu'on pouvait se contenter d'un refroidissement à 4K.

REFERENCES

1. O. Touayar, J.-M. Coutin, J. Bastie : Le radiomètre cryogénique : référence primaire du BNM-INM pour les mesures de rayonnements optiques, Bulletin du BNM N° 177, Volume 1999-3, 35-44.
2. M. Gerlach, M. Krumrey, L. Cibik, P. Müller, G. Ulm, A cryogenic electrical substitution for hard X-rays, Nuclear Instruments and Methods in Physics Research A 580 (2007) 218-221.
3. P. Troussel, N. Coron : BOLUX : a cryogenic electrical-substitution radiometer as high accuracy detector in the 150-11000 eV range, Nuclear Instruments and Methods in Physics Research A 614 (2010) 260-270.

Métrologie des Coefficients d'Atténuation Massique

Y. Ménesguen¹, B. Boyer¹, M.-C. Lépy¹

¹CEA, LIST, Laboratoire National Henri Becquerel 91191 Gif-sur-Yvette cedex, FRANCE.

ABSTRACT

Les applications des rayons X, comme l'analyse par fluorescence ou la caractérisation d'optiques et de filtres en particulier nécessitent la connaissance des données atomiques fondamentales pour une quantification précise. Les utilisateurs des coefficients d'atténuation peuvent retrouver ces valeurs tabulées dans des bases de données et accessibles par internet sur des sites tels que celui du NIST, qui propose la compilation faite par Hubbell¹, sous le nom XCOM. Certaines mesures et calculs faits par Chantler² sont aussi proposés par le NIST sous le nom FFAST. Le CXRO propose de calculer des transmissions de filtres, réflectivité de miroirs ou autre basées sur la compilation faite par Henke³.

Si elles sont pratiques pour l'utilisateur, ces tables sont basées sur des mesures anciennes, ou des calculs théoriques quand les mesures manquent. Cependant, les incertitudes associées peuvent être assez importantes, en particulier pour des énergies de photons inférieures à quelques keV. En effet, plus l'énergie est faible, plus l'élément est absorbant et plus l'échantillon utilisé doit être fin et l'incertitude associée à la mesure d'épaisseur est grande. Des biais systématiques peuvent aussi apparaître. Finalement, les incertitudes estimées des valeurs existantes en-dessous de 1 keV sont de quelques % pour tous les éléments et certainement supérieures à 25 % en-dessous de 500 eV. Des mesures récentes ont aussi révélé des écarts importants, de quelques % au-dessus de certains seuils K⁴.

Ce travail présente ici de nouvelles mesures effectuées par le Laboratoire National Henri Becquerel (laboratoire de métrologie pour les rayonnements ionisants) sur la ligne de métrologie de SOLEIL, pour plusieurs éléments pour une gamme d'énergie allant de 50 eV au minimum à 35 keV au maximum. Ces mesures bénéficient des moyens actuels pour déterminer précisément ces données avec des incertitudes relatives de l'ordre de 0,5 % dans la plus grande partie de la gamme d'énergie. Ces résultats sont obtenus en prenant des précautions pour réduire les causes d'erreur et en quantifiant tous les facteurs d'incertitudes (en particulier, qualité du faisceau de photons et caractéristiques des cibles utilisées). Ces mesures systématiques sont menées dans le cadre de l'initiative internationale « Fundamental Parameters » regroupant plusieurs laboratoires nationaux de métrologie, différents instituts de recherche et des industriels⁵. Ainsi, les résultats obtenus à SOLEIL sont comparées avec des mesures effectuées au PTB et avec les données existantes. Un site internet regroupera à terme ces valeurs expérimentales afin de les mettre à la disposition des utilisateurs.

REFERENCES

1. Hubbell, J. H. "Compilation of Photon Cross-Sections: Some Historical Remarks and Current Status", *X-Ray Spectrometry*, **1999**, *28*, 215-223
2. Chantler, C. T. "Theoretical form factor, attenuation and scattering tabulations for Z=1-92 from E=1-10 eV to E=0.4-1.0 MeV", *Journal of Physical and Chemical Reference Data*, **1995**, *24*, 71-643
3. Henke, B. L.; Gullikson, E. M. & Davis, J. C. "X-ray interactions: photoabsorption, scattering, transmission, and reflection at E = 50-30000 eV, Z = 1-92", *Atomic Data and Nuclear Data Tables*, **1993**, *54*, 181-342
4. Y. Ménesguen, M.-C. Lépy, "Mass attenuation coefficients in the range 3,8<E<11 keV, K fluorescence yield and K β /K α relative X-ray emission rate for Ti, V, Fe, Co, Ni, Cu and Zn measured with a tunable monochromatic X-ray source", 2010, *Nuclear Instruments and Methods in Physics B*.
- 5 http://www.exsa.hu/news/?page_id=13

Crystal Structure of the Hsp90-Sti1 Complex and Mechanism of Client Proteins Recognition

O. Jalmar^{1,2}, L. Qin², C. Caillat², A. Vigouroux², P. Meyer^{1,2}

¹ *Laboratoire de Biologie Moléculaire et Cellulaire des Eucaryotes, FRE 3354 CNRS/UPMC, Institut de Biologie Physico-Chimique, 13, rue Pierre et Marie Curie, 75005 Paris, France.*

² *Laboratoire d'Enzymologie et Biochimie Structurales, UPR 3082 CNRS, 91198 Gif-sur-Yvette, France.*

ABSTRACT

The Hsp90 molecular chaperone is responsible for the conformational activation and assembly of proteins that play essential roles in signaling and cellular regulation. Most of these client proteins control functions involved in malignant transformation such as cell proliferation, immortalization, angiogenesis and apoptosis. Because inhibition of Hsp90 causes the specific degradation of these oncogenic clients by the proteasome, 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. We have focused our attention on Sti1, a cochaperone acting in the early steps of the cycle that helps the transfer of client proteins between the two molecular chaperones Hsp70 and Hsp90. We have solved the structure of the cochaperone Sti1 bound to Hsp90. This structure reveals how Sti1 inhibits the Hsp90 ATPase activity and maintains the Hsp90 molecular clamp in an open conformation in favorable for the loading of client proteins.

ARPES Measurements of Hydrogenated Graphene Layers Grown on SiC using CVD

A. Michon,¹ B. Jabakhanji,² F. Cheynis,³ F. Bertran,⁴ P. Le Fèvre,⁴
A. Taleb-Ibrahimi,⁴ M. Portail,¹ and B. Jouault²

¹ CRHEA, CNRS, Valbonne, France

² L2C, CNRS/Université Montpellier II, France

³ CINA, CNRS/ Université Aix Marseille, France

⁴ Synchrotron SOLEIL, Gif Sur Yvette, France

ABSTRACT

Si sublimation from SiC has been widely studied in the past years because of its ability to grow graphene at the wafer scale with a good uniformity, particularly if using atmospheric pressure annealing. Growing graphene on the Si-face of SiC leads to the formation of a $(6\sqrt{3}\times 6\sqrt{3})$ -R30° reconstructed interface (referred to as the buffer layer), and then to the formation of a monocrystalline graphene film, but its electronic properties are limited by the presence of this interface. However, ex-situ hydrogen treatments can be used to convert the buffer layer into a graphene films which will behave similarly to an isolated graphene film (quasi-free standing graphene).¹

As an alternative to the Si sublimation method, it has been shown that graphene can be grown on SiC from an external source of carbon through a direct growth process using ultra-high vacuum² or CVD^{3,4} conditions with argon or hydrogen as the carrier gas. Among these growth methods, the propane-hydrogen CVD appeared to give original results like the formation of rotational disorder in graphene films grown on the Si-face,⁴ while this has generally been observed only on the C-face using other growth methods. This result has been explained by the presence of hydrogen at the graphene/SiC interface. Propane-hydrogen CVD has also allowed to grow monocrystalline graphene on a $(6\sqrt{3}\times 6\sqrt{3})$ -R30° reconstructed interface. Surprisingly, LEED and XPS observations also suggested the presence of hydrogen at the interface, making expect quasi-free standing behavior.⁵

In order to check this hypothesis, we have grown different graphene samples on the Si-face of SiC using propane-hydrogen CVD and studied their electronic properties using angle-resolved photoemission spectroscopy (ARPES) on the Cassiopée beamline. We have observed that graphene grown on the Si-face of SiC using propane-hydrogen CVD can be either n-type or p-type doped. While the band structure of n-type graphene does not change significantly with annealing up to 1050°C, p-type monolayer graphene can convert to a buffer layer after annealing at 750°C. This proves that p-type graphene lays on a hydrogenated SiC surface, so that a quasi-free standing behavior can be expected. This was verified in magneto-transport measurements, where we have observed mobilities up to 4800 cm²/V.s at 1.5 K with $\mu = 7\times 10^{12}$ /cm² together with a small effect of temperature on the mobility.

REFERENCES

1. C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009).
2. E. Moreau, F. J. Ferrer, D. Vignaud, S. Godey, and X. Wallart, Phys. Status Solidi A **207**, 300 (2009).
3. J. Hwang *et al.*, J. Crystal Growth **312**, 3219 (2010).
4. A. Michon, S. Vézian, A. Ouerghi, M. Zielinski, T. Chassagne, and M. Portail, Appl. Phys. Lett. **97**, 171909 (2010).
5. A. Michon, S. Vézian, E. Roudon, D. Lefebvre, M. Zielinski, T. Chassagne, and M. Portail, J. Appl. Phys. **113**, 203501 (2013).

Sweet Block Copolymer Nanoparticles

E. Minatti¹, R. Borsali², and S. Halila²

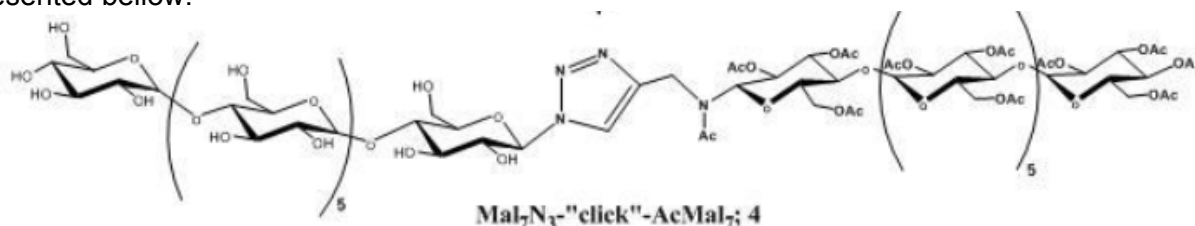
¹ Universidade Federal de Santa Catarina, Departamento de Química, Florianópolis Brazil
edson.minatti@ufsc.br

² Centre de Recherches sur les Macromolécules Végétales (CERMAV), Grenoble, France

ABSTRACT

We present here the design a new class of linear amphiphilic block co-oligomers (BCO) exclusively constituted of biocompatible and biodegradable saccharidic blocks. As an example, we describe herein the preparation and physicochemical studies of a BCO consisting of a bare maltoheptaose derivative as the hydrophilic block “clicked” to its peracetylated maltoheptaose form as the hydrophobic block.

Maltoheptaose is a linear α -(1,4) glucan of seven glucosyl units obtained from the ring-opening of β -cyclodextrin and can be hydrolyzed by starch-degrading enzymes such as glucoamylase or α -amylase. The hydrophobic block was generated by “masking” the hydroxyl groups thanks to ester linkage-mediated hydrophobic. The molecular structure is presented below:



This amphiphilic BCO self-assembles to form spherical micelles in water with an average diameter of 30 nm. The efficient enzymatic hydrolysis of the maltoheptaose that constitutes the shell of the micelles was followed by light scattering (SAXS, DLS and SLS) and colorimetric methods. We have demonstrated, using both light scattering and colorimetric techniques, that the micelles are sensitive to Mal7-degrading enzymes. Moreover, we have clearly observed a reassembly process of the micelles during the course of the shell hydrolysis.

In addition to results previously published elsewhere¹, we demonstrate here the effects of concentration and co-solvents. By increasing the concentration we observed a morphological transition towards worm-like micelles and the addition of THF favored the formation of large compound micelles (LCM).

REFERENCES

1. E. Minatti et al., Sweet Block Copolymer Nanoparticles: Preparation and Self- Assembly of Fully Oligosaccharide-Based Amphiphile, *Biomacromolecules* 2012, 13, 1129–1135

Vibrationally Resolved C 1s Photoionization Cross Section of CF₄

M. Patanen¹, K. Ueda², C. Miron¹, E. Plésiat³, L. Argenti³, K. Kooser⁴,
D. Ayuso⁵, S. Mondal², M. Kimura², K. Sakai², O. Travnikova¹,
A. Palacios³, P. Decleva⁵, E. Kukk⁴, and F. Martín³

¹Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
Sendai 980-8577, Japan

³Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid, Spain

⁴Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland

⁵Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgieri 1,
34127 Trieste, Italy

ABSTRACT

The differential photoionization cross section ratio $\nu = 1 / \nu = 0$ for the symmetric stretching mode in the C 1s photoionization of CF₄ was studied both theoretically and experimentally. The high-resolution measurements in the photon energy range of 330 - 650 eV were carried out at PLEIADES beamline [1] using a VG-Scienta R4000 electron energy analyzer. We observed this ratio to differ from the Franck-Condon ratio and to be strongly dependent on the photon energy, even far from the photoionization threshold.

In a recent study, Ueda *et al.* studied a series of symmetric molecules, CH₄, CF₄, and BF₃, in an attempt to verify if photoelectron diffraction could be selected as a method to extract structural information from conventional photoemission measurements [2]. The performed density functional theory (DFT) calculations showed good agreement with the experiment, but a Born approximation based model providing a simple physical picture to rationalize the results has been also developed. This model was shown to be in a qualitative agreement with the observed cross section oscillations due to the intramolecular photoelectron scattering in CH₄ and BF₃, but was not so successful in the case of CF₄. In this study we investigated the reasons making CF₄ so special.

The DFT computations show that the ratio is significantly modulated by the diffraction of the photoelectrons by the neighboring atoms at high photon energies. At lower energies, the interpretation of the first, very strong maximum observed about 60 eV above the photoionization threshold required detailed calculations of the absolute partial cross sections, which revealed that the absolute cross section has two maxima at lower energies, which turn into one maximum in the cross section ratio because the maxima appear at slightly different energies in the $\nu = 1$ and $\nu = 0$ cross sections. These two strong, low-energy continuum resonances originate from the trapping of the continuum wave function in the molecular potential of the surrounding fluorine atoms and from the outgoing electron scattering by them.

REFERENCES

[1] <http://www.synchrotron-soleil.fr/Recherche/LignesLumiere/PLEIADES>

[2] K. Ueda, C. Miron, E. Plésiat, L. Argenti, M. Patanen, K. Kooser, D. Ayuso, S. Mondal, M. Kimura, K. Sakai, O. Travnikova, A. Palacios, P. Decleva, E. Kukk, and F. Martín, *J. Chem. Phys.* **139**, 124306 (2013).

pH Responsive Peptide Nanotubes: An Atomic View of the pH-induced Conformational Switch that Governs the Assemblies

C. Valéry¹, S. Deville-Foillard², C. Lefebvre³, N. Taberner¹, P. Legrand⁴,
F. Meneau⁴, C. Meriadec³, C. Delvaux², T. Bizien³, E. Kasotakis²,
C. Lopez Iglesias⁵, A. Gall², S. Bressanelli⁶, M.-H. Le Du²,
M. Paternostre^{2*}, F. Artzner^{3*}.

¹Ipsen, 5 Avenue du Canada, 91 Les Ulis, FRANCE

²UMR 8221 CNRS & CEA, CEA-Saclay, 91191 Gif sur Yvette, FRANCE

³IPR, UMR 6251 CNRS & Université Rennes I, 35042 Rennes, FRANCE

⁴Synchrotron Soleil, 91 Gif sur Yvette, FRANCE

⁵Unitat de Microscopia Electronica, Serveis Cientificotecnics, Universitat de Barcelona, SPAIN

⁶UPR CNRS 3296, Avenue de la Terrasse, 91198 Gif-sur-Yvette CEDEX, France

ABSTRACT

From organized biological matter to supramolecular synthetic chemistry, molecular self-assembly is the ubiquitous strategy for the construction of architectures of controlled morphology with 1–100 nm dimensions and single-nanometer precision¹. In this context, we have previously studied the self-assembly process and architecture structure of Lanreotide, a dicationic octapeptide^{2,3}. However, if external stimuli are powerful and typical tools that naturally control protein assemblies and functions, self-assembled nanomaterials hardly possess such responsive properties and bio-inspired approaches could open the way toward tunable self-assembled architectures. Here we study a self-assembling pH sensitive peptide that forms either highly ordered bundles of small nanotubes of 11nm diameter (pH<6.5) or large nanotubes of 50nm diameter (pH>7.5). From our structural multiscale approach, we deduce the mechanism of the peptide conformational changes driving the transition between small and large nanotubes. The sub-angstrom peptide crystal structure (basic pH) reveals a globular conformation stabilized through specific interactions between the lateral chains. Lowering the pH disrupts these interactions and triggers a large change to an extended β -sheet based conformation. We propose that the mechanism discovered in this study can be used to design dual nanostructures that can be switched by a pH change.

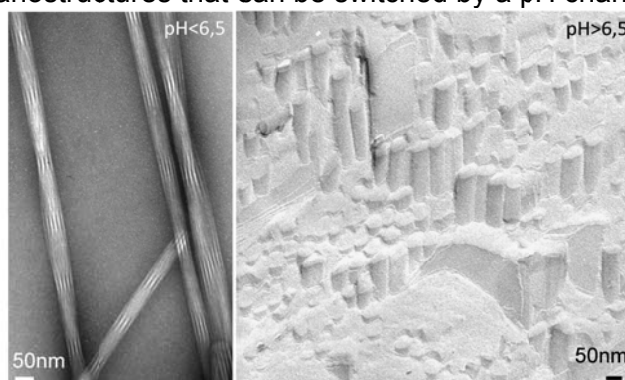


Fig. 1: pH dependent peptide assemblies: low pH (left) and high pH (right)

REFERENCES

[1] C. Valéry, F. Artzner & M. Paternostre, *Soft Matter*, **2011**, 7, 9583

[2] C. Valéry, M. Paternostre, B. Robert, T. Gulik-Krzywicki, T. Narayanan, J-C Dedieu, G. Keller, M. Torres, R. Cherif-Cheikh, P. Calvo, and F. Artzner, *PNAS*, **2003**, 100(18), 10258–10262

[3] E. Pouget, N. Fay, E. Dujardin, N. Jamin, P. Berthault, L. Perrin, A. Pandit, T. Rose, C. Valéry, D. Thomas, M. Paternostre, and F. Artzner, *JACS*, **2010**, 132, 4230–4241

Study of Nanocrystalline Mg-*TM* Complex Hydrides used as Negative Electrodes of Li-ion Batteries by *in-situ* XAS (*TM*=Fe, Co, Ni)

K. Provost¹, W. Zaidi², J. Zhang¹, V. Paul-Boncour¹, A. Michalowicz¹, F. Cuevas¹, M. Latroche¹, J-P. Bonnet², S. Belin³, L. Aymard²

¹ICMPE, CNRS-UPEC, UMR 7182, 2-8 rue Henri Dunant, Thiais, France

²LRCS, CNRS-UMR 7314, 100 rue Saint Leu, Amiens, France

³SOLEIL, L'Orme des Merisiers, Saint-Aubin – BP 48, Gif-sur Yvette, France

ABSTRACT

Metal hydrides (MH_x) are promising candidates for anodes of Li-ion batteries due to their high capacity, suitable potential and low polarization. They operate through the conversion reaction $MH_x + xe^- + xLi^+ \rightarrow M + xLiH$ [1-4]. In this context, Mg₂TMH_x nanocrystalline hydrides (*TM*=Fe, Co, Ni) synthesized by reactive ball milling [5] have been investigated as negative electrodes. From *in situ* XRD patterns collected during electrochemical discharge, an amorphization process has been identified. In order to clarify the reaction mechanism, *in situ* X-ray absorption spectroscopy (XAS) experiments have been performed at the *TM* K-edge during electrochemical cycling of Mg₂TMH_x hydrides. The aim of the study was to ascertain whether electrochemical discharge of Mg₂TMH_x compounds leads either to their decomposition into the constituting elements or to Mg-*TM* alloys, and to study their structural evolution during discharge.

For all Mg₂TMH_x complex hydrides, the shorter *TM*-H contributions are clearly observed in the EXAFS spectra. Upon thermal desorption at 350°C or electrochemical discharge, different behaviors occur depending on *TM*: while Mg₂FeH₆ dehydrogenation induces a demixion into Fe and Mg nanoparticles [6], Mg₂NiH₄ and Mg₂CoH₅ decomposition yields disordered Mg-*TM* alloys. Interestingly, a partial demixion is observed for Co (Mg and MgCo) and no demixion for Ni (Mg₂Ni). The analysis of the Debye-Waller factors shows that in some cases, they are larger for *TM* than for Mg. In addition, although both thermal desorption and electrochemical discharge lead to the formation of similar phases for *TM*=Co, Ni, the disorder effects strongly depend on the process applied to the material, as it is larger for the electrochemical process than for the thermal one.

REFERENCES

1. Y. Oumellal, A. Rougier, G.A. Nazri, J.M. Tarascon, L. Aymard, *Nat. Mater.* **7** (2008) 916-921.
2. Y. Oumellal, A. Rougier, J.M. Tarascon, L. Aymard, *J. Power Sources* **192** (2009) 698-702.
3. W. Zaidi, Y. Oumellal, J.P. Bonnet, J. Zhang, F. Cuevas, M. Latroche, J.L. Bobet, L. Aymard, *J. Power Sources* **196** (2011) 2854-2857.
4. Y. Oumellal, W. Zaidi, J.P. Bonnet, F. Cuevas, M. Latroche, J. Zhang, J.L. Bobet, A. Rougier, L. Aymard, *Int. J. Hydrogen Energy*. **37** (2012) 7831-7835
5. J. Zhang, F. Cuevas, W. Zaidi, J.P. Bonnet, L. Aymard, J.L. Bobet, M. Latroche, *J. Phys. Chem. C* **115** (2011) 4971-4979.
6. J. Zhang, W. Zaidi, V. Paul-Boncour, K. Provost, A. Michalowicz, F. Cuevas, M. Latroche, S. Belin, J.P. Bonnet, L. Aymard, *J. Mater. Chem. A* **1** (2013) 4706-4717.

Structural and Magnetic Properties of $\text{YFe}_2(\text{H,D})_{4.2}$ and $\text{Y}_{0.5}\text{Tb}_{0.5}\text{Fe}_2\text{D}_{4.2}$ under High Pressure

V. Paul-Boncour^{1*}, O. Isnard², K. Provost¹, F. Baudelet³,
L. Nataf³, A. Polian⁴, A. Patissier¹, F. Couturas¹,
J.C. Crivello¹, J. Monnier¹, J.-P. Itié³

¹ICMPE, CNRS-UPEC, UMR7182, 2-8, rue Henri Dunant, Thiais, France

²Institut Néel, CNRS and Univ. Joseph Fourier, BP 166, 38042 Grenoble Cedex 9, France

³SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, 91192 Gif-sur-Yvette, France

⁴IMPMC, UMR 7590, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris CEDEX 05, France

ABSTRACT

Hydrides of RM_2 Laves phases (R = rare earth and M = Mn, Fe, Co) have been widely studied for the influence of hydrogen absorption on their magnetic properties [1]. $R\text{Fe}_2$ compounds form hydrides (deuterides) with different structures derived from the C15 type cubic structure of the parent compounds depending on the H(D) content [2-3]. $\text{YFe}_2\text{D}_{4.2}$ is monoclinic and displays a sharp magnetic variation at $T_{\text{F-AF}}=84$ K, which corresponds to a transition from a ferromagnetic towards an antiferromagnetic structure [4]. A giant isotope effect has been observed on the magnetic properties of $\text{YFe}_2(\text{H,D})_{4.2}$ compounds: the F-AF transition is 47 K higher for the hydride compared to the deuteride [5]. $T_{\text{F-AF}}$ can be also tuned by applying a pressure [6] or replacing Y by another rare earth element [7].

$\text{Y}_{0.5}\text{Tb}_{0.5}\text{Fe}_2\text{D}_{4.2}$ displays the same transition temperature ($T_{\text{F-AF}} = 130(1)$ K) than $\text{YFe}_2\text{H}_{4.2}$. However, its cell volume is only 0.35 % larger than that of $\text{YFe}_2\text{D}_{4.2}$, compared to 0.78 % for $\text{YFe}_2\text{H}_{4.2}$. This indicates that the variation of $T_{\text{F-AF}}$ is not related to a pure magneto-volume effect and that the molecular field of the Tb moment has also a strong influence on the transition temperature.

In order to understand more clearly the relative role played by the volume and the Tb moment on the magnetic transition, we have investigated the influence of the applied pressure on the structural and magnetic properties of these compounds. Applying a pressure allows to decrease the volume and study its influence on the magnetic transition.

$\text{YFe}_2\text{D}_{4.2}$, $\text{YFe}_2\text{H}_{4.2}$ and $\text{Y}_{0.5}\text{Tb}_{0.5}\text{Fe}_2\text{D}_{4.2}$ have been studied by powder diffraction under pressure at the PSICHE beam line of the SOLEIL synchrotron. The evolution of the diffraction patterns shows that several structural transitions occur for pressures above 4 and 13 GPa. XMCD measurements versus pressure and temperature have been also performed at the ODE beam line of the SOLEIL synchrotron at the Fe-K edge for $\text{YFe}_2\text{D}_{4.2}$ and $\text{Y}_{0.5}\text{Tb}_{0.5}\text{Fe}_2\text{D}_{4.2}$ and at the Tb L_{III} edge for $\text{Y}_{0.5}\text{Tb}_{0.5}\text{Fe}_2\text{D}_{4.2}$. The results will be presented and discussed in complement with magnetic measurements under pressure and neutron diffraction experiments.

REFERENCES

- [1] G. Wiesinger, G. Hilscher, in Handbook of Magnetic Materials; Vol. 6, edited by K. H. J. Buschow Elsevier North-Holland, Amsterdam, 1991, p. 511.
- [2] V. Paul-Boncour, L. Guénee, M. Latroche *et al.*, J. Solid State Chem., **142** (1999) 120
- [3] V. Paul-Boncour, S.M. Filipek *et al.* J. Alloys Compds., **317-318** (2001) 83
- [4] V. Paul-Boncour, G. André, F. Bourée, M. Guillot, G. Wiesinger, A. Percheron-Guégan, Physica B, **350** (2004) e27
- [5] V. Paul-Boncour, M. Guillot, G. Wiesinger, G. André, Phys. Rev. B, **72** (2005) 174430
- [6] O. Isnard, V. Paul-Boncour, Z. Arnold, C. V. Colin, T. Leblond, J. Kamarad, H. Sugiura, Phys. Rev. B, **84** (2011) 094429
- [7] M. Guillot, V. Paul-Boncour, T. Leblond, J. Appl. Phys., **107** (2010) 09E144.

X-ray Absorption Spectroscopy during Evolution of the Pd₂Ga-phase used in Methanol Synthesis

H. W. Pereira de Carvalho¹, I. Sharafutdinov², I. Chorkendorff²,
C. Damsgaard³ and J.-D. Grunwaldt¹

¹Institute for Chemical Technology and Polymer Chemistry and Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany

²Center for Individual Nanoparticle Functionality, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

³Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark

ABSTRACT

Intermetallic nanoparticles such as Pd₂Ga supported on SiO₂ are very attractive as catalysts for CH₃OH synthesis from CO₂ by hydrogenation. Pd₂Ga-based catalysts have been prepared by incipient wetness impregnation of Pd and Ga nitrates, drying, calcination in air at 250°C and reduction/alloying in H₂/He at 550°C. *Ex situ* characterization by XRD and TEM has confirmed the formation of Pd₂Ga phase. It is well-known that catalytic activity may be strongly influenced by the shape and size of nanoparticles¹. To rationally design such nanoparticles one has to understand how the intermetallic phases are formed on a nanoscale. Hence, we have followed the reduction and alloying processes towards Pd₂Ga by *in situ* XAS at the SAMBA beamline at SOLEIL. Thanks to the unique facilities available at this beamline, we have traced the alloy formation at the Pd K- and Ga K-edges on the same sample during the annealing under H₂, by alternating rapidly between the Si(311) and Si(111) monochromators, respectively². The phases that resulted from the calcination process were identified as PdO and Ga₂O₃, and the hardly visible second coordination shells pointed to a high dispersion/small particle size. Even at room temperature, the PdO-like phase is converted to Pd under H₂ stream, on the other hand; the Ga₂O₃-like structure is barely affected. During the annealing, around 350°C, the Ga₂O₃-like compound seems to be transformed. EXAFS analysis suggests a mixed Ga_xPd_yO_z, since the inner shell can be assigned as O and outer shells as Pd and Ga. A Ga-Pd scattering path was observed in both Pd K and Ga K edges. At 550°C the alloying process is finished and Pd₂Ga was confirmed by EXAFS. In both Pd K and Ga K edges, only the first coordination shells are clearly defined. For improving our understanding of the alloying process, the same annealing procedure was repeated for Ga(NO₃)₃ supported on SiO₂. During the heating up Ga(NO₃)₃ is nearly fully converted to a Ga₂O₃ like phase around 200°C, and a reduced Ga_xO_y phase starts to be formed from 350°C. These reduced Ga_xO_y species were only stable at high temperatures. During the cooling down step, around 380°C, the reoxidation forming Ga₂O₃ was almost completed. The annealing of Ga(NO₃)₃ has shown that the Pd is necessary to achieve the complete reduction of Ga oxidized species. It may be related to the spillover of H₂ on the surface of Pd forming high reactive atomic H species, which would completely reduce Ga oxide and therefore lead to the Pd₂Ga.

REFERENCES

1. R. A. Van Santen *Acc. Chem. Res.* **42** 56-66 (2009).
2. E. Fonda, A. Rochet, M. Ribbens, L. Barthe, S. Belin, V. Briois *J. Synchr. Rad.* **19**, 417-424 (2012).

Core-hole-clock Spectroscopies in the Tender X-ray Domain

M.N. Piancastelli^{1,2}, G. Goldsztejn¹, T. Marchenko¹, R. Guillemin¹,
R.K. Kushawaha¹, L. Journal¹, S. Carniato¹, J.P. Rueff³,
D. Céolin³, and M. Simon^{1,3}

¹Laboratoire de Chimie Physique-Matière et Rayonnement, CNRS and UPMC, UMR 7614, FR-75231 Paris Cedex 05, France

²Department of Physics and Astronomy, Uppsala University, SE-75120 Uppsala, Sweden

³Synchrotron SOLEIL, l'Orme des Merisiers, FR-91192 Gif-sur-Yvette Cedex, France

ABSTRACT

The core-hole-clock method to observe dynamical phenomena in molecular photoexcitation on the one femtosecond-hundreds of attosecond time scale is illustrated with examples of resonant inelastic x-ray scattering (RIXS) [1,2] and resonant Auger emission experiments on the CH₃I and CH₃Cl prototypical systems in the tender x-ray domain. The resonant Auger electron spectra have been recently measured on the GALAXIES beam line at SOLEIL, with the newly operational endstation dedicated to hard x-ray photoelectron spectroscopy [3]. In particular, a direct comparison between RIXS and resonant Auger data for CH₃Cl allows us to unravel subtle details of nuclear motion and interplay of potential curves of the intermediate and final states reached upon deep core excitation.

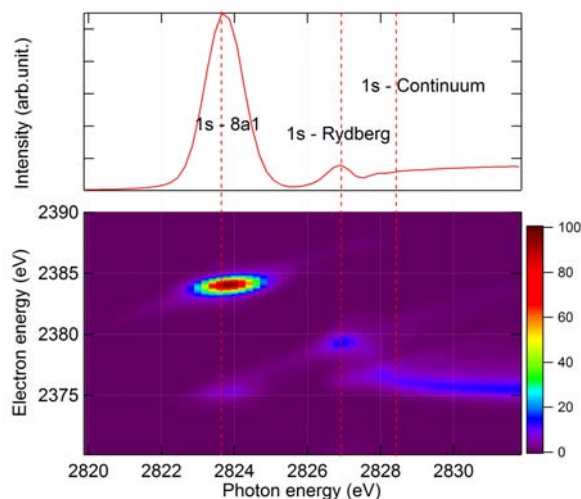


Figure 1. 2D map of KLL Auger decay around the Cl 1s threshold in CH₃Cl. The linear color scale reflects the intensity of the spectral features. The absorption spectrum is shown on top to visually aid to identify the below- and above-threshold processes.

REFERENCES

- [1] T. Marchenko, L. Journal, T. Marin, R. Guillemin, S. Carniato, M. Žitnik, M. Kavčič, K. Bučar, A. Mihelič, J. Hoszowska, W. Cao and M. Simon, *J.Chem.Phys* 134, (2011) 144308 (2011)
- [2] L. El Khoury, L. Journal, R. Guillemin, S. Carniato, W. C. Stolte, T. Marin, D. W. Lindle and M. Simon, *J.Chem.Phys.* 136, (2012) 024319
- [3] D. Céolin *et al.*, *J. Electron Spectrosc. Relat. Phenom.*, in press, <http://dx.doi.org/10.1016/j.elspec.2013.01.006>

Silicene on Silver Reconsidered: Evidence of a Ag(110) Reconstruction Induced by Si Growth.

G. Prévot,¹ R. Bernard,¹ Y. Borensztein,¹ M. Hanbücken,² L. Masson²

¹Institut des Nanosciences de Paris, CNRS UMR 7588 and UPMC, Paris, France

²Aix-Marseille Université, CNRS, CINaM UMR 7325, Marseille, France

ABSTRACT

In the past five years, the Si/Ag interface has proven to be an interesting system with potential intriguing properties. First observations of Si deposition on Ag(110) evidenced the formation of parallel, flat lying isolated nanoribbons (NRs), that self-assembled at higher substrate temperature.^{1,2} These pioneering works have given rise to a number of theoretical and experimental studies concerning the formation and properties of ultrathin Si films on Ag substrates. A graphene-like signature in photoemission spectra has been reported on such films grown on Ag(110) and Ag(111) attributed to the formation of silicene, i.e. sp² bonded silicon atoms arranged in a two-dimensional (2D) honeycomb lattice.^{3,4} Concerning the atomic structure of the NRs, different models have been proposed, some of them being in favor of a Si honeycomb structure. All these models were based on the assumption that the 1D nanostructures are thin pure Si NRs - or nanostripes - on a non-reconstructed Ag substrate.

We have followed in-situ and in real time the Si growth on Ag(110), using grazing incidence X-ray diffraction, scanning tunneling microscopy and surface differential reflectance spectroscopy. We provide compelling evidence of a Ag(110) surface reconstruction associated with the release of Ag atoms induced by the growth of Si nanoribbons.⁵ Our results are in agreement with a missing row reconstruction of the Ag layer underneath the nanoribbons. This shows that the Ag-Si interaction is not negligible and that the structural models of Si atoms arranged in a honeycomb lattice on a flat Ag(110) are inadequate. Moreover, the optical response of the surface cannot be interpreted within the framework of a sp² Si structure.

This challenges the current understanding of the Si structures formed on Ag(110) and currently described as silicene nanoribbons.

REFERENCES

1. C. Leandri, et al., *Surf. Sci.* **574**, L9 (2005).
2. H. Sahaf, L. Masson, C. Léandri, B. Aufray, G. Le Lay, and F. Ronci, *Appl. Phys. Lett.* **90**, 263110 (2007).
3. P. De Padova, et al., *Appl. Phys. Lett.* **96**, 261905 (2010).
4. P. Vogt et al., *Phys. Rev. Lett.* **108**, 155501 (2012).
5. R. Bernard et al. *Phys. Rev. B* **88** (2013) 121411(R)

XANES, a Probe to follow the Reaction of Carboplatin and Oxaliplatin with Cl⁻ and Sulfur Nucleophiles

K. Provost¹, D. Bazin², M. Dedon³, C. Jouanneau³,
D. Bouvet Muller¹ and A. Michalowicz¹

¹ICMPE, UMR 7182 CNRS-UPEC, 2-8 rue Henri Dunant, 94320 Thiais, France

²CNRS, LCMCP-UPMC, Collège de France, 11 place Marcelin Berthelot, 75231 Paris Cedex 05

³UMR S702, INSERM-UPMC, 4 rue de la Chine, 75970 Paris Cedex 20, France

ABSTRACT

Cisplatin, carboplatin and oxaliplatin are largely used worldwide as anticancer drugs. Their reactions with sulfur nucleophiles are implied in many *in-vivo* and *in-vitro* detoxification processes [1]. These complexes and their degradation products, obtained in the presence of chloride or sulfur molecules, have been characterized by EXAFS [2-6]. In these studies, little attention had been paid to the XANES part of the absorption spectra. Few data are available in literature about XANES spectra of Pt-based anticancer drugs. All of them deal with the *in vitro* and *in vivo* reduction of Pt(IV) precursors of Pt(II) potential drugs [7-8]. Thus, the Pt-L_{III} edge white line intensity was used to quantify the Pt(IV)/Pt(II) ratios in biological samples. However, to our knowledge, no study has been performed on Pt-L_{III} edges of the degradation products of Pt(II) anticancer drugs.

We present a quantitative study of the experimental XANES features evolutions, for a large number of model compounds and carboplatin and oxaliplatin degradation products, with various N/(Cl-S) contents and Cl/S ligands, based on the joined analysis of both EXAFS and XANES part of the absorption spectra. We show how the white line intensity can be used to monitor the average N/S content in the Pt(II) first coordination sphere. Furthermore, post-edge features in the first 20eV after the white line are sensitive to the ligand chemical natures, and could be used as ligand signatures. These results may define new tools for further determination of Pt average environment in biological samples through μ -XANES studies.

REFERENCES

1. L. Kelland, *Nature Rev. Cancer* **7** (2007) 573-584
2. K. Provost, D. Bouvet-Muller, S. Crauste-Manciet, J. Moscovici, L. Olivi, G. Vlaic and A. Michalowicz, *Biochimie* **91** (2009) 1301-1306
3. E. Curis, K. Provost, I. Nicolis, S. Bénazeth, D. Bouvet, F. Brion, S. Crauste-Manciet and D. Brossard, *New J. Chem.* **24** (2000) 1003-1008
4. D. Bouvet, A. Michalowicz, S. Crauste-Manciet, E. Curis, I. Nicolis, D. Brossard and K. Provost, *J. Synchrotron Radiat.* **13** (2006) 477-483
5. D. Bouvet, A. Michalowicz, S. Crauste-Manciet, D. Brossard and K. Provost, *Inorg. Chem.* **45** (2006) 3393-3398
6. K. Provost, D. Bouvet-Muller, S. Crauste-Manciet, L. Olivi, G. Vlaic and A. Michalowicz, *J. Phys. Conf. Ser.* **190** (2009) 012206
7. M. D. Hall, G. J. Foran, M. Zhang, P. J. Beale and T. W. Hambley, *J. Am. Chem. Soc.* **125** (2003) 7524-7525
8. M. D. Hall, H. L. Daly, J. Z. Zhang, M. Zhang, R. A. Alderden, D. Pursche, G. J. Foran and T. W. Hambley, *Metallomics* **4** (2012) 568-575

Mg₆Pd Nanoparticles in a Porous Carbon Matrix: EXAFS Characterization of Native and Hydrogenated Nanoparticles

K. Provost¹, M. Ponthieu¹, C. Zlotea¹, Y.S. Au², P. E. de Jongh²,
M. Latroche¹ and F. Cuevas¹

¹ICMPE, UMR 7182 CNRS-UPEC, Thiais, France

²Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands

ABSTRACT

Magnesium, a low-cost and abundant metal, is seen as one of the most promising hydrogen stores. It forms a stoichiometric hydride, MgH₂, that holds 7.6 wt.% hydrogen with high volumetric density (109 g_H l⁻¹). However, MgH₂ is too stable for room temperature use and its formation suffers from slow kinetics. To overcome these drawbacks, alloying of magnesium with transition metals and its nanostructuring are the most encouraging strategies.^{1,2} In this context, intermetallic Mg₆Pd is particularly interesting. Its high Mg content warrants high hydrogen capacity and the presence of Pd ensures good catalytic properties. Moreover, Mg₆Pd crystalizes in a complex structure with large unit cell parameters of ~ 2 nm and one may expect singular structural properties as the particle size decreases to the nanoscale range.³

Mg₆Pd nanoparticles with average size of 4 nm have been synthesized inside of porous carbon following a two-step process: first impregnation and reduction of H₂PdCl₄ to generate Pd nanoparticles embedded in the carbon matrix Pd@C; and then melt-infiltration of magnesium at 923 K to form nanoconfined Mg₆Pd@C. For subsequent structural studies, this hybrid material was hydrogenated at 573 K under at 5 MPa H₂(g). In addition, a Mg₆Pd bulk ingot was synthesized by induction melting for being used as a reference.

Mg₆Pd bulk, Mg₆Pd@C native and hydrogenated samples were structurally characterized by EXAFS spectroscopy at Pd K-edge in transmission mode. Measurements were performed at Doris beamline C of the Desy synchrotron facility in Hamburg, Germany. Through a challenging EXAFS analysis of the Mg₆Pd complex structure, we demonstrate that the nanoparticles exhibit close structural arrangement to Mg₆Pd bulk, though more disordered and simple. This may be attributed to the small difference between the nanoparticles size and Mg₆Pd cell parameters. Under hydrogenation, we observe Mg₆Pd disproportionation into intermetallic MgPd and MgH₂ phases.

REFERENCES

1. F. Aguey-Zinsou and J. R. Ares-Fernandez, *Energy Environ. Sci.*, **3**, 526–5435 (2010)
2. C. Zlotea and M. Latroche, *Colloids Surf., A* **439**, 117–130 (2013).
3. S. Samson, *Acta Cryst., B* **28**, 936-945 (1972)

Structural Basis of Myosin V Cargo Recognition

O. Pylypenko^{a,b}, W. Attanda^{a,b}, C. Gauquelin^{a,b}, M. Lahmani^{a,b},
D. Coulibaly^{a,b}, B. Baron^{c,d}, S. Hoos^{c,d}, M.A. Titus^e,
P. England^{c,d}, A. Houdusse^{a,b}

^a *Structural Motility, Institut Curie, 26 rue d'Ulm, 75248 Paris cedex 05, France*

^b *CNRS, UMR 144*

^c *Institut Pasteur, Proteopole, Department of Structural Biology and Chemistry.*

^d *CNRS, UMR 3528*

^e *Department of Genetics, Cell Biology and Development,
University of Minnesota, Minneapolis, MN 55455, USA.*

ABSTRACT

Class V myosins are present in most eukaryotes and function as molecular motors transporting or tethering of a wide variety of membrane cargoes. Specific recognition of the cargo allows the myosins to perform precise cellular functions at particular time and position in cells. However, very little is known about how evolution has favored conservation of functions for some isoforms while also allowing for the generation of new recognition sites and specialized cellular functions. Crystal structures of the human Myosin Va and the Myosin Vb globular tail domain give insights into how the motor is linked to the recycling membrane compartments via Rab11, or to the melanosome membrane via recognition of the melanophilin adapter that binds to Rab27a. The structures illustrate how the Rab11 binding site has been conserved during evolution and how divergence at another site of the globular tail domain allows specific recognition of melanophilin by the Myosin Va isoform. The structures show how either the partner or the globular tail domain structural plasticity is important for selective recruitment of the motor.

Small-angle X-ray Solution Scattering Study of the Multi-aminoacyl-tRNA Synthetase Complex Reveals an Elongated and Multi-armed Particle

J. Dias¹, J. Pérez², M. Mirande^{1,@} and L. Renault^{1,@}

¹Laboratoire d'Enzymologie et Biochimie Structurales, Centre de Recherche de Gif, C.N.R.S., 1 Avenue de la Terrasse, 91190 Gif-sur-Yvette, France

; ²SOLEIL Synchrotron, L'Orme des Merisiers Saint-Aubin, Gif-sur-Yvette, France.

Co-corresponding authors: mirande@lebs.cnrs-gif.fr, renault@lebs.cnrs-gif.fr

ABSTRACT

In animal cells, nine functionally different aminoacyl-tRNA synthetases are associated with the three auxiliary proteins p18, p38 and p43 to form a stable and conserved, large Multi-Aminoacyl-tRNA Synthetase complex (MARS), whose molecular mass has been proposed to be between 1.0 and 1.5 MDa [1]. The complex acts as a molecular hub for coordinating protein synthesis and diverse regulatory signal pathways. Electron microscopy studies defined its low resolution molecular envelope as an overall rather compact, asymmetric triangular shape [2].

Here, we have analyzed the composition and homogeneity of the native mammalian MARS isolated from rabbit liver, and characterized its overall internal structure, size, and shape at low resolution by hydrodynamic methods and small-angle X-ray scattering in solution near physiological ionic conditions.

Our data reveal that the MARS exhibits a much more elongated and multi-armed shape than expected from previous reports [3]. The hydrodynamic and structural features of the MARS are large compared to other supramolecular assemblies involved in translation, including ribosome. The large dimensions and non-compact structural organization of MARS favor a large solvent-accessible surface for all its components. This helps to understand how the fourteen catalytic components clustered in total in the mammalian MARS may work simultaneously in translation and accommodate concerted structural rearrangements of their catalytic and *cis*-acting tRNA-binding domains upon binding bulky tRNA substrates. This non-compact architecture may also contribute to the spatio-temporal controlled release of some of its components, which participate in non-canonical functions after dissociation from the complex.

REFERENCES

1. Mirande, M. (2005). Multi-Aminoacyl-tRNA Synthetase Complexes. In *The Aminoacyl-tRNA Synthetases*, M. Ibba, C. Francklyn, and S. Cusack, eds. (Georgetown, Texas, USA: Landes Bioscience), pp. 298-308.
2. Norcum, M.T., and Boisset, N. (2002). Three-dimensional architecture of the eukaryotic multisynthetase complex determined from negatively stained and cryoelectron micrographs. *FEBS Lett.* 512, 298-302.
3. Dias, J., Renault L.#, Pérez, J. Mirande M.# (2013) Small-angle X-ray solution scattering study of the multi-aminoacyl-tRNA synthetase complex reveals an elongated and multi-armed particle. *J. Biol. Chem.* 288(33):23979-89.

Probing Deeper by HAXPES: Inelastic Background Analysis of Layered Systems for Transistor Devices

O. Renault¹, P. Risterucci¹⁻³⁻⁴, E. Martinez¹, D. Ceolin²,
J.-P. Rueff², G. Grenet⁴, S. Tougaard³,

¹CEA, LETI, MINATEC Campus, 17 rue des Martyrs, 38054 GRENOBLE Cedex 9, France.

²Synchrotron SOLEIL - L'Orme des Merisiers Saint-Aubin - BP 48 91192 GIF-sur-YVETTE.

³Dept. of Physics, Chemistry and Pharmacy, University of Southern Denmark, DK-5230 Odense M, Denmark.

⁴Institut des nanotechnologies de Lyon (INL), UMR CNRS 5270, Ecole Centrale de Lyon, 36 avenue Guy de Collongue 69 134 ECULLY Cedex.

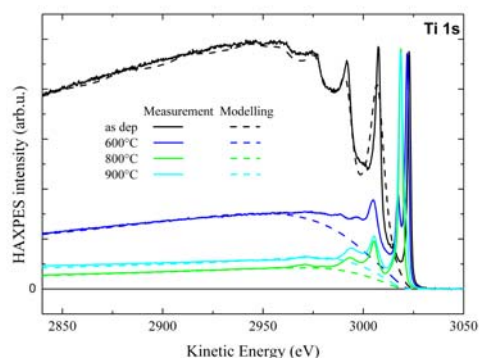
ABSTRACT

The enhanced probing depth offered in HARD X-ray Photoelectron Spectroscopy (HAXPES) up to about 20 nm in core-level analysis [1] was recently further extended up to 50 nm [2] with the additional use of inelastic background analysis. We present here the results for two different technological samples, giving a scope of the sensitivity and parameters influencing the method.

We report on inelastic background analysis following Tougaard's method [3] applied to HAXPES spectra measured at GALAXIES beamline [4] on layered systems of technological interest. The first sample studied is a high-k metal gate stack (TiN(6.5 nm)/LaOx(0.7 nm)/HfSiON(1.4 nm)/SiON(1.8 nm)/Si(100)) capped with 50 nm Si. The high sensitivity of the experiment is shown with the case of the sub-nanometric La layer being quantitatively analyzed at the extreme burying depth of 56 nm. The second sample is designed to perform ohmic contacts in power transistor devices and is composed of Al(10 nm)/Ti(15 nm)/AlGaN(25 nm)/GaN.

Inelastic background analysis of Ti1s transition is shown in Fig. 1. The depth distributions obtained provide an overall understanding of the annealing process and ohmic contact formation. These two different cases also illustrate an important parameter used for modeling of the inelastic losses, namely the inelastic scattering cross-section. For the high-k samples where Si plasmon excitations within the 50 nm Si capping layer dominate, the inelastic scattering cross-section derived from REELS measurements of pure Si at 10keV must be used; for the AlGaN sample, the unannealed sample is dominated by metallic Al plasmon losses, but after annealing these features disappear from the inelastic background, showing the disappearance of the metallic Al layer. The depth distribution of Ti obtained allows to get an insight in the ohmic contact formation process.

We show various case study of inelastic background analysis of technological samples. We highlight the sensitivity of our method and the key choice of the inelastic scattering cross-section.



REFERENCES

1. G. Panaccione and K. Kobayashi, *Surface Science* **606** (3–4), 125-129 (2012).
2. P. Risterucci, O. Renault, B. Dettlefs, E. Martinez, J. Zegenhagen, G. Grenet, S. Tougaard, *Surf Interface Anal.*, accepted (2014); *Appl. Phys. Lett.* 2014 (in press).
3. S. Tougaard, *Journal of Electron Spectroscopy and Related Phenomena* **178–179**, 128-153 (2010).
4. D. Céolin, J. M. Ablett, D. Prieur, T. Moreno, J. P. Rueff, T. Marchenko, L. Journal, R. Guillemin, B. Pilette, T. Marin and M. Simon, *J. of Elec. Spec. and Rel. Phen.* **190, Part B**, 188-192 (2013).

Synchrotron X-ray Footprinting Coupled with Mass Spectrometry for the Structural Study of Large Macromolecular Complexes

A. Młynarczyk[§], P. Jolivet^{*}, Y. Gohon^{*}, L. Aymé^{*}, M. Froissard^{*},
R. Tâche^{*}, K. Brodolin[°], P. Roblin[®], P. Da Silva[¥], P. Mercere[¥],
F. Gonnet[§], R. Daniel[§], A. Giuliani^Δ, B. Sclavi[□], T. Chardot^{*}

*Δ Ligne DISCO, ¥ Ligne Metrology, ®Ligne Swing, Synchrotron Soleil, BP 48
91192 GIF-sur-YVETTE CEDEX*

** INRA, AgroParisTech, UMR1318 Institut Jean-Pierre Bourgin, Saclay Plant Sciences,
78000 Versailles*

*§Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, CNRS UMR 8587,
Université d'Evry-Val-d'Essonne, F-91025 Evry, France.*

□ LBPA, CNRS UMR 8113, ENS Cachan, Cachan, 94235

° CPBS, CNRS UMR 5236 - UM1 / UM2, BP 14491, 34093 MONTPELLIER Cedex 5

ABSTRACT

Synchrotron X-ray footprinting relies on the microsecond timescale production of hydroxyl radicals by the radiolysis of water. These radicals can attack the solvent accessible residues of macromolecules. The identification of the sites of cleavage or modification permits the creation of a map of the change in the solvent accessibility of the macromolecule in the presence of a specific interaction partner as a function of time.

Thanks to the evolution of mass spectrometry analysis techniques this approach allows for the study of macromolecular complexes in solution that are difficult to study by other means, such as those mediated by protein-lipid interactions in lipid bodies and membranes or those made of large, flexible, multimeric proteins.

We have recently set up this technique at the Metrology beamline at Soleil. These early experiments have allowed us to characterize different kinds of samples, to develop data analysis protocols and to thus reproducibly identify specific protein or DNA regions that become modified upon X-ray exposure depending on different experimental conditions, such as the binding of inhibitor molecules (i.e. antibiotics).

Structure and Electronic Properties of the Giant Rashba-split BiTeCl and BiTel Semiconductors

O.E. Tereshchenko^{1,2}, K.A. Kokh^{3,2}, V.A. Golyashov¹,
M.G. Gorynina², A.S. Kozhukhov¹

¹ Rzhzanov Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russian Federation

² Novosibirsk State University, Novosibirsk 630090, Russian Federation

³ Sobolev Institute of Geology and Mineralogy, SB RAS, Novosibirsk 630090, Russian Federation

ABSTRACT

The growing interest in studying of the narrow semiconductors based on the bismuth tellurohalides BiTeX (X=I, Br, Cl) with a noncentrosymmetric unit cell is related to a giant Rashba-type spin splitting of the bulk and surface states, which makes these materials attractive for spintronics applications. Recently, an ARPES and spin-resolved ARPES study by several groups proved that the BiTeX semiconductors show a very large spin-splitting of two-dimensional state at the surface, in agreement with by ab initio calculations, arising from the broken inversion symmetry in the crystal bulk and a strong spin-orbit interaction [1,2]. The bismuth tellurohalides BiTeX (X=Cl,Br,I) are layered materials and have a hexagonal crystal structure of alternating layers of bismuth, tellurium and chlorine (iodine) atoms with the weakest bonding between the Te and Cl(I) layers providing a natural cleaving plane. In ideal case, the surface layer should be either purely iodine- or tellurium-terminated depending on the stacking order of the underlying layers.

Photoemission and AFM in Kelvin mode shown that on various BiTel samples and for both crystal mounting orientations the surface states of both terminations were presented. This leads to the conclusion, that both terminations are present on the surface with domain sizes smaller than the synchrotron light spot. In contrast to BiTel, the BiTeCl samples are single crystalline on a macroscopic scale (mm) with well-defined surface terminations. An aging effect was observed on the BiTel surfaces in terms of band bending downward shift on I-terminated part of the surface caused by preferential adsorption on I-termination. The measured in-plane Seebeck coefficient of BiTeCl samples demonstrated a rather high value, reaching approximately $-280 \mu\text{V}/\text{K}$ at room temperature, suggesting an n-type conductivity. The influence of the ferromagnetic dopants on the electronic structure of Rashba-type surface and bulk states are discussed.

REFERENCES

1. K. Ishizaka, M. S. Bahramy, H. Murakawa, M. Sakano, T. Shimojima, T. Sonobe, K. Koizumi, S. Shin, H. Miyahara, A. Kimura, et al. *Nature materials* **10**, 521-526 (2011).
2. G. Landolt, S. V. Eremeev, O. E. Tereshchenko, S. Muff, B. Slomski, K. A. Kokh, M. Kobayashi, T. Schmitt, V. N. Strocov, J. Osterwalder, E. V. Chulkov, J Hugo Dil, *New Journal of Physics* **15**, pp. 085022-11 (2013).

Build-in Lateral p-n Junction on (0001) $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ Topological Insulators

O.E. Tereshchenko^{1,2}, K.A. Kokh^{2,3}, V.A. Golyashov²

¹ Rzhanov Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russian Federation

² Novosibirsk State University, Novosibirsk 630090, Russian Federation

³ Sobolev Institute of Geology and Mineralogy, SB RAS, Novosibirsk 630090, Russian Federation

ABSTRACT

This report is focused on the preparation of single Bi_2Te_3 crystal with as grown built in p-n junction formed perpendicular to the cleavage plane. As-received crystals, grown by modified Bridgman method using rotating heat field, were cleaved and characterized by ARPES, Hall measurements, atomic force microscopy and scanning tunneling microscopy. Photoemission with spatial resolution was used to identify surface states in p- and n-type region. The Bi_2Te_3 crystals can be grown both p- and n-type conductivity depending on the Bi/Te ratio in the solution. We assumed to receive switching from p- to n type using the effect of Te segregation in the vertical Bridgman method and successfully realized built in p-n junction along the boule of Bi_2Te_3 single crystal. The results demonstrate high crystallographic quality and chemical stability of the cleaved surfaces even after month of the air exposure. In the vicinity of the p-n junction, Seebeck and Hall coefficients changed sign abruptly, electron concentration decreased by two orders of magnitude (down to 10^{17} cm^{-3}) and the electron mobility reached the value of $70000 \text{ cm}^2/\text{Vs}$ at 4 K. It was found that on both part of the (0001) surface (p- and n-type) 2D electron gas was formed caused by downward band bending. Alternative p-n junction was constructed by using solidification of n-type Bi_2Te_3 and p-type Sb_2Te_3 compounds. The p-n junctions demonstrated only ohmic behavior. Possible effects of intermixing between topological surface state and 2D electron gas and their influence on the charge transport will be considered.

Towards a Better Understanding of Atmospheric Pressure Photoionization using APEX (DISCO) Endstation

D. Touboul, M. Méjean, A. Giuliani, A. Brunelle

*Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS,
Avenue de la Terrasse, 91198 Gif-sur-Yvette, France
DISCO beamline, Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin,
91192 Gif-sur-Yvette, France
UAR 1008 CEPIA, INRA, Rue de la Géraudière, F-44316 Nantes, France*

ABSTRACT

Atmospheric Pressure Photo-ionization (APPI) offers the unique capability to analyze hydrophobic and hydrophilic compounds with a reasonable sensitivity. The ionization mechanism is occurring at a high temperature (200-500°C) and at atmospheric pressure. It involves the direct photoionization of the analyte or of a dopant molecule which can exchange a proton or an electron with the analyte. Previous studies tried to explain the complex photochemistry under APPI by using the tabulated thermochemical parameters (adiabatic ionization energy, proton affinity,...) without taking into account that the reactions are occurring in a hot dense medium.

Using a commercial APPI source coupled to the DISCO beamline at the SOLEIL synchrotron radiation facility, we were able to discriminate among the previously proposed mechanisms and to obtain a better understanding of the photochemistry occurring in the ion source.

For that purpose, different model molecules were analyzed: guanine, substance P peptide, and monoterpenes.

For guanine,¹ depending on the photon energy in the VUV range, we are able to selectively produce either radical cation species or protonated species and thus to propose a complete model for the ionization of small molecules in the presence of a dopant.

For substance P, we were able to determine the threshold energy for the production of b-, y-, and c-type fragment ions, allowing the determination of the complete amino acid sequence without the need of tandem mass spectrometry. Peptides bearing post translational modifications were also successfully analyzed.

Finally, using the tunable energy of the synchrotron radiation, we determined the vertical ionization energy of 12 different monoterpenes and modified monoterpenes, which can be considered as a good model for secondary organic aerosol. This new method only requires few µg of each analyte that is significantly lower compared to other experiment based using oven.

REFERENCE

1. J. Allegrand, D. Touboul, A. Giuliani, A. Brunelle and O. Laprévote, *Int. J. Mass Spectrom.* **321-322**, 14-18 (2012)

ESUO, a Pan–european organization to Promote Access to Synchrotrons and Free Electron Lasers

M.C. Feiters¹⁾ and U. Pietsch²⁾

*1) Radboud University Nijmegen, Faculty of Science,
Institute for Molecules and Materials*

*2) Faculty of Science and Engineering, Department of Physics,
University of Siegen, Germany*

ABSTRACT

The European Synchrotron Users Organization (ESUO) was founded in 2010 (<http://www.esuo.org>; U. Pietsch & M. J. Cooper, 'European Synchrotron User Organization established', *J. Synchrotron Rad.* (2010). 17, 428–429) and is composed of national user delegates plus the representatives of the European facility users' organisations. It has as its most important aims to facilitate direct access to European national accelerator based radiation sources (including synchrotrons and lasers, hereafter for brevity collectively referred to as SR sources) throughout programmes of the European Union solely on the basis of scientific merit, and to promote an integrated approach throughout Europe to the use of SR sources.

LIST OF PARTICIPANTS

SOLEIL Users' Meeting 2014
List of participants

TITLE	FAMILY NAME	FIRST NAME	ORGANISM	CITY	COUNTRY	EMAIL
Dr	ABLETT	James	Synchrotron SOLEIL	Gif-sur-Yvette	France	james.ablett@synchrotron-soleil.fr
Mme	AIT AMIR	Dalila	MICRO-CONTROLE SPECTRA-PHYSICS	Evry	France	dalila.aitamir@newport.com
Dr	ALCARAZ	Christian	LCP - CNRS - Univ. Paris Sud 11	Orsay	France	christian.alcaraz@u-psud.fr
Dr	ANDREAZZA	Pascal	Centre de Recherche sur la Matière Divisée	Orléans	France	Pascal.Andreazza@univ-orleans.fr
Dr	ANTONSSON	Egill	Synchrotron SOLEIL	Saint-Aubin	France	antonsson@synchrotron-soleil.fr
Mr	ASTRUC	Thierry	INRA de Theix - Unité de Recherches "QuaPA"	Saint Genés Champanelle	France	astruc@clermont.inra.fr
Mr	AUBERT	Arnaud	ALTEC Equipment	Houilles	France	a.aubert@altec-equipment.com
Dr	AVILES MORENO	Juan Ramon	Laboratoire PHLAM, UMR8523 CNRS ' Université Lille 1	Villeneuve d'Ascq	France	Juan-Ramon.Aviles-Moreno@univ-lille1.fr
Mlle	AYME	Laure	INRA Centre de Versailles	Versailles	France	laure.ayme@versailles.inra.fr
Dr	BARRETT	Nicholas	DSM, IRAMIS	Gif-sur-Yvette	France	nick.barrett@cea.fr
Dr	BENDOUNAN	Azzedine	Synchrotron SOLEIL	Gif-sur-Yvette	France	azzedine.bendounan@synchrotron-soleil.fr
Mme	BENKOULA	Safia	Synchrotron SOLEIL	Saint-Aubin	France	safia.benkoula@synchrotron-soleil.fr
Mlle	BERBEL MANAIA	Eloisa	Faculté de Pharmacie - Université Paris-Sud	Châtenay-Malabry	France	eloisa.berbel-manaia@u-psud.fr
Mlle	BERNARD	Anne-Sophie	Laboratoire des Biomolécules, Ecole Normale Supérieure, Université Paris 6, CNRS	Paris	France	anne-sophie.bernard@ens.fr
Dr	BERRIER	Elise	UCCS	Villeneuve d'Ascq	France	elise.berrier@univ-lille1.fr
Dr	BERTIN	Mathieu	LPMAA - Université Pierre et Marie Curie	Paris	France	mathieu.bertin@upmc.fr
Dr	BERTRAN	Francois	Synchrotron SOLEIL	Gif-sur-Yvette	France	francois.bertran@synchrotron-soleil.fr
Dr	BES	René	Synchrotron Synchrotron SOLEIL, Ligne MARS et CEA Cadarache DEN/DEC/SESC/LL	Gif-sur-Yvette	France	bes@synchrotron-soleil.fr
Dr	BEUTIER	Guillaume	SIMaP	Saint-Martin d'Hères	France	guillaume.beutier@simap.grenoble-inp.fr
PROF	BIANCONI	Antonio	Rome International Center for Materials Science Superstripes	Rome	Italy	antonio.bianconi@ricmass.eu
Dr	BIOU	Valerie	CNRS, UMR7099	Paris	France	biou@ibpc.fr
Dr	BLAUD	Magali	LCRB UMR8015	Paris	France	magali.blaud@parisdescartes.fr
PROF	BLEUZEN	Anne	Université Paris-Sud	Orsay	France	anne.bleuzen@u-psud.fr
Mr	BOUAMRANE	Fayçal	Unité Mixte CNRS/THALES et Université Paris sud 11	Palaiseau	France	faycal.bouamrane@thalesgroup.com
PROF	BOUCHER	Florent	Institut des Matériaux Jean Rouxel (IMN)	Nantes	France	Florent.Boucher@cnrs-imn.fr
Dr	BOUCKAERT	Julie	UNITE DE GLYCOBIOLOGIE STRUCTURALE ET FONCTIONELLE	Villeneuve D'Ascq	France	julie.bouckaert@univ-lille1.fr
Dr	BOUDON	Vincent	Lab. Interdisciplinaire Carnot de Bourgogne	DIJON	France	Vincent.Boudon@u-bourgogne.fr
Mme	BOUHIER	Sylvie	OMICRON TECHNOLOGIES	EYBENS	France	sbouhier@mor-cal.eu
Dr	BOURNEL	Fabrice	Université P. et M. Curie, Laboratoire de Chimie Physique Matière et Rayonnement / Syn	Paris	France	fabrice.bournel@upmc.fr
Mme	BRIGNOLO	Stefania	Laboratoire de Chimie Physique Matière et Rayonnement	Paris	France	bristefa@gmail.com
Dr	BROUTIN	Isabelle	CNRS	Paris	France	isabelle.bROUTIN@parisdescartes.fr
Dr	BRUBACH	Jean-blaise	Synchrotron SOLEIL	Gif-sur-Yvette	France	jean-blaise.brubach@synchrotron-soleil.fr
Mr	BUSSA	Stéphane	PI France	Montrouge	France	s.bussa@pi.ws
Dr	CAETANO	Bruno	Instituto de Química, UNESP and Université Pierre et Marie Curie, UPMC-Univ Paris 06,	Paris	Brazil and France	bruno.caetano@upmc.fr
Dr	CAMMELLI	Sebastiano	MARS beamline Synchrotron SOLEIL	Gif-sur-Yvette	France	sebastiano.cammelli@synchrotron-soleil.fr
Dr	CAMPANACCI	Valerie	LEBS CNRS UPR3082	Gif-sur-Yvette	France	campanacci@lebs.cnrs-gif.fr
Dr	CAO	Jing	Université Paris-Sud XI-ICMMO	Orsay	France	jing.cao@u-psud.fr
Dr	CARENCO	Sophie	Collège de France	Paris	France	sophie.carenco@college-de-France.fr
PROF	CARNIATO	stéphane	laboratoire de chimie physique matière et rayonnement, UPMC	Paris	France	stephane.carniato@upmc.fr
Dr	CARRASCO	Nathalie	LATMOS - UVSQ	Guyancourt	France	nathalie.carrasco@latmos.ipsl.fr
PROF	CARRIER	Xavier	Université Pierre et Marie Curie - UPMC	Ivry-sur-Seine	France	xavier.carrier@upmc.fr
Dr	CARRIERE	David	CEA de Saclay	Gif-sur-Yvette	France	david.carriere@cea.fr
Dr	CEOLIN	Denis	Synchrotron SOLEIL	Gif-sur-Yvette	France	denis.ceolin@synchrotron-soleil.fr
Mme	CHABANNE	Corinne	Synchrotron SOLEIL	Gif-sur-Yvette	France	corinne.chabanne@synchrotron-soleil.fr
Mme	CHAGNOT	Caroline	INRA	saint genes champanelle	France	caroline.chagnot@hotmail.fr
Mlle	CHAIX	Laura	Institut Laue-Langevin	Grenoble	France	chaixl@ill.fr
Mme	CHAOUCHI	Karine	Synchrotron SOLEIL	Gif-sur-Yvette	France	karine.chaouchi@synchrotron-soleil.fr
Mr	CHAPUIS	Franck	OMICRON TECHNOLOGIES	Eybens	France	fchapuis@omicron-technologies.com
Dr	CHARDOT	Thierry	INRA Centre de Versailles	Versailles	France	thierry.chardot@versailles.inra.fr
Dr	CHEN	Kai	Synchrotron SOLEIL	Gif-sur-Yvette	France	kai.chen@synchrotron-soleil.fr
Dr	CHERFILS	Jacqueline	CNRS	Gif-sur-Yvette	France	cherfils@lebs.cnrs-gif.fr
Dr	CHOUËIKANI	Fadi	Synchrotron SOLEIL	Gif-sur-Yvette	France	choueikani@synchrotron-soleil.fr
Dr	CHWIEJ	Joanna	AGH University of Science and Technology	Krakow	Poland	joanna.chwiej@fis.agh.edu.pl
Dr	CINQUIN	Bertrand	Synchrotron SOLEIL	Gif-sur-Yvette	France	Bertrand.cinquin@synchrotron-soleil.fr
Dr	CIOCI	Gianluca	LISBP	Toulouse	France	cioci@insa-toulouse.fr
Dr	CLEDE	Sylvain	LBM - ENS PARIS	Paris	France	sylvain.clede@ens.fr
Mr	CLEMENT	François	kURT J.LESKER COMPANY	HASTINGS	United Kingdom	francoisc@lesker.com
Dr	COATI	Alessandro	Synchrotron SOLEIL	Gif-sur-Yvette	France	alessandro.coati@synchrotron-soleil.fr
Mr	COLLET	Nicolas	PI France	Montrouge	France	n.collet@pi.ws
Mr	COOK	Philip	IPANEMA / Synchrotron SOLEIL	Gif-sur-Yvette	France	philip.cook@synchrotron-soleil.fr
Dr	CREFF	Gaelle	Institut de Chimie de Nice	Nice	France	gaelle.creff@unice.fr
PROF	CRISTOL	sylvain	Unité de Catalyse et Chimie du Solide	Villeneuve d'Ascq	France	sylvain.cristol@univ-lille1.fr
PROF	CROSET	Bernard	Institut des Nanosciences de Paris	Paris	France	bernard.croset@insp.jussieu.fr
Dr	CUBAYNES	Denis	ISMO & Synchrotron SOLEIL	Orsay	France	Denis.cubaynes@U-psud.fr
Dr	CUISSET	Arnaud	Laboratoire de Physico-Chimie de l' Atmosphère	Dunkerque	France	arnaud.cuisset@univ-littoral.fr
Dr	CUNHA DE MIRANDA	Barbara	Laboratoire de Chimie Physique - Université Paris Sud XI	Orsay	France	barbara.miranda@u-psud.fr
Mme	CZJZEK	Mirjam	UMR7139 Végétaux Marins et Biomolécules, Station Biologique de Roscoff	Roscoff	France	czzek@sb-roscoff.fr
Dr	D ASTUTO	Matteo	IMPMC UMR7590 UPMC-CNRS	Paris	France	matteo.dastuto@impmc.upmc.fr
Mlle	DAFFE	Niéli	UPMC-Synchrotron SOLEIL	Paris	France	Nieli.Daffe@impmc.upmc.fr
PROF	DAILLANT	Jean	Synchrotron SOLEIL	Gif-sur-Yvette	France	jean.daillant@synchrotron-soleil.fr
Mlle	DALLA BERNARDINA	Simona	Synchrotron SOLEIL	Gif-sur-Yvette	France	simona.dalla-bernardina@synchrotron-soleil.fr
Dr	DAMAY	Françoise	Laboratoire Léon Brillouin	Gif-sur-Yvette	France	francoise.damay@cea.fr
Dr	DAVID	Gabriel	Synchrotron SOLEIL	Gif-sur-Yvette	France	gabriel.david@synchrotron-soleil.fr
Dr	DAVYDOK	Anton	Im2np	Marseille	France	anton.davydok@im2np.fr
Dr	DE BOISSIEU	Marc	SIMAP, CNRS, Université de Grenoble	Saint Martin d'Hères	France	Marc.de-boissieu@simap.grenoble-inp.fr
Mr	DE OLIVEIRA	Nelson	Synchrotron SOLEIL	St Aubin	France	nelson.de.oliveira@synchrotron-soleil.fr
Mr	DEBESSE	Frédéric	AEROTECH	Tadley	United Kingdom	fdebesse@optoprim.com

SOLEIL Users' Meeting 2014
List of participants

TITLE	FAMILY NAME	FIRST NAME	ORGANISM	CITY	COUNTRY	EMAIL
Mr	DEGUT	Clément	CNRS UMR 8015 LCRB	Paris	France	clement.degut@parisdescartes.fr
PROF	DEN AUWER	Christophe	Université Nice Sophia Antipolis	Nice	France	christophe.denuwer@unice.fr
Mlle	DENDEN	Ibtihel	Subatech Laboratory	Suce sur Erdre	France	ibtihel.denden@subatech.in2p3.fr
Mlle	DUCROT	Camille	Synchrotron SOLEIL	Gif-sur-Yvette	France	camille.ducrot@synchrotron-soleil.fr
Mme	DUGET	Anne	SYMETRIE	Nîmes	France	anne.duget@symetrie.fr
Dr	DUMAS	Paul	Synchrotron SOLEIL	Gif-sur-Yvette	France	dumas@synchrotron-soleil.fr
PROF	DUMAS	Thomas	CEA	Bagnols sur ceze	France	thomas.dumas@cea.fr
Mr	DUPRAZ	Maxime	SIMAP	Saint-Martin d'Hères	France	maxime.dupraz@simap.grenoble-inp.fr
Dr	DUPUIS	Vincent	MDC, UPMC, Laboratoire PECSA	Orsay	France	vincent.dupuis@upmc.fr
Dr	DURAND	Dominique	IBBMC CNRS UMR8619 Université Paris-Sud	Paris	France	dominique.durand@u-psud.fr
Mr	EL SAHILI	Abbas	LEBS CNRS UPR 3082	Gif-sur-Yvette	France	abbas.el-sahili@lebs.cnrs-gif.fr
Mlle	FATIMA	Sadaf	Institut de Minéralogie et de Physique des Milieux Condensés IMPMC, UPMC	Paris	France	sadaf.fatima@impmc.upmc.fr
Dr	FEITERS	Martin	Radboud University Nijmegen, Faculty of Science, Institute of Molecules and Materials	Nijmegen	Netherlands	m.feiters@science.ru.nl
Dr	FERNANDEZ GOMEZ-RECUERO	Laura Isabel	Donostia International Physics Center	San Sebastian	Spain	lauraisabel.fernandez@ehu.es
Mme	FERNANDEZ-VARELA	Paloma	Laboratoire d'Enzymologie et Biochimie Structurales (LEBS)	Gif-sur-Yvette	France	fernandez-varela@lebs.cnrs-gif.fr
Dr	FETICS	Susan	CNRS - LEBS	Gif-sur-Yvette	France	susan.fetics@lebs.cnrs-gif.fr
PROF	FILLION	Jean-Hugues	LPMAA	Paris	France	jean-hugues.fillion@upmc.fr
Dr	FINET	Stéphanie	IMPMC CNRS-UPMC-IRD-MNHN	Paris	France	stephanie.finet@impmc.upmc.fr
Mr	FLOROT	Claude	Mclennan Servo Supplies	Ash Vale	United Kingdom	claudefloro@mclennan.fr
Mlle	FOLLY-KLAN	Marcia	LEBS-CNRS UPR 3082	Gif-sur-Yvette	France	marcia.folly-klan@lebs.cnrs-gif.fr
PROF	FONTAINE	Alain	Fondation Nanosciences	Grenoble	France	alain.fontaine@fondation-nanosciences.fr
Dr	FOUCAULT-COLLET	Alexandra	CBM CNRS	Orléans	France	alexandra.foucault@cnrs-orleans.fr
Dr	FOURNIER	Jean-Baptiste	Station Biologique de Roscoff - UMR7139	Roscoff	France	jbournier@sb-roscoff.fr
Mme	FRAISSARD	Frédérique	Synchrotron SOLEIL	Saint Aubin	France	frederique.fraissard@synchrotron-soleil.fr
Dr	GALLET	Jean-Jacques	LCP-MR, Université Pierre et Marie Curie	Paris	France	jean-jacques.gallet@upmc.fr
Dr	GARCIA	Gustavo	Synchrotron SOLEIL	Gif-sur-Yvette	France	gustavo.garcia@synchrotron-soleil.fr
Dr	GATTI	Matteo	LSI, Ecole Polytechnique, Synchrotron SOLEIL	Palaiseau	France	matteo.gatti@polytechnique.fr
Dr	GIRARDON	Jean-Sébastien	UCCS Unité de Catalyse et de Chimie du Solide	Villeeneuve d'Ascq	France	jean-sebastien.girardon@univ-lille1.fr
Dr	GIULIANI	Alexandre	Synchrotron SOLEIL	Gif-sur-Yvette	France	alexandre.giuliani@synchrotron-soleil.fr
Mlle	GONZALEZ	Sara	DSM / IRAMIS / SPEC	Gif-sur-Yvette	France	sara.gonzalez@cea.fr
Mr	GRANDAMAS	Stéphane	AGILENT TECHNOLOGIES	Leini	Italy	stephane.grandamas@agilent.com
Mr	GRIESSL	Stefan	HUBER Diffraktionstechnik GmbH & Co.KG	Rimsting	Germany	sg@xhuber.com
PROF	GRIONI	Marco	EPFL	Lausanne	Suisse	marco.grioni@epfl.ch
Dr	GRUET	Sébastien	Synchrotron SOLEIL	Gif-sur-Yvette	France	sebastien.gruet@synchrotron-soleil.fr
Mr	GUERIAU	Pierre	Muséum national d'Histoire naturelle	Paris	France	gueriau@mnhn.fr
Mr	GUIBERT	Clément	UPMC, PECSA	Paris	France	clement.guibert@upmc.fr
Dr	GUILLOU	Emmanuel	Inst. de Chimie Moléculaire	Reims	France	emmanuel.guillon@univ-reims.fr
Dr	GUILLOU	Raphaëlle	Institut P'	Futuroscope	France	raphaëlle.guillon@univ-poitiers.fr
PROF	GUINEBRETIERE	René	Centre Européen de la Céramique, ENSCI, 12 rue Atlantis	Limoges	France	rene.guinebretiere@unilim.fr
Dr	GUYOT	Herve	Institut NEEL	Grenoble	France	guyot@grenoble.cnrs.fr
Mr	HACHET	Vincent	AGILENT TECHNOLOGIES	Leini	Italy	vincent.hachet@agilent.com
Dr	HAJLAOUI	Mahdi	Synchrotron SOLEIL	Bures sur Yvette	France	mahdi.hajlaoui@synchrotron-soleil.fr
Dr	HAMACEK	Josef	CNRS UPR4301	Orléans	France	sandrine.villette@cnrs-orleans.fr
Dr	HEAYS	Alan	Leiden Observatory	Leiden	Netherlands	ahays@yahoo.com
Dr	HENRI	Julien	CNRS/UPMC FRE3354 Laboratoire de Biologie Moléculaire et Cellulaire des Eucaryotes	Paris	France	henri@ibpc.fr
PROF	HRICOVINI	Karol	Université de Cergy-Pontoise	Cergy-Pontoise	France	karol.hricovini@u-cergy.fr
Mlle	ISABET	Tatiana	Synchrotron SOLEIL	Gif-sur-Yvette	France	tatiana.isabet.old@orange.fr
Dr	ISAURE	Marie-Pierre	Université de Pau et des Pays de l'Adour/ LCABIE- IPREM	Pau	France	marie-pierre.isaure@univ-pau.fr
Dr	ITIE	Jean-Paul	Synchrotron SOLEIL	Gif-sur-Yvette	France	jean-paul.itie@synchrotron-soleil.fr
Dr	ITO	Kenji	LCPMR	Paris	France	kenji.ito@kek.jp
Dr	JACQUES	Vincent	CNRS	Orsay	France	vincent.jacques@u-psud.fr
Dr	JAMME	Frederic	Synchrotron SOLEIL	Gif-sur-Yvette	France	frederic.jamme@synchrotron-soleil.fr
Mme	JAUBERT	Anne-Sophie	MDC VACUUM PRODUCTS SARL	Lyon	France	asiaubert@mdcvacuum.fr
Mr	JEAN	Fabien	Institut Néel (CNRS)	Grenoble	France	fabien.jean@neel.cnrs.fr
Mlle	JIA	Juanjuan	Institut des Sciences Moléculaires d'Orsay	Orsay	France	jiajuan@gmail.com
Dr	JOURNEL	Loic	UPMC-LCPMR	Paris	France	loic.journal@upmc.fr
Dr	JUJIN	Amélie	IMPMC - CNRS, UNIVERSITE P. ET M. CURIE	Paris	France	amelie.jujin@impmc.upmc.fr
PROF	KALPYRIS	Ioannis	imec	Leuven	Belgium	ioannis.kalpyris@imec.be
PROF	KENNEDY	Eugene	Dublin City University	Dublin	Ireland	eugene.kennedy@dcu.ie
Dr	KUBSKY	Stefan	Synchrotron SOLEIL	Gif-sur-Yvette	France	stefan.kubsky@synchrotron-soleil.fr
Mlle	KUTZER	Pia	Universitaet Kassel	Kassel	Germany	p.kutzer@physik.uni-kassel.de
Dr	LA FONTAINE	Camille	Synchrotron SOLEIL	Gif-sur-Yvette	France	camille.lafontaine@synchrotron-soleil.fr
Dr	LABLANQUIE	Pascal	LCP-MR	Paris	France	pascal.lablanquie@upmc.fr
Mr	LANGLAIS	Simon	SIMaP, Grenoble INP	Saint Martin d'Hères	France	simon.langlais@gmail.com
Mr	LAPIERRE	Olivier	SYMETRIE	Nîmes	France	info@symetrie.fr
Dr	LE HA'	Anne-Solenn	C2RMF - Centre de recherche et de restauration des musées de France	Paris	France	anne-solenn.leho@culture.gouv.fr
Dr	LEBLANC	Catherine	CNRS - UPMC	Roscoff	France	catherine.leblanc@sb-roscoff.fr
Dr	LECLERC	Joan	CNRS UPR4301	Orléans	France	sandrine.villette@cnrs-orleans.fr
Pr	LECOMTE	Claude	Cristallographie, Résonance Magnétique et Modélisations	Vandoeuvre Les Nancy	France	claudefcomte@lcm3b.uhp-nancy.fr
Dr	LEGROS	Samuel	CIRAD	Paris	France	samuel.legros@cirad.fr
Dr	LEJEUNE	Julien	UNIVERSITY OF SOUTHAMPTON, SCHOOL OF CHEMISTRY	Southampton	United Kingdom	julien.lejeune@ens-lyon.org
Mlle	LEMOINE	Asseline	Synchrotron SOLEIL / CRMD	Saint-Aubin	France	asseline.lemoine@synchrotron-soleil.fr
Dr	LEPY	Marie-Christine	Laboratoire National Henri Becquerel	Gif-sur-Yvette	France	marie-christine.lepy@cea.fr
Mlle	LETOUQUART	Juliette	Laboratoire de Biochimie - Ecole Polytechnique	Palaiseau	France	juliette.letoucart@polytechnique.edu
Mme	LI	sha	Institut des Sciences Moléculaires d'Orsay	orsay	France	sha.li@u-psud.fr
PROF	LI DE LA SIERRA- GALLAY	Ines	IBBMC, UMR8619, Univ. Paris Sud	Orsay	France	ines.gallay@u-psud.fr
Dr	LINGUERRI	Roberto	Laboratoire MSME Université Paris-Est Marne-la-Vallée	Champs sur Marne	France	roberto.linguerrri@u-pem.fr

SOLEIL Users' Meeting 2014
List of participants

TITLE	FAMILY NAME	FIRST NAME	ORGANISM	CITY	COUNTRY	EMAIL
Mr	LIU	Dan	SIMaP-Laboratoire de Science et Ingénierie des Matériaux et Procédés	Saint Martin d'Hères	France	dan.liu@simap.grenoble-inp.fr
Mme	LORY	Céline	Synchrotron SOLEIL	Saint Aubin	France	celine.lory@synchrotron-soleil.fr
Mr	LUCACCHIONI	Jean-Marc	Synchrotron SOLEIL	Gif-sur-Yvette	France	jean-marc.lucacchioni@synchrotron-soleil.fr
Dr	LUGAN	Noel	Laboratoire de Chimie de Coordination du CNRS	Toulouse	France	noel.lugan@lcc-toulouse.fr
PROF	LUNING	Jan	LCPMR / Synchrotron SOLEIL	Paris	France	jan.luning@upmc.fr
Dr	LYONNARD	Sandrine	CEA	Grenoble	France	sandrine.lyonnard@cea.fr
Mme	MAKAMTÉ KEMDIB	Staelle Sonia	Institut de biologie Physico-chimique	Paris	France	makamte@ibpc.fr
Mme	MAMEDE	Stéphanie	UCCS	Villeneuve d'Ascq	France	anne-sophie.mamede@ensc-lille.fr
Dr	MANCERON	Laurent	Synchrotron SOLEIL- AILES	Saint Aubin	France	laurent.manceron@synchrotron-soleil.fr
Dr	MARCEAU	Eric	Lab. de Réactivité de Surface	Ivry sur Seine	France	eric.marceau@upmc.fr
Mr	MARIJON	Jean-baptiste	laboratoire PIMM arts et metier de paris	Paris	France	jean-baptiste@marijon.fr
Mlle	MARTINIC	Ivana	CNRS UPR4301	Orléans	France	sandrine.villette@cnrs-orleans.fr
Mr	MARTY	Loïc	Laboratoire d Enzymologie et de Biochimie Structurale	Gif-sur-Yvette	France	loic.marty@lebs.cnrs-gif.fr
Mr	MASION	Armand	CEREGE UMR7330 CNRS - Aix Marseille Université	Aix-en-Provence	France	masion@cerge.fr
Dr	MATHIEU	Claire	CEA	Gif-sur-Yvette	France	claire.mathieu@cea.fr
Mme	MENEGHEL	Julie	INRA Grignon / Synchrotron SOLEIL Synchrotron	Thiverval-Grignon	France	julie.meneghel@grignon.inra.fr
Dr	MENESGUEN	Yves	CEA	Gif-sur-Yvette	France	yves.menesguen@cea.fr
PROF	MENEZ	Benedicte	IPGP-Université Paris Diderot	Paris	France	menez@ipgp.fr
Mr	MENUT	Denis	CEA Saclay	Gif-sur-Yvette	France	denis.menut@cea.fr
PROF	MERROUN	Mohamed L.	University of Granada, Department of Microbiology	Granada	Spain	merroun@ugr.es
Mr	MEYER	Michael	SPECS Surface Nano Analysis GmbH	Berlin	Germany	marketing@specs.com
Dr	MEYER	Philippe	LBMCE IBPC	Paris	France	philippe.meyer@ibpc.fr
PROF	MICHALOWICZ	Alain	Institut de Chimie et des Matériaux Paris Est (CNRS and UPEC)	Thiais	France	michalov@u-pec.fr
Dr	MICHON	Adrien	CNRS-CRHEA	Valbonne	France	am@crhea.cnrs.fr
PROF	MINATTI	Edson	UFSC - Universidade Federal de Santa Catarina	Florianopolis	Brazil	edson.minatti@ufsc.br
Dr	MIRON	Catalin	Synchrotron SOLEIL	Gif-sur-Yvette	France	catalin.miron@synchrotron-soleil.fr
Mlle	MLYNARCZYK	Anna	Laboratoire Analyse et Modélisation pour la Biologie et l Environnement, Université d'Avoyry	Evry	France	ana.mlynarczyk@gmail.com
Mr	MOBERG	Robert	VG SCIENTA	Uppsala	Sweden	robert.moberg@vgscienta.com
Mr	MONNIER	Christophe	AEROTECH	Tadley	United Kingdom	cmonnier@aerotech.com
Dr	MONNIER	Judith	UPEC	Thiais	France	monnier@icmpe.cnrs.fr
Dr	MORERA	Solange	LEBS-CNRS	Gif-sur-Yvette	France	morea@lebs.cnrs-gif.fr
PROF	MORIN	Paul	SYNCHROTRON Synchrotron SOLEIL	Gif-sur-Yvette	France	paul.morin@synchrotron-soleil.fr
Dr	NAHON	Laurent	Synchrotron Synchrotron SOLEIL	Gif-sur-Yvette	France	laurent.nahon@synchrotron-soleil.fr
Mlle	NAZARENKO	Iulilia	CNRS UPR4301	Orléans	France	sandrine.villette@cnrs-orleans.fr
Mr	NEEMAN	Elias	Laboratoire PhLAM, UMR8523 CNRS ' Université Lille 1	Villeneuve d'Ascq	France	elias.neeman@univ-lille1.fr
Mr	NEMAUSAT	Ruidy	Institut de Minéralogie et de Physique des Milieux Condensés	Paris	France	ruidy.nemausat@impmc.upmc.fr
Dr	NEVEU	Sophie	UPMC- Laboratoire PECSA	Paris	France	sophie.neveu@upmc.fr
PROF	NEVILLE	John	University of New Brunswick	Fredericton, NB	Canada	jneville@unb.ca
Dr	NICOLAI	Béatrice	faculté de pharmacie- Université Paris Descartes	Paris	France	beatrice.nicolai@parisdescartes.fr
Dr	NINET	Sandra	IMPMC	Paris	France	sandra.ninet@impmc.jussieu.fr
Dr	NIOCHE	Pierre	UFR BIOMEDICALE	Paris	France	pierre.nioche@univ-paris5.fr
Dr	NONIN-LECOMTE	Sylvie	CNRS	Paris	France	sylvie.nonin@parisdescartes.fr
Mlle	NOVIKOVA	Anastasiia	Synchrotron SOLEIL	Gif-sur-Yvette	France	anastasiia.novikova@synchrotron-soleil.fr
Dr	OHRESSER	Philippe	Synchrotron SOLEIL	Gif-sur-Yvette	France	philippe.ohresser@synchrotron-soleil.fr
Dr	OHTSUBO	Yoshiyuki	Synchrotron SOLEIL	Gif-sur-Yvette	France	yoshiyuki.ohtsubo@synchrotron-soleil.fr
Dr	OLIVIERI	Giorgia	Synchrotron SOLEIL	Gif-sur-Yvette	France	giorgia.olivieri@synchrotron-soleil.fr
Dr	OUERGI	Abdelkarim	LPN/CNRS	Marcoussis	France	abdelkarim.ouerghi@lpn.cnrs.fr
Dr	PALACIO	Irene	Synchrotron SOLEIL	Gif-sur-Yvette	France	irene.palacio@synchrotron-soleil.fr
Dr	PALANCHER	Herve	CEA-Cadarache	Saint Paul lez Durance	France	herve.palancher@cea.fr
Dr	PARENT	Philippe	Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), CNRS and Aix-Marseille	Marseille	France	parent@cinam.univ-mrs.fr
Dr	PATANEN	Minna	Synchrotron SOLEIL	Gif-sur-Yvette	France	patanen@synchrotron-soleil.fr
PROF	PATERNOSTRE	Maité	CNRS	Gif-sur-Yvette	France	maite.paternostre@cea.fr
Dr	PAUL-BONCOUR	Valérie	Institut de Chimie et des Matériaux de Paris Est, UMR 7182, CNRS et UPEC	Thiais	France	paulbon@icmpe.cnrs.fr
Mme	PAVAN	Sylvie	Synchrotron SOLEIL	Gif-sur-Yvette	France	sylvie.pavan@synchrotron-soleil.fr
Mr	PELLI	Mario	ALLECTRA	Sheffield Park	United Kingdom	mario@allectra.com
Dr	PENENT	Francis	LCP-MR	Paris	France	francis.penent@upmc.fr
Dr	PEREIRA DE CARVALHO	Hudson Wallace	Karlsruhe Institute of Technology -ITCF	Karlsruhe	Germany	hudson.carvalho@kit.edu
Mme	PEREZ	Anne	Laboratoire Géomatériaux et Environnement	Marne-la-Vallée	France	anne.perez@univ-mlv.fr
Dr	PERRIN	Agnes	LISA UMR 7583	Creteil	France	agnes.perrin@lisa.u-pec.fr
Mr	PERRON	Jonathan	Université Pierre et Marie Curie	Paris	France	jonathan.perron@etu.upmc.fr
Mr	PETOU	Stéphane	Centre de Biophysique Moléculaire UPR4301	ORLEANS	France	stephane.petoud@cnrs-orleans.fr
PROF	PIANCATELLI	Maria Novella	LCPMR-UPMC	Paris	France	maria-novella.piancastelli@fysik.uu.se
Mme	PINEAU	Blandine	Synchrotron SOLEIL	Gif-sur-Yvette	France	blandine.pineau@synchrotron-soleil.fr
Mr	PINOT	Yoann	Université de Haut-Alsace	Mulhouse	France	yoann.pinot@uha.fr
Mme	POCHARD	France	Synchrotron SOLEIL	Gif-sur-Yvette	France	France.pochard@synchrotron-soleil.fr
Dr	POPESCU	Horia	Synchrotron SOLEIL	Gif-sur-Yvette	France	horia.popescu@synchrotron-soleil.fr
Mr	POUDEL	Purushottam	UPMC Paris- VI	Paris	France	alonepp@gmail.com
PROF	POUMELLE	Bertrand	PSUD	Orsay	France	Bertrand.Poumellec@u-psud.fr
Dr	PREVOT	Geoffroy	Institut des NanoSciences de Paris	Paris	France	prevot@insp.jussieu.fr
Dr	PRIGENT	Pascale	Synchrotron SOLEIL	Gif-sur-Yvette	France	pascale.prigent@synchrotron-soleil.fr
Mr	PROPERZI	Leonardo	Universita di Camerino	Recanati	Italia	leonardo.properzi@unicam.it
Dr	PROVOST	Karine	ICMPE, UMR7182 CNRS-UPEC	Thiais	France	provost@u-pec.fr
Dr	PUTTNER	Ralph	Freie Universität Berlin	Berlin	Germany	puettner@physik.fu-berlin.de
Dr	PYLYPENKO	Olena	Curie Institute	Paris	France	pylypenk@curie.fr
Dr	RADNIK	Joerg	Leibniz Institute for Catalysis	Rostock	Germany	joerg.radnik@catalysis.de
Mme	RADZIWIŁL-BIENKOWSKA	Joanna	Micalis UMR 1319 - Equipe ProbiHA 'te	Jouy-en-Josas	France	Joanna.Radziwill-Bienkowska@jouy.inra.fr
Dr	RAOIX	Denis	Synchrotron SOLEIL	Engins	France	denis.raoux0750@orange.fr

SOLEIL Users' Meeting 2014
List of participants






TITLE	FAMILY NAME	FIRST NAME	ORGANISM	CITY	COUNTRY	EMAIL
Mr	RAPHANEL	Jean	HUBER Diffractionstechnik GmbH & Co.KG	Rimsting	Germany	raphanel@lms.polytechnique.fr
Dr	RAULT	Julien	Synchrotron SOLEIL	Gif-sur-Yvette	France	julien.rault@synchrotron-soleil.fr
Dr	RECEVEUR-BRECHOT	Véronique	Centre de Recherche en Cancérologie (CRCM)	Marseille	France	veronique.brechot@ibsm.cnrs-mrs.fr
Dr	REFREGIERS	Matthieu	Synchrotron SOLEIL	Gif-sur-Yvette	France	refregiers@synchrotron-soleil.fr
Dr	RENAULT	Louis	LEBS, CNRS-Gif-Sur-Yvette	Gif-sur-Yvette	France	renault@lebs.cnrs-gif.fr
Dr	RENAULT	Olivier	CEA-LETI	Grenoble	France	olivier.renault@cea.fr
PROF	RENEVIER	Hubert	Grenoble INP	Grenoble	France	hubert.renevier@grenoble-inp.fr
Dr	RESTA	Andrea	Synchrotron SOLEIL	Saint Auban	France	andrea.resta@synchrotron-soleil.fr
Dr	RETY	Stéphane	LCRB UMR8015	Paris	France	magali.blaud@parisdescartes.fr
Dr	RIETVELD	Ivo	Université Paris Descartes	Paris	France	ivo.rietveld@parisdescartes.fr
Mr	RISTERUCCI	Paul	CEA-LETI	Grenoble	France	paul.risterucci@cea.fr
Dr	ROCCO	Mattia	Biopolimeri e Proteomica, IRCCS AOU San Martino-IST, Istituto Nazionale per la Ricerca	Genova	Italy	mattia.rocco@istige.it
Dr	ROGNIAUX	Hélène	INRA UR1268 BIA - BiBS Plateform Mass Spectrometry lab	Nantes	France	Helene.Rogniaux@nantes.inra.fr
Dr	ROMANZIN	Claire	Laboratoire de Chimie Physique	Orsay	France	claire.romanzin@u-psud.fr
Mr	ROPARTZ	David	INRA UR1268 BIA - BiBS Platform - Mass Spectrometry Lab	Nantes	France	David.Ropartz@nantes.inra.fr
Dr	ROSSANO	Stéphanie	Lab. Géomatériaux et Environnement	Marne la Vallée	France	Stephanie.Rossano@univ-mlv.fr
Mme	ROUAM	Valérie	Synchrotron SOLEIL	Gif-sur-Yvette	France	valerie.rouam@synchrotron-soleil.fr
Mlle	ROULOT	Alexandra	Synchrotron SOLEIL	Gif-sur-Yvette	France	alexandra.roulot@synchrotron-soleil.fr
Mr	RUSE	Ludovic	PHYSICAL INSTRUMENT	Meylan	France	ludovic.ruse@physical-instrument.fr
Mlle	SALADO LEZA	Daniela Edith	Institut des Sciences Moléculaires d Orsay	Orsay	France	daniela.salado-leza@u-psud.fr
Mr	SAMBOU	Aliou	PI MICOS	ESCHBACH	Germany	a.sambou@pimicos.com
Dr	SCHLUTIG	Sandrine	Synchrotron SOLEIL	Gif-sur-Yvette	France	sandrine.schlutig@synchrotron-soleil.fr
Mr	SCHMITT	Julien	Laboratoire de Physique des Solides UMR 8502	Orsay	France	julien.schmitt@u-psud.fr
PROF	SCHNEIDER	Jochen	DESY-CFEL	Hamburg	Germany	jochen.schneider@desy.de
Dr	SCLAVI	Bianca	CNRS, ENS Cachan	Cachan	France	sclavi@lpa.ens-cachan.fr
Dr	SETKOWICZ	Zuzanna	AGH University of Science and Technology	Krakow	Poland	zuzanna.setkowicz@gmail.com
Dr	SIBERT	Eric	LEPMI	Saint Martin d'Hères	France	eric.sibert@lepmi.grenoble-inp.fr
Mr	SIMPFENDOERFER	Martin	PI MICOS	D-79427 ESCHBACH	Germany	M.Simpfendoerfer@pimicos.com
PROF	SIROTTI	Fausto	CNRS - Synchrotron SOLEIL	Gif sur yvette	France	fausto.sirotti@synchrotron-soleil.fr
Dr	SOEP	Benoit	LFP/IRAMIS	Gif-sur-Yvette	France	benoit.soep@cea.fr
Dr	SOLARI	Pier Lorenzo	Synchrotron SOLEIL	Saint-Aubin	France	pier-lorenzo.solari@synchrotron-soleil.fr
Dr	SOMOGYI	Andrea	Synchrotron SOLEIL	Saint-Aubin	France	somogyi@synchrotron-soleil.fr
Dr	SOTTILE	Francesco	Ecole Polytechnique	Palaiseau	France	Francesco.sottile@polytechnique.fr
PROF	SOUKIASSIAN	Patrick	CEA and Université de Paris-Sud	Gif-sur-Yvette	France	patrick.soukiassian@cea.fr
PROF	STIEVANO	Lorenzo	Institut Charles Gerhardt - AIME, UMR CNRS 5253, Université Montpellier 2	Montpellier	France	lorenzo.stievano@univ-montp2.fr
Dr	SULZENBACHER	Gerlind	Architecture et Fonction des Macromolécules Biologiques, UMR7257 CNRS, AMU	Marseille	France	Gerlind.Sulzenbacher@afmb.univ-mrs.fr
Mr	SURROCA	Yannick	EXPEDEON	Cambridge	United Kingdom	yannick.surroca@expedeon.com
Dr	SWARAJ	Sufal	Synchrotron SOLEIL	Saint-Aubin	France	swaraj@synchrotron-soleil.fr
Dr	TANG	Xiaofeng	Synchrotron SOLEIL	Gif-sur-Yvette	France	xiaofeng.tang@synchrotron-soleil.fr
Dr	TEJEDA	Antonio	Synchrotron SOLEIL	Gif-sur-Yvette	France	antonio.tejeda@synchrotron-soleil.fr
Dr	TERESHCHENKO	Oleg	Rzhanov Institute of Semiconductor Physics	Novosibirsk	Russian Federation	teresh@isp.nsc.ru
Dr	TESTARD	Fabienne	CEA	Gif-sur-Yvette	France	fabienne.testard@cea.fr
Mlle	TISSOT	Héloïse	Synchrotron SOLEIL	Saint Aubin	France	TISSOT@synchrotron-soleil.fr
Dr	TOUBOUL	David	ICSN CNRS UPR2301	Gif-sur-Yvette	France	david.touboul@cnrs.fr
Dr	TRCERA	Nicolas	Synchrotron SOLEIL	Gif-sur-Yvette	France	trcera@synchrotron-soleil.fr
Dr	VACHETTE	Patrice	IBBMC, CNRS UMR8619 Université Paris-Sud	Orsay	France	patrice.vachette@u-psud.fr
PROF	VAN DER BEEK	Cornelis	CNRS	Palaiseau	France	kees.vanderbeek@polytechnique.edu
Mr	VAUVRE	Jean-Michael	UMR 1145	Massy	France	jean-michael.vauvre@agroparistech.fr
Mlle	VERGER	Louisiane	IMPMC (Institut de Minéralogie et de Physique des Milieux Condensés)	Paris	France	louisiane.verger@impmc.upmc.fr
Mlle	VIGOUROUX	Armelle	LEBS CNRS	Gif-sur-Yvette	France	vigouroux@lebs.cnrs-gif.fr
Mr	VILAIN	Jean	MICRO-CONTROLE SPECTRA-PHYSICS	Evry	France	jean.vilain@newport.com
Dr	VILLETTE	sandrine	Synchrotron SOLEIL CNRS CBM	Orléans	France	sandrine.villette@cnrs-orleans.fr
Mlle	VUILLAMY	Alexandra	CNRS UPR4301	Orléans	France	sandrine.villette@cnrs-orleans.fr
Mme	WILLIS	Béatrice	ALLECTRA	Sheffield Park	United Kingdom	bwillis@ellectra.com
Mr	WILSON	Axel	Synchrotron SOLEIL - INSP	Paris	France	wilson@insp.jussieu.fr
Mr	WINGATE	Graham	Mclennan Servo Supplies	Ash Vale	United Kingdom	graham.wingate@mclennan.co.uk
Mlle	ZAMBOLIN	Silvia	IBPC Paris	Paris	France	silvia.zambolin@alice.it
Mme	ZHANG	Zailan	IMPMC UMR7590 UPMC-CNRS	Paris	France	zailan.zhang@impmc.upmc.fr
Mr	ZHOU	Tao	CEA-Grenoble/INAC	Grenoble	France	tao.zhou@cea.fr

LIST OF COMMERCIAL EXHIBITORS

List of Commercial Exhibitors

Company	Contacts	Phone numbers	Email	Web site
AEROTECH 	Christophe MONNIER Frédéric DEBESSE	33 1 64 93 58 67 33 1 41 90 61 88	cmonnier@aerotech.com fdebese@optoprim.com	http://www.aerotech.com
AGILENT Technology 	Vincent HACHET Stéphane GRANDAMAS	33 1 78 73 51 77 33 1 07 67 66 51	vincent.hachet@agilent.com stephane.grandamas@agilent.com	https://www.home.agilent.com/
ALECTRA 	Béatrice WILLIS Mario PELLI	33 2 97 27 23 07 44 1825 721 900	bwillis@allectra.com mario@allectra.com	http://www.allectra.com
ALTEC 	Arnaud AUBERT	33 1 39 15 69 85	a.aubert@altec-equipment.com	http://www.altec-equipment.com
EXPEDEON 	Yannick SURROCA	33 7 50 40 07 07	yannick.surroca@expedeon.com	http://www.expedeon.com/
HUBER DIFFRACTIONSTECKNIK 	Jean RAPHANEL Stefan GRIESSL		raphanel@lms.polytechnique.fr sg@xhuber.com	http://www.xhuber.com
LESKER 	Francois CLEMENT	33 6 98 50 00 11	francoisc@lesker.com	http://www.lesker.com/
Mclennan 	Claude FLOROT Graham WINGATE	33 6 16 28 83 70 44 8707 700 666	claud.florot@mclennan.fr graham.wingate@mclennan.co.uk	http://www.mclennan.co.uk/
MDC VACUUM PRODUCTS SARL 	Anne-Sophie JAUBERT	33 9 75 77 62 81	asjaubert@mdcvacuum.fr	http://www.mdcvacuum.fr/
NEWPORT 	Dalila AIT AMIR Jean VILAIN	33 1 60 91 68 68 33 2 38 40 50 00	dalila.aitamir@newport.com jean.vilain@newport.com	http://www.newport.com

List of Commercial Exhibitors

Company	Contacts	Phone numbers	Email	Web site
OMICRON 	Franck CHAPUIS Sylvie BOUHIER	33 4 76 99 22 60	fchapuis@omicron-technologies.com sbouhier@nor-cal.eu	http://www.omicron-technologies.com/
PHYSICAL INSTRUMENTS 	Ludovic RUSE	33 6 27 74 53 38	ludovic.ruse@physical-instruments.fr	http://www.physical-instruments.fr
PI France SAS 	Nicolas COLLET Stéphane BUSSA	33 1 55 22 60 01 33 1 55 22 60 00	n.collet@pi.ws s.bussa@pi.ws	http://www.pi.ws
SPECS 	Michael MEYER	49 304 678 240	marketing@specs.com	http://www.specs.de
SYMETRIE 	Olivier LAPIERRE Anne DUGET	33 4 66 29 43 88	info@symetrie.fr anne.duget@symetrie.fr	http://www.symetrie.fr
VG SCIENTA 	Robert MOBERG	4670 325 23 45	robert.moberg@vgscienta.com	http://www.vgscienta.com

COMPANIES ADVERTISEMENTS

DISCOVER VALUE IN VACUUM TECHNOLOGY

The New Agilent IDP-15 Dry Scroll Pump

- Hermetic pump with motor and bearings completely isolated from the vacuum path
- Provides rapid pump-down
- Single-sided scroll design allows simple, fifteen minute service
- Designed specifically for low noise (<50 dBA) and vibration



Agilent TwisTorr 304 FS

- Proven best performance on the market, with new TwisTorr stages optimized for H₂ Compression Ratio
- Agilent Floating Suspension, the breakthrough bearing technology that reduces acoustical noise and vibration



Agilent Technologies France

Tel: +33 (0) 1 64 53 61 15

vpf.sales@agilent.com

The Measure of Confidence

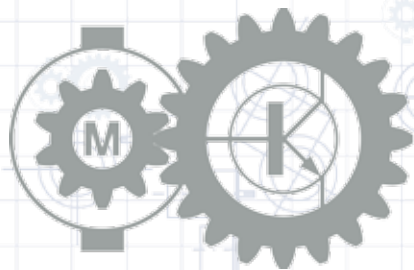


Learn more:

www.agilent.com/chem/TwisTorr304FS

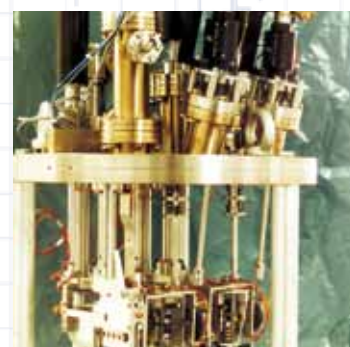
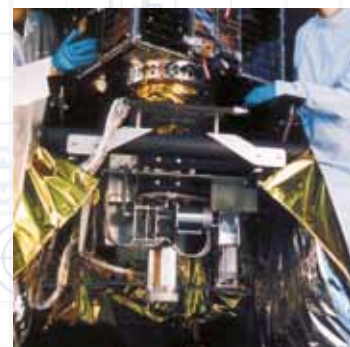
www.agilent.com/chem/IDP-15





McLennan

*motion and
mechatronics*



Over thirty years experience in Motion Control & Mechatronics



Design & manufacture motors, geared motors, drives and controls for science projects all over the world



We specialise in custom designs to suit the specific requirements of the scientific research market including vacuum and high radiation



We supply everything from a motor to complete control system or mechatronic mechanism



Supply equipment from the world's leading manufacturers



Large stocks for rapid delivery or on-time schedules (including Kanban and JIT)

SCIENCE IS OUR BUSINESS!

McLennan Servo Supplies Ltd

Unit 1, The Royston Centre
Lynchford Lane, Ash Vale
Surrey, GU12 5PQ
UK

Tel: +44 (0) 8707 700700

McLennan (France)

118-122 Avenue de France,
75013 Paris,
France.

Tel: +33 (0) 146 461 495

Email: sales@mclennan.co.uk , ventes@mclennan.fr

www.mclennan.co.uk