th SOLEIL USERS' MEETING

JANUARY 22nd and 23rd, 2015

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

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) Emmnuel GUILLON (ICM, Reims) Sandrine LYONNARD (INC/SPrAM-CEA, Grenoble) Judith MONNIER (ICMPE, Paris) Sandra NINET (IMPMC, Paris) Francis PENENT (LCPMR, Paris) Stéphanie ROSSANO(LG2I, Marne-Ia-Vallée) Antonio TEJEDA (LPS, Orsay)

Satellite Workshop

INRA-SOLEIL: The synchrotron approach in agriculture, food and

environment sciences.

January 21st, 2015

Information and registration: www.synchrotron-soleil.fr/Workshops/2015/SUM15





Welcome

The 10th SOLEIL Users' Meeting takes place on January 22nd and 23rd, 2015 at Polytechnique (Palaiseau) and at SOLEIL.

The meeting provides an invaluable forum for the synchrotron radiation user community, presenting an important opportunity to obtain the latest information on beamline performance at SOLEIL, to hear about the latest and most exciting results obtained at SOLEIL and to share scientific, technical and practical issues about the synchrotron radiation use.

The meeting takes the form of 4 plenary lectures in the following field:

- Diluted matter,
- Ancient materials Environment and Earth,
- Chemistry and Physico-chemistry in situ reactivity Soft matter
- Matter and material properties: Structure, Organisation, Characterisation, Elaboration

For the first time, technical workshops are organized on the following topics:

- Samples environments : extreme conditions
- Data storage and analysis
- Combined measurements

Half-day parallel sessions in which scientific presentations, selected from submitted abstracts, are presented.

On the afternoon of January 22nd, the visit of HERMES, MARS and ROCK beamlines is organized in conjunction with the poster session and commercial exhibitions.

The day ends with the best students' poster award and the buffet dinner at SOLEIL.

Bienvenue

Le 10ème Colloque des Utilisateurs de SOLEIL se tient les jeudi 22 et vendredi 23 janvier 2015, 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 dernières informations sur la machine, sur les performances des lignes, et d'échanger ensemble sur les aspects scientifiques, techniques et pratiques de l'utilisation du synchrotron.

Il est constitué de 4 conférences plénières couvrant différents thèmes de recherche de la communauté des utilisateurs de SOLEIL :

- Matière diluée,
- Matériaux anciens Terre et Environnement,
- Chimie et physico-chimie Réactivité in situ Matière molle,
- Propriétés de la matière et des matériaux : Structure, Organisation, Caractérisation, Elaboration.

Pour la première fois, des ateliers techniques transversaux sont organisés sur les thèmes suivants :

- Environnement échantillons : conditions extrêmes
- Stockage et analyse des données
- Mesures couplées

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

Un temps de convivialité et de discussions est organisé à SOLEIL le jeudi 22 janvier après-midi avec la session posters et les stands d'entreprises ainsi que la visite des lignes de lumière : HERMES, MARS et ROCK.

La journée se termine par la remise du prix au meilleur poster étudiant et du buffet dînatoire.

SOLEIL Users' Meeting 2015

January 22nd – 23rd, 2015

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

Summary

- Programme
- Plenary Session
- Technical Workshops
- 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 Commercial Exhibitors
- Companies Advertisements



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

Programme

Thursday, January 22nd

ECOLE POLYTECHNIQUE – AUDITORIUM GAY-LUSSAC

- 09:00 10:00 Registration & coffee
- 10:00 10:15 Welcome / Introduction Elise Berrier - ORGUES Chairperson
- 10:15 10:30 The word of SOLEIL General Director *Jean Daillant*
- 10:30 10:50 Last improvements of the Machine *Amor Nadji*
- 10:50 11:20 Scientific highlights and prospective of SOLEIL Paul Morin / Andy Thompson
- 11:20 11:50 Hydrogen and nitrogen under pressure: Towards a "killer application"? *Paul Loubeyre CEA, Bruyères-le-Chatel, France*
- 11:50 12:20 In situ X-ray absorption spectroscopy applied to hydrothermal Geochemistry *Denis Testemale Institut Neel , Grenoble, France*
- 12:20 12:50 Photon induced desorption of interstellar relevant ices in the VUV *Jean Hugues Fillion LERMA, Paris, France*
- 13:00 14:30 Lunch

Transfer to SOLEIL (14h30)



Technical Workshops:

-Samples environments : extreme conditions

Conference Room, Reception Building

"Samples environment:The sample environment available on a beam-line is crucial for the success of your experiment. We will discuss the different possibilities offered on beam-lines as specific ancillary equipment or as a common pool shared among beamlines, and the relative perspectives.This year special focus we will be on extreme condition, in particular on high pressure, high and low temperatures, electric and magnetic fields".

Contributors: L. Joly et A. Polian

 15:00 - 16:30

 Data storage and analysis Auditorium BLOCH, CEA L'Orme des Merisiers
 Synchrotron data at SOLEIL, what do users expect?
 How to deal with the rapid evolution of the size, storage and access of generated data and of the processing programs?
 Contributors : P. Legrand, P. Ohresser, A. Buteau and B. Gagey
 Combined measurements

Auditorium SOLEIL, Main Building

"Coupled experiments: what you can do and what do you want to do? We often want to perform simultaneously several analyzes of our samples, to obtain maximum information. We will discuss the various options available on the SOLEIL beamlines for coupled experiments". Contributors: V. Briois, P. Fertey, S. Réguer and D. Vantelon

- 16:30 17:00 Coffee break
- 17:00 19:30 Posters session / Commercial exhibition / Users' questions Booth
- 18:00 19:30 Visit of HERMES, MARS & ROCK Beamlines
- 19:30 21:00 Buffet / Award of the best student poster

Friday, January 23rd

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

ECOLE POLYTECHNIQUE – AUDITORIUM GAY-LUSSAC

- 14:30 15:00 High resolution structural and dynamical Synchrotron studies of aperiodic materials **Bertrand Toudic -** Université de Rennes, France
- 15:00 16:00 Synthesis of technical workshops and discussion with SOLEIL Management
- 16:00 16:15 Conclusions



Biology - Health Chairpersons: Valérie BIOU and Isabelle BROUTIN ECOLE POLYTECHNIQUE – AUDITORIUM MONGE

09:00 - 09:30 (25'+5')	Structural insights into the dimerization and the DNA binding of the response regulator ComE from <i>Streptococcus pneumonia</i>
()	Sophie Quevillon-Cheruel - invited speaker (I2BC, Orsay, France)
09:30 - 09:50 <i>(15'+5')</i>	Structural basis for the assembly of the human CSF-1:CSF-1R extracellular signaling complex Jan Felix - (L-ProBE, Ghent, Belgium)
09:50 - 10:10 <i>(15'</i> +5')	Specificity of periplasmic binding proteins in <i>Agrobacterium Tumefaciens</i> Loïc Marty – (LEBS, Gif-sur-Yvette, France)
10:10 - 10:30 <i>(15'</i> +5')	Structural study on molecular switch involved in quorum sensing in <i>Bacillus cereus</i> Antoine Talagas – (IBBMC, Orsay, France)
10:30 - 10:50 <i>(15'</i> +5')	Structure determination of the central domain of human dystrophin by coupling SAXS and new interactive flexible fitting method <i>Olivier Delalande – (IGDR, Rennes, France)</i>
10:50 - 11:10	Coffee break
11:10 - 11:40 (25'+5')	Speciation of a group I ribozyme into a lariat capping ribozyme Benoit Masquida - invited speaker (GMGM, Strasbourg, France)
11:40 - 12:00 <i>(15'</i> +5')	1-methyladenosine in transfer RNA Clément Dégut – (LBC-NMR, Paris, France)
12:00 - 12:20 <i>(15'</i> +5')	The ATP-mediated formation of the YgjD-YeaZ-YjeE complex is required for the biosynthesis of tRNA t ⁶ A in <i>E. coli</i> Wenhua Zhang – (IBBMC, Orsay, France)
12:20 - 12:40 <i>(15'</i> +5')	TRF2/RAP1 complex: The whole is greater than the sum of its parts <i>Guillaume Gaullier – (CEA, iBiTecS, Gif-sur-Yvette, France)</i>
12:40 - 13:00 <i>(15'+5')</i>	Cell localisation of radiosensitizing gadolinium-based nanoparticles in glioblastoma cells Lenka Štefančíková – (ISMO, Orsay, France)



Chemistry & Physico-Chemistry, In Situ Reactivity, Soft Matter Chairpersons: Sandrine LYONNARD and Elise BERRIER ECOLE POLYTECHNIQUE – AUDITORIUM CARNOT

- 09:00 09:30 (25'+5') The near-ambient pressure XPS at TEMPO beamline, first results Jean-Jacques Gallet - invited speaker (LCPMR, Paris, France)
- 09:30 09:50 (15'+5') Recent applications and results in near ambient pressure XPS: In-situ cell designs for liquid environments *Michael Meyer* – (SPECS, Berlin, Germany)

In situ site-selective K-edge XAS: New insights into the transformation of monometallic compounds (15'+5') Amélie Bordage – (ICMMO, Orsay, France)

- 10:10 10:30 (15'+5') Modeling hydrodesulfurization (HDS) reactions, multivariate curve resolution chemometric technique applied to in-Situ XAFS **Danilo Oliveira de Souza** – (UCCS, Villeneuve d'Asq, France)
- 10:30 10:50 (15'+5') Use of model materials for fission products release study in severe accidents conditions *Ernesto Geiger* – (*CEA*, *Saint-Paul-Lez-Durance*, *France*)
- 10:50 11:10 Coffee break
- 11:10 11:40 (25'+5') Shape control in wet synthesis of anisotropic gold nanoparticles **Fabienne Testard** - invited speaker (CEA Saclay, Gif-sur-Yvette, France)
- 11:40 12:00 (15'+5') Determination of gold nanoparticles formation step by in situ time-resolved XANES in a microfluidic device **Jean-Sébastien Girardon** – (UCCS, Villeneuve d'Asq, France)
- 12:00 12:20 (15'+5') Self-assembly of CdSe nanoplatelets **Benjamin Abécassis** – (LPS, Orsay, France)
- Assembly and disassembly kinetics of virus-like particles probed by time-resolved small-12:20 - 12:40 (15'+5') Didier Law-Hine – (LPS, Orsay, France)
- 12:40 13:00 (15'+5') Controlling self-assembly of ferrofluids during evaporation in PDMS *Clément Guibert* – (*PHENIX, Paris, France*)



Cultural heritage, archaeology, environment, geosciences Chairpersons: Stéphanie ROSSANO and Emmanuel GUILLON ECOLE POLYTECHNIQUE – MEETING ROOM N°16

- 10:00 10:30 (25'+5') Actinide speciation in sea water and in a model biomarker *Christophe den Auwer* - *invited speaker (ICN, Nice France)*
- 10:30 10:50 (15'+5') Sub-critical alkaline stabilization archaeological iron conservation: Transformation of akaganeite followed by in-situ XAS at the iron K-edge and completed by XRD analysis **Marine Bayle** - (CEA Saclay, Gif-sur-Yvette, France)
- 10:50 11:10 Coffee break

Complementarity of X-rays techniques for the conservation of iron cultural heritage 11:10 - 11:40 materials

(25'+5') **Solenn Reguer** - invited speaker (Synchrotron SOLEIL, Gif-sur-Yvette, France)

- 11:40 12:00 (15'+5') Interest of high resolution X-ray absorption spectroscopy in environmental sciences Isabelle Kieffer - (OSUG, Grenoble, France)
- 12:00 12:20 (15'+5') Melting properties of the deep earth's mantle investigated by in situ measurements Denis Andrault - (LMV, Clermont-Ferrand, France)
- 12:20 12:40 Precipitation in "old" duralumin used in airplanes
- (15'+5') Audrey Cochard (CEMES, Toulouse, France)
- 12:40 13:00 (15'+5') PSICHE: In-situ imaging and tomography for materials science at SOLEIL. Presentation and perspectives. Andrew King - (Synchrotron SOLEIL, Gif-sur-Yvette, France)



Diluted Matter

Chairpersons: Vincent BOUDON and Francis PENENT ECOLE POLYTECHNIQUE –SAUVY MEETING ROOM

09:00 - 09:30 <i>(25'+5')</i>	Relaxation dynamics of atoms and molecules in the tender x-ray region <i>Marc Simon - invited speaker (LCPMR, Paris, France)</i>
09:30 - 09:50 (15'+5')	XUV induced fragmentation dynamics of 5-halouracils investigated in the time and energy domain <i>Raluca Cireasa – (ISMO, Orsay, France)</i>
09:50 - 10:10 <i>(15'+5')</i>	Understanding the internal torsion and bending motion of dimethyl ether via isotopic studies <i>Pia Kutzer</i> – (<i>University of Kassel Kassel, Germany</i>)
10:10 - 10:30 <i>(15'</i> +5')	Einstein–Bohr recoiling double-slit Gedanken experiment performed at the molecular level <i>Minna Pattanen - (Synchrotron SOLEIL, Gif-sur-Yvette, France)</i>
10:30 - 10:50 <i>(15'</i> +5')	Gas-phase ion-molecule chemistry: An experimental study of $CH_3^+ + CH_4$ Allan Lopes – (LCP, Orsay, France)
10:50 - 11:10	Coffee break
11:10 - 11:40 <i>(</i> 25'+5')	Rotational doppler effect Faris Gel'mukhanov - invited speaker (Royal Institute of Technology, Stockholm, Sweden)
11:40 - 12:00 <i>(15'</i> +5')	New information on HC_3N^+ using Synchrotron- and laser-based photoelectron studies Séverine Boyé-Péronne – (ISMO, Orsay, France)
12:00 - 12:20 <i>(15'</i> +5')	Ultrafast dynamics and electronic state: Lifetime interferences in chlorine-containing molecules <i>Gildas Goldsztejn – (LCPMR, Paris, France)</i>
12:20 - 12:40 <i>(15'+5')</i>	X-ray photoionization of atomic oxygen ions Brendan M. McLaughlin – (CTAMOP, Belfast,UK & ITAMP, Cambridge,USA)
12:40 - 13:00 <i>(15'</i> +5')	High density THz frequency comb produced by coherent Synchrotron radiation Stefano Tammaro - (Synchrotron SOLEIL, Gif-sur-Yvette, France)



Electronic & Magnetic Property of Matter, Surfaces and Interfaces Chairpersons: Antonio TEJEDA and Matteo d'ASTUTO ECOLE POLYTECHNIQUE – AUDITORIUM BECQUEREL

Infrared near-field imaging and spectroscopy with broadband sources 09:00 - 09:30 Y. De Wilde - invited speaker (Institut Langevin, Paris, France) (25'+5') One dimensional π -conjugated band dispersion in ordered polymeric chains 09:30 - 09:50 Yannick Fagot-Revurat – (Institut Jean Lamour, Vandoeuvre-les-Nancy, France) (15'+5') Coexistence of metallic and semiconducting nanoribbons on a continuous graphene 09:50 - 10:10 laver (15'+5') Arlensiu Celis – (LPS, Orsay, France) Orientational tuning of the two-dimensional electron gases at the low-index surfaces of 10:10 - 10:30 SrTiO₃ (15'+5') Tobias C. Rödel – (CSNSM, Orsay, France) In depth atomic structure of the pentacene/Cu(110) interface in the monolayer coverage 10:30 - 10:50 regime: Theory and X-ray diffraction results (15'+5') Michèle Sauvage - (Synchrotron SOLEIL, Gif-sur-Yvette, France) 10:50 - 11:10 Coffee break Magnetic cooling at molecular level: Two case studies by XAS and XAMCD investigation 11:10 - 11:40 Marco Affronte - invited speaker (Università di Modena e Reggio Emilia, Modena, (25'+5') Italy) Direct determination of the chemical ordering of Co_{1.5}Fe_{1.5}Ge epitaxial thin films 11:40 - 12:00 Alexandre M. Bataille – (Institut Jean-Lamour, Nancy, France) (15'+5') Laser induced dynamics in FeRh 12:00 - 12:20 Federico Pressacco - (Synchrotron SOLEIL, Gif-sur-Yvette, France) (15'+5') Investigation of the magnetic spin structure with X-ray absorption spectroscopy in 12:20 - 12:40 transmission mode (15'+5') Kai Chen - (Synchrotron SOLEIL, Gif-sur-Yvette, France) XMCD at Co and Fe L2,3 edges of photomagnetic Co/Fe dinuclear complex 12:40 - 13:00 Fatima Sadaf – (IMPMC, Paris, France) (15'+5')



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

Chairpersons: Judith MONNIER and Sandra NINET

ECOLE POLYTECHNIQUE – AUDITORIUM GAY-LUSSAC

09:00 - 09:30 About nuclear fuels on MARS

(25'+5') **Philippe Martin** - invited speaker. (CEA, Cadarache, France)

- 09:30 09:50 (15'+5') The local environment of substitutional Al³⁺ in goethite probed by XANES and firstprinciples calculations **Manoj Ducher** - (IMPMC, Paris, France)
- 09:50 10:10 (15'+5') Tracking the chemical composition of embedded magnetic nanowires by X-ray absorption spectroscopy **Anastasiia Novikova** - (Synchrotron SOLEIL, Gif-sur-Yvette & GEMC, Versailles, France)
- 10:10 10:30 (15'+5') In situ anomalous X-ray scattering: chemical order in Ag-M nanoparticles during growth and annealing Asseline Lemoine - (CRMD, Orléans, France)
- 10:30 10:50 (15'+5') The new RIXS-MCD end-station at GALAXIES: a photon-in, photon-out tool to probe magnetism under extreme conditions using hard X-rays James M. Ablett - (Synchrotron SOLEIL, Gif-sur-Yvette, France)
- 10:50 11:10 Coffee break
- 11:10 11:40 (25'+5') Anomalous single crystal diffraction technique: the ideal tools to investigate the Cu/Zn disorder in kesterite photovoltaic compound Alain Lafond - invited speaker (Institut des Matériaux Jean Rouxel, Nantes, France)
- Laue diffraction microscopy on French CRG-IF BM32 at ESRF
- 11:40 12:00 (15'+5') Jean-Sébastien Micha - (Université Grenoble Alpes/CEA-INAC, Grenoble, France)
- 12:00 12:20 (15'+5') In situ combined Synchrotron X-ray diffraction and wafer curvature measurements on chalcogenide films **Toufik Ouled-Khachroum** – (Aix-Marseille Université, IM2NP, Marseille, France)
- 12:20 12:40 (15'+5') Mechanical study of metallic thin films under controlled biaxial deformation **Raphaelle Guillou** - (Institut P', Poitiers, France)
- 12:40 13:00 (15'+5') Ammonia monohydrate at high pressure Jean-Antoine Queyroux - (IMPMC, Paris, France)

PLENARY SESSION

PLENARY SESSION

22/01/2015

PT-01	Hydrogen and nitrogen under pressure: Towards a "killer application"? <i>P. Loubeyre</i>
PT-02	In situ X-ray absorption spectroscopy applied to hydrothermal Geochemistry <i>D. Testemale</i>
PT-03	Photon induced desorption of interstellar relevant ices in the VUV <i>J. H. Fillion</i>
23/01/2015	

PT-04 High resolution structural and dynamical Synchrotron studies of aperiodic materials *B. Toudic*

Hydrogen and Nitrogen under Pressure. Towards a 'Killer Application' ?

P. Loubeyre

CEA , DIF, Bruyères-le-Châtel, 91297 Arpajon. Paul.loubeyre@cea.fr

ABSTRACT

Twice in the past, high pressure has enabled a major rupture in the synthesis of materials with high societal impact, namely: the synthesis of ammonia in 1909 (at ~200 bars and 500°C) and the synthesis of diamond in 1954 (at ~5GPa and 1500°C). In both cases, the scaling up from forefront laboratory research to industrial production took only few years. A legitimate question is whether modern high pressure research is capable of bringing a new material rupture? We believe so and I will try to show why.

Modern High Pressure research has shown that the properties of matter in the 100 GPa regime differ drastically from those at ambient pressure. There is a new chemistry at work [1]. That has been primarily revealed by the routine use of the diamond anvil cell in front of synchrotrons over the past 15 years. In particular, quite spectacular phenomena have been observed for low Z systems. For example solid molecular nitrogen has been transformed into a single bonded polymeric form [2], solid oxygen into an extended molecular metal [3] and hydrogen into a graphene type structure [4]. Pressure is also a powerful driving force for self-assembly of molecular compounds. A remarkable guest-host structure has been discovered in the N2/H2 system [5]. So, there is a unique possibility to tailor molecular interactions for material synthesis. Two classes of promising novel materials are emerging: High Tc H-rich superconductors as analogous to metal H; High energy density materials as analogous to poly-N.

- 1. W.Grochala, R. Hoffmann, J. Feng and N. Ashcroft. Angew. Chem. Int. ed. 46, 3620 (2007).
- 2. M. Eremets, A.Gavriliuk, I. Trojan, D. Dzivenko and R. Boehler. Nature Materials 3, 558 (2004).
- 3. G. Weck, S. Desgreniers, P. Loubeyre and M. Mezouar, Phys. Rev. Lett. 102, 255503 (2009).
- 4. I. Naumov, R. Cohen and R. Hemley. Phys. Rev. B 88, 045125 (2013).
- 5. D. Spaulding, G. Weck, P. Loubeyre, F. Datchi, P. Dumas and M. Hanfland, Nature Comm. 5, 5739 (2014).

D. Testemale^{1,2}, E. Lahera^{2,3}, A. Prat^{1,2}, O. Proux^{2,3}, W. Del Net^{2,3} and J.-L. Hazemann^{1,2}

Institut Néel - CNRS, 25 rue des Martyrs, BP 166, 38042 Grenoble FAME beamline, ESRF, 71 avenue des Martyrs, 38043 Grenoble. OSUG – CNRS, 414 rue de la piscine, 38400 Saint-Martin d'Hères

ABSTRACT

Within the study of fluid-rock interactions at hydrothermal conditions, relevant for a broad range of scientific topics (transport of metals, dissolution/precipitation of minerals, CO2 sequestration), there is a strong necessity of understanding the processes taking place at the molecular scale. Indeed, the hydrothermal conditions, in particular the pressure and temperature conditions about the critical point of aqueous fluids, are at the origin of some of their peculiar properties (rock solubility, species partitioning, diffusivity, etc.). In this context we set up a research program to explore the structure of those fluids, by looking both at solvents (H₂O-CO₂-NaCl system) and solutes (dissolved metals), and mainly based on X-ray absorption spectroscopy techniques that are employed on FAME beamline.

We'll introduce first our autoclave system which is at the core of our methodology [1]. This set-up was designed and is being developed to reach challenging hydrothermal pressure and temperature conditions and with a strong adaptability to different techniques (x-ray spectroscopy, small angle x-ray scattering, inelastic scattering, Raman spectroscopy, etc.). It is integrated on the FAME beamline and available to the community.

Then we'll use iron geochemistry as the common theme to present several of our recent collaborative studies that clearly depict the technological and scientific possibilities of our method. That ranges from the speciation of iron in H₂O-NaCl solvents [2] to the solubility of fayalite and magnetite [3]. Other Earth Sciences applications that benefit from our set-up will also be evoked.

Finally we'll explore the most recent developments in our research: first how molecular dynamics data constitute a clear step forward to interpret spectroscopy results; then the scientific perspectives open by the use of high-resolution fluorescence detection [4].

- D. Testemale et al., *Rev. Sci. Instrum.* **76**, 043905 (2005).
 D. Testemale et al., *Chem. Geol.* **264**, 295-310 (2009).
- 3. D. Daval et al., Chem. Geol. 275, 161-175 (2010).
- 4. I. Llorens et al., Rev. Sci. Instrum. 83, 063104 (2012).

Photon Induced Desorption of Interstellar Relevant Ices in the VUV

<u>J.-H. Fillion^(1,2)</u>, E.C. Fayolle⁽³⁾, X. Michaut⁽¹⁾, L. Philippe⁽¹⁾, M. Doronin⁽¹⁾, J. Rakovsky⁽¹⁾, K. Öberg⁽²⁾, H. Linnartz⁽⁴⁾, C. Romanzin⁽⁵⁾ and M. Bertin⁽¹⁾

 (1) Sorbonne Universités, UPMC Univ Paris 06, UMR 8112, LERMA, F-75005, Paris, France
 (2) LERMA, Observatoire de Paris, PSL Research University, CNRS, UMR 8112, F-75014, Paris, France

 (3) Harvard-Smithsonian Center For Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA.
 (4) Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands.

(5) Laboratoire de Chimie Physique, CNRS UMR 8000, Univ Paris Sud, F-91400 Orsay, France.

ABSTRACT

During the cold and dense phase of star- and planet-formation, ices accreted onto microscopic interstellar dust particles, are the dominant reservoir of molecules other than H_2 . When exposed to UV radiation from protostars, background stars or through secondary H_2 emission induced by cosmic rays, the mantle molecules non-thermally desorb into the gas phase. Because of negligible thermal evaporation in these cold regions, this process is crucial to explain the abundance of gas phase species below their accretion temperatures.

Previous estimates of the photodesorption rates have been largely based on broadband discharge lamps, peaking at Ly- α wavelength (10.2 eV), which limits both the understanding of the desorption mechanisms and the applicability to various astrophysical environments where UV field spectral profiles can be very different. In recent years, we have developed a novel approach based on the coupling of the "Surface Processes and ICES" set-up to the DESIRS beamline at SOLEIL, enabling tunable monochromatic excitation of interstellar ice analogs at low temperature (10 K). Instead of probing the depletion of the solid-state molecular concentration to obtain an average desorption rate, the high photon fluxes provided by DESIRS have offered, for the first time, the opportunity to measure the wavelength dependency of absolute desorption rates for individual particles ejected into the gas phase. This approach has led to revisit the mechanism in the context of astrophysical media.

In this talk, I will review results obtained on amorphous ice films of various composition (pure, binary) and various structures (mixed, layered). The Photon Induced Desorption spectra (PSD) from simples ices (CO, N₂, O₂) and isotopologues, reveal an *indirect desorption mechanism* induced by electronic transition, occurring within the upper layers of the ice film. The role of CO absorption below 10 eV, as a promoter of the photodesorption of other neighbouring species such as N₂ or CO photodesorption will be demonstrated, as well as the interconnection with CO₂ photolysis. Indirect desorption appears to be very promising to explain the presence of larger organic molecules in the coldest parts of interstellar medium.

- 1. E.C. Fayolle, M. Bertin, C. Romanzin, X. Michaut, K.I. Öberg, H. Linnartz, J.-H. Fillion, Astrophys. J. 739, L36 (2011)
- 2. M. Bertin, E.C. Fayolle C. Romanzin, , K.I. Öberg X. Michaut, A. Moudens, L. Philippe, P. Jeseck, H. Linnartz, J.-H. Fillion, *Phys. Chem. Chem. Phys.* **14**, 9929 (2012)
- 3. E.C. Fayolle, M. Bertin, C. Romanzín, H.A.M. Poderoso, L. Philippe, X. Michaut, P. Jeseck, H. Linnartz, K.I. Öberg, J.-H. Fillion, Astron. Astrophys. 526, A122 (2013)
- 4. M. Bertin, E.C. Fayolle, C. Romanzin, H.A.M. Poderoso, X. Michaut, L. Philippe, P. Jeseck, K.I. Öberg, H. Linnartz & J.-H. Fillion, Astrophys. J. **779**, 120 (2013)
- J.-H. Fillion, E.C. Fayolle, X. Michaut, M. Doronin, L. Philippe, J. Rakovsky, C. Romazin, N. Champion, K.I. Öberg, H. Linnartz and M. Bertin, Faraday Discussions 168, 533 (2014)

High Resolution Structural and Dynamical Synchrotron Studies of Aperiodic Materials

B. Toudic, P. Rabiller, L. Guérin, C. Mariette

Institut de Physique de Rennes, Université de Rennes 1, F 35042 Rennes

ABSTRACT

Since 1992, there is a new definition of the crystal in order to include compounds which do not posses translation symmetry but do present long range order¹. This definition can no more be given in the real space as a periodic repetition of a unit cell, so it is given in the reciprocal space by its diffraction image "essentially made of Bragg peaks". There are three families of such aperiodic crystals¹: the incommensurately modulated ones, the aperiodic composites and the quasicrystals² A common feature of all these crystals is to recover the translational symmetry within crystallographic superspaces of dimension larger than the one of the physical space. The number of allowed space groups quickly increases with the dimension of the superspace. Such space groups are tabulated at the dimensions 3+1³, 3+2, and 3+3⁴. All the physics had then to be determine within theses superspaces. The first challenge was of course to know where the atoms are. The next question concerns the phase transitions which may occur within such crystallographic superspaces, defining order parameters and critical phenomena. A third question concerns the collective dynamics within aperiodic materials where the absence of a generating unit cell means the absence of any Brillouin zone. No standard theory based on Bloch theorem exists anymore. Supplementary specific dynamical modes are predicted since the real crystal in the physical space is the result of an arbitrary cut of a higher dimensional space. These modes are associated to the infinite degeneracy of the ground state, generating zero energy excitations called phason modes.

During this talk, we will give several illustrations of these physical original properties. Synchrotron radiation plays there an important role combined with other approaches such as neutron scattering⁵⁻⁹. The main forces of the synchrotron radiation are the very high spatial resolution, the possibility of time and energy analysis over a huge region within the reciprocal space, the very high flux which combined with zero noise multidetector allowing a full three dimensional Pair Distribution Function analysis...

REFERENCES

2. D. Shechtman, I. Blech, D. Gratias and J. W. Cahn, *Metallic Phase with Long-Range Orientational Order and No Translational Symmetry*, Phys. Rev. Lett. 53, 1984, p. 1951-1953.

3. P. M. de Wolff, T. Janssen and A. Janner, *The superspace groups for incommensurate crystal structures with a one-dimensional modulation*, Acta Cryst. A37, 1981, p. 625-636.

4. T. Janssen et al., *Incommensurate and Commensurate Modulated Structures*, in The International Tables for Crystallography, Vol. C, 2008.

 C. Mariette, M. Huard, B. Toudic, P. Rabiller, S. M. Nichols, C. Ecolivet, T. Janssen and M. D.Hollingsworth, A molecular « phase ordering » phase transition leading to a modulated aperiodic composite in n-heptane/urea, J. Chem. Phys., 2012, 136.
 C. Mariette, L. Guérin, P. Rabiller et al., *Critical phenomena in higher dimensional spaces: Thehexagonal-to-orthorhombic phase transition in aperiodic n-nonadecane/urea*, Phys. Rev. B87, 2013, 104101.

8. B. Toudic, R. Lefort, C. Ecolivet, et al., *Mixed acoustic phonons and phase modes in an aperiodic composite crystal*, Phys. Rev. Lett. 107, 2011, p. 205502.

^{1.} T. Janssen, *Fifty years of aperiodic crystals*, Acta Crystallogr. A68, 2012, p. 667-674.

^{5.} B. Toudic, P. Garcia, C. Odin, P. Rabiller, C. Ecolivet, E. Collet, P. Bourges, G. J. McIntyre, M. D.Hollingsworth and T. Breczewski, *Hidden Degrees of Freedom in Aperiodic Materials*, Science, 319, 2008, 5859, 69-71.

^{9.} C. Mariette, Thèse Université de Rennes 1, unpublished, 2013.

TECHNICAL WORKSHOPS

Technical Workshops

Samples Environment: Extreme Conditions

Conference Room, Reception Building

"Samples environment: The sample environment available on a beam-line is crucial for the success of your experiment.

We will discuss the different possibilities offered on beam-lines as specific ancillary equipment or as a common pool shared among beam-lines, and the relative perspectives.

This year special focus we will be on extreme condition, in particular on high pressure, high and low temperatures, electric and magnetic fields".

Contributors: L. Joly and A. Polian

Samples environments: extreme conditions



Left: Schematic view of a Membrane Diamond Anvil Cell (MDAC) for high pressure/temperature. Photo of a crystal inside the cell with its ruby pressure gauge

The attractiveness of a beam-line station can be greatly enhanced by the **sample environment**: it can offer to users, either a specific ancillary equipment or a common pool shared among beamlines in a synchrotron.

Introductory examples. In this workshop, two short talks will give examples of both cases at SOLEIL and in other synchrotrons for particularly demanding environments:

high pressure and high temperature conditions (Alain Polian, IMPMC, Paris)
high magnetic/electric fields and very low temperature (Loïc Joly IPCMS, Strasbourg).

Round table. We hope these examples will stimulate discussion between the users and the SOLEIL staff and management, in particular on possible applications, other systems on different beamlines, possibilities for exciting novel experiments...



Top: DEIMOS Cryomagnet (maker: Air Liquid). Bottom: Copper sample holder on cryostat insertion, with gold connections for applying electric stimuli.

Technical Workshops

Data Strorage and Analysis

Auditorium BLOCH, CEA L'Orme des Merisiers

Synchrotron data at SOLEIL, what do users expect ?

How to deal with the rapid evolution of the size, storage and access of generated data and of the processing programs ?

Contributors: P. Legrand, P. Ohresser, A. Buteau and B. Gagey

Synchrotron data at SOLEIL: a workshop about storage and analysis



Store, reduce, analyse, model ... what part should SOLEIL play?

In the context of a strong expansion of data volume produced at SOLEIL due to large detectors and time resolved measurements, this workshop aims to discuss the following questions:

data storage

should raw data be stored and kept?

how can we bring them back home?

how should they be stored?

should synchrotrons be responsible for their storage? if yes, should there be a common storage for all synchrotron sources in Europe for example?

if the data is stored in a "cloud" system, what is the

ownership / legal status of the data?

data processing/ analysis/ modelling

to what level do we expect synchrotrons to provide software and help (data processing, interpretation...)

two talks will be given to trigger discussion

- a member of the Computing Services will talk about data storage and developments in the context of PANDATA and PANDAAS European projects;
- a beamline scientist will present his point of view.

Image credits

Technical Workshops

Combined Measurements

Auditorium SOLEIL, Main Building

"Coupled experiments: what you can do and what do you want to do?

We often want to perform simultaneously several analyzes of our samples, to obtain maximum information. We will discuss the various options available on the SOLEIL beamlines for coupled experiments".

Contributors: V. Briois, P. Fertey, S. Réguer and D. Vantelon

Synchrotron experiments at SOLEIL: a workshop about combined measurements



Considering the technical possibilities at SOLEIL synchrotron, an increasing part of users would like to perform "coupled experiments". In this context, this workshop would like to address the following questions:

Possible coupling

What kind of coupling exists? What kind of coupling is possible? Which beamlines are involved? ...

Users' activities

How can users act to use/implement/develop coupled experiments?

Two talks will be given to trigger discussion

- A user will share his experience of developing a coupled experiment on a SOLEIL beamline.
- Beamline scientists will present their point of view on opportunities and relevance of coupled experiments.

PARALLEL SESSIONS

PARALLEL SESSION

Biology - Health ECOLE POLYTECHNIQUE – AUDITORIUM MONGE

Chairpersons: Valérie BIOU and Isabelle BROUTIN

IT-01	Structural insights into the dimerization and the DNA binding of the response regulator ComE from <i>Streptococcus pneumoniae S. Quevillon-Cheruel</i>
OC-01	Structural basis for the assembly of the human CSF-1:CSF-1R extracellular signaling complex <i>J. Felix</i>
OC-02	Specificity of periplasmic binding proteins in <i>Agrobacterium Tumefaciens L. Marty</i>
OC-03	Structural study on molecular switch involved in quorum sensing in <i>Bacillus cereus A. Talagas</i>
OC-04	Structure determination of the central domain of human dystrophin by coupling SAXS and new interactive flexible fitting method <i>O. Delalande</i>
IT-02	Speciation of a group I ribozyme into a lariat capping ribozyme <i>B. Masquida</i>
OC-05	1-methyladenosine in transfer RNA <i>C. Dégut</i>
OC-06	The ATP-mediated formation of the YgjD-YeaZ-YjeE complex is required for the biosynthesis of tRNA t^6A in <i>E. coli W. Zhang</i>
OC-07	TRF2/RAP1 complex: The whole is greater than the sum of its parts <i>G. Gaullier</i>
OC-08	Cell localisation of radiosensitizing gadolinium-based nanoparticles in glioblastoma cells L. Štefančíková

The New RIXS-MCD End-station at GALAXIES: A Photon-in, Photon-out Tool to Probe Magnetism under Extreme Conditions using Hard X-rays

M. Boudes, D. Sanchez, M. Graille, H. van Tilbeurgh, D. Durand, <u>S. Quevillon-Cheruel</u>

Institute for Integrative Biology of the Cell (I2BC), Université Paris-Saclay, CEA, CNRS, Université Paris-Sud, Bât 430, 91405 Orsay Cedex, France

ABSTRACT

Natural transformation contributes to the maintenance and to the evolution of the bacterial genomes. In the human pathogen *Streptococcus pneumoniae*, this function is reached by achieving the competence state, which is under the control of the ComD-ComE two-component system. We investigated the binding interplay among ComD, ComE and the promoter region *comcde* using X-ray, SAXS (Proximas and Swing beamlines of SOLEIL) and biochemistry.

We present the crystal and solution structures of ComE. The active and non-active states are mimics by the phosphorylated mimetic ComE^{D58E} and the unphosphorylatable ComE^{D58A} mutants. In the crystal, full-length ComE^{D58A} dimerizes through its canonical REC receiver domain but with an atypical mode, which is also adopted by the isolated REC^{D58A} and REC^{D58E}. The LytTR domain adopts a tandem arrangement consistent with the two direct repeats of its promoters. However ComE^{D58A} is monomeric in solution, as seen by SAXS, by contrast to ComE^{D58E} that dimerizes. For both, a relative mobility between the two domains is assumed.

ComD is a dimer that adapts two monomers of ComE, one on each side, placing ^{ComE}D58 in front of ^{ComD}H248, a location that is convenient for the intermolecular transfer reaction of the phosphoryl group. The LytTR, ComE^{D58A} and ComE^{D58E} complexes with *comcde* are composed of two protein molecules per DNA duplex. Modeling the complexes against SAXS data indicated that ComE^{D58E} bound to *comcde* forms a compact dimer similar to the crystal structure, whereas ComE^{D58A}–*comcde* adopts more than one conformation with or without dimer contacts.

The various oligomeric states of ComE induce different bending angles of the promoter, which provides a mechanistic scenario for the activation of ComE: the phosphorylation of ComE forces additional bending of *comcde*, and the release of this bending strain on DNA via the disruption of the ComE dimer may signal the shut-off of the competence state. We conclude that the ComD-ComE two-component system controls the competence state of *S. pneumoniae* via the phospho-regulation of ComE, which fluctuates between monomeric and dimeric states.

Structural Basis for the Assembly of the Human CSF-1:CSF-1R Extracellular Signaling Complex

<u>J. Felix¹</u>, S. De Munck¹, K. Verstraete¹, L. Meuris², N. Callewaert² J. Elegheert¹, and S.N. Savvides¹

 ¹Unit for Structural Biology, Laboratory for Protein Biochemistry and Biomolecular Engineering (L-ProBE), Ghent University, K.L. Ledeganckstraat 35, 9000 Ghent, Belgium.
 ²Unit for Medical Biotechnology, Inflammation Research Center (IRC), VIB, Rijvisschestraat 120, 9052 Ghent, Belgium.

ABSTRACT

Colony Stimulating Factor 1 receptor (CSF-1R or FMS) is unique among the hematoietic class-III Receptor Tyrosine Kinases (RTKIII) because it is activated by two distinct cytokines ligands, CSF-1 and interleukin 34 that share no recognizable sequence similarity¹. CSF-1R plays pivotal roles in innate and adaptive immunity and is involved in inflammatory diseases and cancer².

Despite nearly three decades of research in the (patho)physiology and cellular context of human CSF-1R signaling mediated by human CSF-1R and as therapeutic antagonism of CSF-1R is gaining relevance in tumor therapy³, detailed structural and mechanistic insights of the interaction interface between human CSF-1R and CSF-1 interaction interface and a synthesis of mechanistic principles underlying their its extracellular assembly have remained elusive.

Here, we show via a series of structural undertakings and analyses that dimeric human CSF-1 dramatically restructures its cognate receptor to establish a cytokine-receptor interaction interface dominated by electrostatic interactions to drive the assembly of a ternary extracellular signaling complex featuring homotypic receptor interactions mediated by the fourthits fourth Ig-like domain proximal to the membrane. In this context, the inherent intersubunit plasticity of human CSF-1 in the unbound state as well as structural plasticity in its receptor enables switching to a single signaling-competent conformation.

In addition, details of the CSF-1:CSF-1R interaction interface and comparisons with the functional counterpart observed in the human IL-34:CSF-1R complex⁴ delineate the structural determinants of the functional duality of CSF-1R. Importantly, recapitulation of diverse structural snaphots of CSF-1R and CSF-1 complexes in light of available structure-function data^{5,6} now establishes that concerted structural plasticity both in the cytokine and the receptor play critical roles in the assembly of a highly cooperative CSF-1:CSF-1R signaling complex.

Finally, we map somatic somatic mutations to the extracellular human CSF-1R segment associated with cancer and provide insights into their possible mechanistic consequences. Together, such structural insights allow consolidation of a wide array of available data and will be catalytic in future mechanistic interrogation of CSF-1R mediated signaling and its targeting for therapeutic purposes.

- 1. Lin, H., Lee, E., Hestir, K., Leo, C., Huang, M., Bosch, E., Halenbeck, R., Wu, G., Zhou, A., Behrens, D., et al. Science 320, 807-811 (2008).
- 2. Stanley, E.R., and Chitu, V. Cold Spring Harbor perspectives in biology 6 (2014).
- 3. Ries, C.H., Cannarile, M.A., Hoves, S., Benz, J., Wartha, K., Runza, V., Rey-Giraud, F., Pradel, L.P., Feuerhake, F., Klaman, I., et al. *Cancer cell* 25, 846-859 (2014)
- 4. Ma, X., Lin, Wei Y., Chen, Y., Stawicki, S., Mukhyala, K., Wu, Y., Martin, F., Bazan, J.F., and Starovasnik, Melissa A. Structure 20, 676-687 (2012).
- Elegheert, J., Desfosses, A., Shkumatov, A.V., Wu, X., Bracke, N., Verstraete, K., Van Craenenbroeck, K., Brooks, B.R., Svergun, D.I., Vergauwen, B., et al. *Structure* 19, 1762-1772 (2011).
- Felix, J., Elegheert, J., Gutsche, I., Shkumatov, A.V., Wen, Y., Bracke, N., Pannecoucke, E., Vandenberghe, I., Devreese, B., Svergun, D.I., et al. Structure 21, 528-539 (2013).

Specificity of Periplasmic Binding Proteins in Agrobacterium Tumefaciens

L. Marty¹, A. Vigouroux¹, D. Faure² and S. Morera¹

¹ Laboratoire d'Enzymologie et de Biochimie Structurales (LEBS), UPR CNRS 3082, Gif-sur-Yvette, ² Institut des Sciences du Végétal (ISV), UPR CNRS 2355, Gif-sur-Yvette

ABSTRACT

Agrobacterium tumefaciens induces the crown gall disease characterized by the formation of a tumor at the infection site in plants. This bacterium hijacks the plant cells machinery by integrating a fragment of its virulence plasmid, the pTi, into the plant genome. Genes expression from this fragment allows anarchic cell proliferation, leading to tumor formation and allows the synthesis of small molecules, called opines, used as specific nutrients by the bacterium. Hence, assimilation of these molecules confers a selective advantage to *Agrobacterium tumefaciens*. Almost twenty different opines are known but all of them cannot be catabolized by the same strains. Indeed, each opine is imported with its own transport system, composed of a Periplasmic Binding Protein (PBP) which binds and brings the molecule to a membrane transporter, usually an ABC-transporter type.

Two very similar opines, one used by the strain *A. tumefaciens* R10 and the other by the strain C58, are imported by two different transport systems. In order to understand how two different systems can import similar opines, we have undertaken biophysical and structural studies.

We solved several PBP-opine structures using data from PX1 at SOLEIL. Structural comparison combined with measured affinity constants allowed us to determine PBP specificity towards similar opines.

Structural Study on Molecular Switch Involved in Quorum Sensing in *Bacillus cereus*

<u>A. Talagas¹</u>, S. Zouhir², S. Perchat³, D. Lereclus³, S. Nessler^{1,2}

¹Institut de Biochimie et Biophysique Moléculaire et Cellulaire, Université Paris-sud, Orsay ²Laboratoire d'Enzymologie et de Biochimie Structurale, CNRS, Gif-sur-Yvette ³Unité de Génétique Microbienne et Environnement, INRA, Jouy-en-Josas

ABSTRACT

Bacteria use a mode of communication, called quorum sensing (QS) to regulate gene expression in a population-density dependent manner and thus control processes such as sporulation, competence, or virulence, in a multicellular way. In Gram-positive, QS is mainly based on the production, secretion and detection of small signal peptides.

The project focuses on the study of the *Bacillus cereus* QS system involving the sensor NprR and its signal peptide NprX. NprR belongs to the superfamily of direct QS sensors called RNPP (for Rap, NprR, PlcR and PrgX). RNPP are characterized by a peptidebinding domain composed of 6 to 9 TPR motifs. An additional HTH-type DNA-binding domain is present in NprR and the transcription factors PlcR and PrgX, but not in the Rap proteins displaying a phosphatase activity. NprR is a bifunctional QS sensor. When the QS is achieved, i.e. when sufficient amounts of NprX are produced, secreted and reabsorbed to interact with NprR, the NprR/NprX complex activates the expression of a regulon of 42 genes. In the absence of NprX, NprR acts as inhibitor of sporulation similar to the Rap proteins. To understand how NprX regulates the activity of NprR, we solved the crystal structures of NprR alone and in complex with NprX.

We used two forms of the effector: full-length NprR and the truncated form NprR Δ HTH where the HTH domain was deleted. Isothermal microcalorimetry measurements (ITC) and *in vivo* activity assays demonstrated that the minimal active form of NprX is an heptapeptide whereas higher affinity is observed with an octapeptide (1). Solution analysis using SEC-MALS, DLS and SAXS experiments showed that the apo form of NprR is dimeric and that NprX binding stabilizes a tetrameric form. Comparison of the crystal structures of NprR Δ HTH / NprX complex (2), and apo form NprR Δ HTH (3) helped explain why peptide-induced tetramerization is necessary for DNA binding. Further comparison with the Rap structures allowed us to propose a molecular mechanism for the sporulation inhibitor activity of NprR.

⁽¹⁾ Perchat, S., Dubois, T., Zouhir, S., Gominet, M., Poncet, S., Lemy, C., Aumont-Nicaise, M., Deutscher, J., Gohar, M., Nessler, S. and Lereclus, D. A cell–cell communication system regulates protease production during sporulation in bacteria of the Bacillus cereus group. Molecular Microbiology, 2011, 82: 619–633.

⁽²⁾ Zouhir S, Perchat S, Nicaise M, Perez J, Guimaraes B, Lereclus D, Nessler S. Peptide-binding dependent conformational changes regulate the transcriptional activity of the quorum-sensor NprR. Nucleic Acids Res. 2013, 16:7920-7933.

⁽³⁾ Talagas, A., Perchat S., Poncet S., Christelle Lemy, Nathalie Gilois, Michel Gohar, Lereclus D., Nessler S. A bifunctional quorum sensor couples necrotrophism and sporulation in *B. thuringiensis*. In preparation

Structure Determination of the Central Domain of Human Dystrophin by Coupling SAXS and New Interactive Flexible Fitting Method

<u>O. Delalande^{a,*}</u>, A.-E. Molza^a, J.-F. Hubert^a, A. Chéron^a, C. Ragénès-Nicol^a, J. Perez^b, P. Roblin^{b,c}, C. Tascon^a, A. Nicolas^a, E. Giudice^a, N. Férey^d, M. Baaden^e, M. Czjzek^f and E. Le Rumeur^a

^a Institut de Génétique et Développement de Rennes, CNRS, UMR6290, Univ. Rennes 1, Campus Santé, 2 av du Pr Léon Bernard, 35043 Rennes Cedex, France. ^b Synchrotron SOLEIL, L'orme des merisiers, Saint Aubin, BP 48,

91192 Gif sur Yvette Cedex, France

^c INRA, UR1268 Biopolyme res Interactions Assemblages, F-44300 Nantes, France ^d Laboratoire d'Informatique pour la Mécanique et les Sciences de l'Ingénieur, CNRS, UPR3251, Univ Paris XI, Bât 508, 512 et 502 bis, 91403 Orsay Cedex, France.

^e Laboratoire de Biochimie Théorique, CNRS, UPR9080, Univ. Paris Diderot, Sorbonne Paris Cité, 13 rue Pierre et Marie Curie, 75005 Paris, France.

^f Laboratoire Végétaux Marins et Biomolécules, CNRS, UMR7139, Univ. Pierre et Marie Curie-Paris 6, Station Biologique, 29682 Roscoff, France.

ABSTRACT

Nowadays, our molecular knowledge of dystrophin, the protein encoded by the *DMD* gene that is mutated in myopathy patients, still remains very limited. Dystrophin is crucial for the structural properties and dynamics of striated muscles. It ensures the maintenance of the plasma membrane integrity against stresses upon muscle and heart contraction through a network of interactions with proteins and phospholipids. However, the molecular principles underlying dystrophin function and interactions remain elusive.

To get around the absence of its atomic structure, we conceived an approach combining Small Angle X-Ray Scattering data and interactive flexible fitting at low-resolution to propose the first high resolution models of the central domain of dystrophin. This domain made of 24 spectrin-like repeats was studied by a 'dissect and build' strategy using multirepeat fragments. SAXS scattering curves analysis of the fragments indicated worm-like rather than long cylinder structure type. *Ab initio* computation and further reconstruction by interactive flexible fitting showed that inter-repeats regions present specific twists and bends. This results into a filamentous protein with numerous local tortuosities significantly far from the straight rod that has been suggested for the last two decades.

Dystrophin topology thus remarkably illustrates the hypothetic structural role it should play in muscle cells: allowing flexible movements to dampen or transmit lateral forces without unfolding the molecule. We also structurally characterized the most observed deletion mutant in patients bearing a Becker muscular dystrophy. Its central domain filamentous structure showed to be profoundly modified by comparison with the native protein.

Speciation of a Group I Ribozyme into a Lariat Capping Ribozyme

B. Masquida

GMGM, UMR7156, CNRS-Université de Strasbourg, Strasbourg, France

ABSTRACT

The lariat capping (LC) ribozyme (formerly named GIR1) is a natural ribozyme isolated from eukaryotic microorganisms. It catalyzes cleavage by branching, leaving a three-nucleotide lariat cap, which substitutes for a conventional mRNA cap. We have solved the crystal structures of the ~200 nt *Didymium iridis* LC ribozyme with a regulatory domain locked in a conformation corresponding to the active state (1). One of the crystal structures shows the architecture of the ribozyme right after cleavage. The overall structure demonstrates the interlocking of the core by the regulatory domain with exquisite tertiary interactions between loops from the core and the specific regulatory domain. These interactions result from an unanticipated reorganization of elements that were thought to be typical of group I introns. At the active site, a tight binding pocket binds a preformed lariat fold. The structure represents an important addition to the ensemble of large metallo-ribozymes that perform splicing and branching reactions and is discussed in relation to the evolution of intron splicing.

REFERENCES

1. Meyer, M., Nielsen, H., Olieric, V., Roblin, P., Johansen, S.D., Westhof, E. and Masquida, B. (2014) Speciation of a group I intron into a lariat capping ribozyme. *Proceedings of the National Academy of Sciences of the United States of America*, **111**, 7659-7664.

1-Methyladenosine in Transfer RNA

<u>C. Dégut</u>¹, M. Roovers², F. Brachet¹, J.Caillet³, L. Droogmans², V.Larue¹, C. Tisné¹

¹ Laboratory of Biological cristallography and NMR, Paris, France ² Laboratory of microbiology, Bruxelles, France ³IBPC, Paris, France

ABSTRACT

RNA modification is a post-transcriptional process by which certain nucleotides are altered after their initial incorporation into an RNA chain. Transfer RNA is the most heavily modified class of RNA molecules. These modifications expand the chemical and functional diversity of tRNA, and enhance its structural stability. We focussed our research on m¹A tRNA modification. m¹A nucleotide is found at position 9, 14, 22, 57 and 58 in tRNA. We solved the X-ray structures of the *B. subtilis* m¹A₂₂ tRNA (TrmK) methyltransferases. We then conducted biophysical studies using ITC, NMR, site-directed mutagenesis and molecular docking to obtain data on the tRNA recognition mode specific to the methyltransferase and on the reaction mechanism. TrmK presents two domains : the 'Rossman-fold' domain responsible for the methyltransferase activity and a domain that presents two helices that formed a coiled-coil, probably necessary to bind to tRNA. These two domains form a concave surface of positive electrostatic potentials favorable to the tRNA binding just below the catalytic pocket.

Recent results regarding the specific recognition with tRNA substrates and the reaction mechanism of this enzyme will be presented.

The ATP-mediated Formation of the YgjD-YeaZ-YjeE Complex is Required for the Biosynthesis of tRNA t⁶A in E. Coli

W. Zhang¹, B. Collinet^{1,2,*}, D. Durand¹ and H. van Tilbeurgh^{1,*}

¹ Institut de Biochimie et Biophysique Moléculaire et Cellulaire, UMR 8619, CNRS, Bâtiment 430, Université de Paris-Sud, 91405 Orsay Cedex, France

² Sorbonne Universités, UPMC Univ Paris 06, UFR 297, Sciences de la vie, F-75005, Paris, France * To whom correspondence should be addressed:

Tel: +33 1 69 15 31 55; Fax: +33 1 69 85 37 15; Email: <u>herman.van-tilbeurgh@u-psud.fr</u> Correspondence may also be addressed to Bruno Collinet. Tel: +33 1 69 15 79 68; Fax: +33 1 69 85 37 15; Email: <u>bruno.collinet@u-psud.fr</u>

ABSTRACT

The essential and universal *N*⁶-threonylcarbamoyladenosine (t⁶A) modification at position 37 of ANN-decoding tRNAs plays a pivotal role in translational fidelity through enhancement of the cognate codon recognition and stabilization of the codon-anticodon interaction. In *E. coli*, the YgjD, YeaZ, YjeE and YrdC proteins are necessary and sufficient for the *in vitro* biosynthesis of t⁶A, using tRNA, ATP, *L*-threonine and bicarbonate as substrates. YrdC synthesizes the short-lived *L*-threonylcarbamoyladenylate (TCA), and YgjD, YeaZ and YjeE cooperate to transfer the *L*-threonylcarbamoyl-moiety from TCA onto adenosine at position 37 of substrate tRNA. We determined the crystal structure of the heterodimer YgjD-YeaZ at 2.3 Å, revealing the presence of an unexpected molecule of ADP bound at an atypical site situated at the YgjD-YeaZ interface. We further showed that the ATPase activity of YjeE is strongly activated by the YgjD-YeaZ and YjeE form a compact ternary complex only in presence of ATP. The formation the ternary YgjD-YeaZ-YjeE complex is required for the *in vitro* biosynthesis of t⁶A but not its ATPase activity.

Key words: crystal structure of YgjD-YeaZ, ATPase, ternary complex YgjD-YeaZ-YjeE, *N*⁶-threonylcarbamoyladenosine (t⁶A) of tRNA

TRF2/RAP1 Complex: The Whole is Greater than the Sum of its Parts

<u>G. Gaullier^{1,2}</u>, S. Miron^{1,2}, S. Pisano³, R. Buisson³, Y.-V. Le Bihan^{1,2}, C. Tellier-Lebègues^{1,2}, W. Messaoud^{1,2}, P. Roblin⁴, R. Thai¹, B.G. Guimarães⁵, M.-J. Giraud-Panis³, E.Gilson³ and M.-H. Le Du^{1,2}

1: CEA, iBiTecS, F-91191 Gif-sur-Yvette, France

2: Université Paris-Sud & CNRS, UMR 8221, F-91191 Gif-sur-Yvette, France 3: IRCAN, CNRS UMR 7284, INSERM U1081, Université de Nice Sophia Antipolis, Nice, France 4: SWING beamline, SOLEIL synchrotron, Saint-Aubin, France 5: PROXIMA 1 beamline, SOLEIL synchrotron, Saint-Aubin, France

ABSTRACT

Telomeres are nucleoprotein complexes that cap the ends of linear eukaryotic chromosomes. Their integrity is essential to maintain genome stability, and their dysfunctions are associated with cancer and ageing pathologies [1].

In human, the telomere is formed by 6 proteins TRF1, TRF2, RAP1, TIN2, TPP1 and POT1, in complex with TTAGGG DNA repeats [2]. TRF2 is central at the telomere: more than it's interaction with double-stranded DNA and RAP1, it is able to interact with a large number of proteins [3].

The main question of our study is to understand how TRF2 can undergo conformational adjustments to form functional assemblies with its various partners.

We first observed that the presence of RAP1 affects TRF2 interaction properties with linear DNA and Holliday junction. But current available data describing the interaction between TRF2 and RAP1 [4] are not sufficient to explain these effects. We therefore studied the effect of RAP1 on TRF2 interaction using an integrative structural biology approach. SAXS study of TRF2 and RAP1 and their complex revealed that both proteins are highly flexible and undergo major conformational adjustment upon binding. Combining crystallography, ITC and protein footprinting, we could complete at the molecular scale the description of the interaction between TRF2 and RAP1.

Altogether, our results show that TRF2 and RAP1 flexibility is an essential property that allows them to form specific structural entities with their functional partners.

^[1] Donate LE & Blasco MA (2011) Telomeres in cancer and ageing. Phil. Trans. R. Soc. B 366: 76-84

^[2] De Lange T (2005) Shelterin: the protein complex that shapes and safeguards human telomeres. Genes Dev. 19: 2100–2110

 ^[3] Kim H, et al (2009) TRF2 functions as a protein hub and regulates telomere maintenance by recognizing specific peptide motifs. Nat. Struct. Mol. Biol. 16: 372–379

^[4] Chen Y, et al (2011) A conserved motif within RAP1 has diversified roles in telomere protection and regulation in different organisms. Nat. Struct. Mol. Biol 18: 213–221

Cell Localisation of Radiosensitizing Gadolinium-based Nanoparticles in Glioblastoma Cells

<u>L. Štefančíková¹</u>, E. Porcel¹, P. Eustache¹, S. Li¹, D. Salado¹, S. Marco^{2,3}, J.-L. Guerquin-Kern^{2,3}, M. Réfrégiers⁴, O. Tillement⁵, F. Lux⁵, and S. Lacombe¹

 ¹Institut des Sciences Moléculaires d'Orsay (UMR 8214) Bât 351, Université Paris Sud, CNRS, 91405, Orsay Cedex, France
 ² Institut Curie, centre de recherche, bat 112, centre Universitaire, 91405 Orsay Cedex, France
 ³ INSERM U759, bat 112, centre Universitaire, 91405 Orsay Cedex, France
 ⁴ Synchrotron SOLEIL, BP48 Saint-Aubin, 91192 Gif-sur-Yvette, France
 ⁵ Institut Lumière Matière, Université Claude Bernard Lyon 1, CNRS, 69622 Villeurbanne cedex, France

lenka.stefancikova@u-psud.fr

ABSTRACT

Radiotherapy is the most common therapeutic modality used to fight against cancer in about 50 % of all cancer patients. Recently, the addition of nanoparticles (NPs) has been proposed as a new strategy to enhance the effect of radiotherapy particularly in the treatment of aggressive tumors such as glioblastoma. The physical processes involved in radiosensitization by NPs have been well studied. Nonetheless, further understanding of its biological impact, including the localisation of the NPs in the target cells, is still lacking. Most studies were performed with NPs tagged with fluorescent markers. However, the presence of these markers can affect the NPs uptake and localisation. In this study, a set of methods was used to unambiguously and fully characterize the uptake of *label-free* NPs, their co-localisation with cell organelles, and their radiosensitizing efficacy.

U87 glioblastoma cells extracted from highly aggressive human tumor were used to study the radiosensitizing effects and localization of gadolinium-based nanoparticles (GdBN). For the first time, Synchrotron Radiation Deep UV (SR-DUV) microscopy is proposed as a new tool to track *label-free* GdBN. This highly innovative technique certified the localisation of the NPs in the cytoplasm of U87 cells and the absence of NPs in the nucleus. In a second step, Transmission Electron Microscopy (TEM) demonstrated that GdBN are taken up by cells via endocytosis. Third, using confocal microscopy it was found that GdBN co-localise with lysosomes but not with mitochondria. Finally, clonogenic assay measurements proved that the presence of NPs in the lysosomes induces a neat amplification of the killing of glioblastoma cells irradiated by gamma rays. The set of combined experimental protocols—SR-DUV, TEM and confocal microscopy — demonstrates a new standard method to study the localisation of NPs together with their radiosensitizing properties. This information is crucial to the understanding of NP-induced radiosentization and will contribute to the development of nanoagents for radiotherapy.
PARALLEL SESSION

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

ECOLE POLYTECHNIQUE – AUDITORIUM CARNOT

Chairpersons: Sandrine LYONNARD and Elise BERRIER

IT-03	The near-ambient pressure XPS at TEMPO beamline, first results <i>J.J. Gallet</i>
OC-09	Recent applications and results in near ambient pressure XPS: In-situ cell designs for liquid environments <i>M. Meyer</i>
OC-10	In situ site-selective K-edge XAS: New insights into the transformation of monometallic compounds <i>A. Bordage</i>
OC-11	Modeling hydrodesulfurization (HDS) reactions, multivariate curve resolution chemometric technique applied to in-Situ XAFS <i>D. Oliveira de Souza</i>
OC-12	Use of model materials for fission products release study in severe accidents conditions <i>E. Geiger</i>
IT-04	Shape control in wet synthesis of anisotropic gold nanoparticles <i>F. Testard</i>
OC-13	Determination of gold nanoparticles formation step by in situ time-resolved XANES in a microfluidic device <i>J.S. Girardon</i>
OC-14	Self-assembly of CdSe nanoplatelets <i>B. Abécassis</i>
OC-15	Assembly and disassembly kinetics of virus-like particles probed by time- resolved small-angle X-ray scattering <i>D. Law-Hine</i>
OC-16	Controlling self-assembly of ferrofluids during evaporation in PDMS C. Guibert

Near-ambient Pressure XPS at Tempo Beamline: First Results

<u>J.-J. Gallet</u>,^{1,2} F. Bournel,^{1,2} C. Chauvet,¹ G. Olivieri,¹ H. Tissot,¹ F. Rochet,^{1,2} and F. Sirotti¹

1 Laboratoire de Chimie Physique Matière et Rayonnement, Université Pierre et Marie Curie, Sorbonne Universités, Paris, France 2 Synchrotron SOLEIL, Saint-Aubin, France

ABSTRACT

The Near Ambient Pressure XPS (NAP-XPS) recently installed at TEMPO beamline of synchrotron SOLEIL is available for users since September 2014. This new setup that can operate under pressures up to 25 mbar opens promising perspectives in the field of environmental molecular chemistry, catalysis and chemical vapor deposition. I will briefly describe the NAP-XPS available tools the set up. the for sample preparation/characterization that make it a full-fledged surface science experiment, and I will focus on the originality of the various sample environments. Illustrative examples will be essentially taken from the environmental molecular chemistry studies carried out recently by our group during the commissioning period (hydration of a swelling clay, ion segregation at the vapor/liquid water interface). I will also present some results obtained in collaboration in the fields of catalysis and atomic layer deposition. Finally I will say a few words on the ongoing technical developments concerning the building of a reaction cell that will reveal the full potential of the machine for fast photoemission experiments.

Recent Applications and Results in Near Ambient Pressure XPS – In-situ Cell Designs for Liquid Environments

A. Thissen, S. Bahr, T. Kampen, O. Schaff, M. Meyer*

SPECS Surface Nano Analysis GmbH, Voltastrasse 5, 13355 Berlin, Germany <u>*Michael.Meyer@specs.com</u>

ABSTRACT

Modern devices are often only functional in environments far away from ultrahigh vacuum, still being the standard operation conditions for all Surface Science techniques. In parallel the importance of surfaces for the correct device operation is continuously increasing due to miniaturization down to the nanoscale. To contribute to advanced materials analysis in future means using Photoelectron spectroscopy combined with Scanning Probe Microscopies and related techniques in the generic or near generic device environments. This means high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields applied. Also extremely low or high temperatures might be necessary. In past all standard Surface Science Techniques did not work under these extreme environments. As a route to in situ sample analysis Near Ambient Pressure XPS has already been used for a longer time with tremendous success. Nowadays steps are made to utilize this analysis technique not only at synchrotrons and in academic environments, but also as standard analysis tools in user friendly laboratory systems. This work summarizes and presents existing solutions and future development routes to new instruments and materials analysis methods being functional under these working conditions. Opportunities and limits will be discussed from the perspective of a supplier of scientific instruments. Finally applications, examples and results from existing In situ methods like high pressure treatments cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in highest or lowest temperatures, high magnetic fields and static or dynamic potentials will be demonstrated.

In Situ Site-selective K-edge XAS: New Insights into

A. Bordage¹, V. Trannoy¹, O. Proux^{2,3}, R. Moulin¹, A. Bleuzen¹

the Transformation of Monometallic Compounds

¹ ICMMO, Université Paris-Sud, UMR CNRS 8182, rue du Doyen G. Poitou, 91405 Orsay, France
 ² OSUG, UMR CNRS 832, Université Grenoble-Alpes, F-38041 Grenoble Cedex 9, France
 ³ BM30B/FAME, ESRF, F-38043 Grenoble Cedex 9, France

ABSTRACT

The understanding of chemical processes under working conditions has been a longstanding challenge, in particular for compounds in which the element of interest is present under several oxidation states and/or in different sites. In situ and operando x-ray absorption spectroscopy (XAS)¹ is now a mature technique widely used to study chemical processes. Site-selective XAS² has recently brought new opportunities, for instance to investigate monometallic core-shell nanoparticles³ and active site in enzyme⁴. However, in situ and site-selective XAS had not been combined yet. We demonstrate here that in situ site-selective XAS is a powerful tool to follow the transformation of a monometallic compound. As a proof-of-principle study, we choose the calcination in air up to 400°C of a monometallic Co^{II}₄[Co^{III}(CN)₆]_{2,7}.20H₂O Prussian Blue Analogue (Co-PBA) into Co₃O₄. In Co-PBA, Co²⁺ high-spin (HS) and Co³⁺ low-spin (LS) cations are both present in an octahedral site but with different neighbours; in Co_3O_4 , the $Co^{2+}(HS)$ cations occupy the tetrahedral site of the spinel structure, while the Co³⁺(LS) ones occupy the octahedral site. The Co K-edge site-selected XANES spectra were recorded using the high-resolution spectrometer⁵ of the FAME beamline (BM30B, French CRG, ESRF). The pure site-selective Co²⁺(HS) and Co³⁺ (LS) spectra were extracted from XAS spectra measured at two energy positions of the spectrometer. Indeed, experimentally, whatever the energy chosen for the spectrometer, the spectrum includes a contribution from both sites. The Co²⁺:Co³⁺ ratio was determined for the two positions of the spectrometer from the corresponding Co K_β x-ray emission spectra of reference compounds and the compound of interest. Despite no significant changes in the xray emission spectra during the calcination, the pure Co²⁺(HS) and Co³⁺(LS) XANES spectra display well-marked differences with temperature, particularly in the spectral features of the Co²⁺(HS) site from the octahedral geometry at room-temperature (in Co-PBA) to the tetrahedral one at 400°C (in Co_3O_4). It is to be noted that the experimental $Co^{2+}(HS)$ spectrum in Co_3O_4 is presented here for the first time and is in excellent agreement with multiple scattering calculations⁶.

These first in situ site-selective XAS experiments successfully enabled to individually resolve the evolution of the $Co^{2+}(HS)$ and $Co^{3+}(LS)$ XANES spectra during the calcination of Co-PBA to Co_3O_4 . These results thus pave the way for new experiments to investigate in situ catalytic systems and materials used for data storage, battery, renewable energies, etc.

- 4. N. Leidel et al., Inorg. Chem. 51, 4546-4559 (2012); C. Lambertz et al., Chem. Sci. 5, 1187-1203 (2014).
- 5. I. Llorens et al., Rev. Sci. Instrum. 83, 063104 (2012).

^{1.} J. Singh et al., Chem. Soc. Rev 39, 4754-4766 (2010).

^{2.} M. Grush et al., J. Am. Chem. Soc. 117, 5895-5896 (1995) ; F. de Groot, Topics in catalysis 10, 179-186 (2000) ; P. Glatzel et al., Inorg. Chem. 41, 3121-3127 (2002).

^{3.} T-J. Kühn et al., Appl. Organometal. Chem 25, 577-584 (2011) ; T-J. Kühn et al., Inorg. Chem 53, 8367-8375 (2014).

^{6.} T. Jiang and D.E. Ellis, J. Mat. Res. 11, 2242-2256 (1996).

Modeling Hydrodesulfurization (HDS) Reactions, Multivariate Curve Resolution Chemometric Technique Applied to *In-situ* XAFS.

D. Oliveira de Souza, C. Lancetot, C. Lamonier, A. Tougerti, S. Cristol

UCCS, Bâtiment C3, Université Lille 1, 59655 – Villeneuve d'Ascq CEDEX, France

ABSTRACT

Nowadays synchrotron light sources are well consolidate as a tool for cutting edge research in different branches of science, such as, basics and applied physics, chemistry, biology, health science, environment, geology, art, archaeology and so on. Particularly, in the 3rd generation sources scientist are able to perform high quality *in situ* experiments with short time scale, typically, microseconds. For that reason, it is necessary to develop analysis tools allowing users to treat totally this huge amount of data in friendly (and fast) way and get fruitful information. Chemometrics, and particularly MCR-ALS technique seems well suited to cope with this problem¹.

In our work, we perform *in situ* QEXAFS experiments in two series of CoMo-based HDS catalysts supported on TiO₂-anatase by increasing the amount of MoO₃ loading. The solids were prepared with two different methods, namely, one-pot sol-gel and insipient wetness impregnation². The goal of this study is to probe structural changes at the molecular level during the activation of the catalyst and correlate it with the catalytic activity. For that, we have applied MCR-ALS to the data in order the resolve the kinetics of the reaction and to obtain information on concentration profile and pure intermediate compound spectra.

As an example of the results, we found that for impregnated catalysts the initial structure evolves to the final active phase (MoS_2) passing by two intermediate compounds (Figure 1). The first step is a reduction of the oxide precursor followed by a partial sulfidation leading to an oxysulfide specie and then the final active phase is formed. MCR-ALS method has been proving as promising one to resolve atomic structure of compounds and kinetics of a reaction on *in situ* based experiments.



- 1. A. de Juan, R. Tauler, Analytica Chimica Acta, 500 (2003) 195-210
- 2. D. L. Nguyen et al, ChemCatChem, 4 (2012) 2112-2120.

Use of Model Materials for Fission Products Release Study in Severe Accidents Conditions

E. Geiger¹; R. Bès²; Y. Pontillon¹; P. Martin²; G. Ducros¹

¹: CEA, DEN, DEC, SA3C, 13108 Saint-Paul-Lez-Durance, France ²: CEA, DEN, DEC, SESC, 13108 Saint-Paul-Lez-Durance, France

ABSTRACT

Many international research programs have been carried out aiming to understand the fission products (FP) and actinides behaviours and release mechanisms during a Severe Accident occurring in a Nuclear Power Plant. Most of them used irradiated nuclear fuels. The high radioactivity associated with such samples limits strongly the characterization techniques available. To overcome this limitation, model materials can be used as an alternative to irradiated fuels. One of the best candidates is a SIMFUEL material which consists in sintered UO2 doped with stable FP during manufacturing. FP concentrations are chosen in order to be representative of those of a specific irradiated fuel Burn-Up. Despite that no volatile FP are present in SIMFUEL (since they volatized during the sintering process), such material can be used in this field of research when an adequate approach is chosen: annealing test coupled to well defined pre and post-test characterizations. Among their main advantages, there is the possibility of performing synchrotron radiation analyses, yet unavailable for irradiated fuels.

This general approach was applied on SIMFUEL samples, in which FP concentration ranges from 0.03 to 0.9 at. %, submitted to different annealing conditions representative of intermediate stages of a severe accident (up to 1700°C). HR-XRD and XAS characterization techniques have been performed on MARS beam line of SOLEIL. HR-XRD diffractograms were collected in the 2-80° 2O range at 17 KeV and XAS measurements on most relevant FP relative to severe accident such as molybdenum, ruthenium, zirconium and barium were performed. Results obtained have demonstrated that SIMFUEL are chemically representative to irradiated nuclear fuels since the same common chemical phases have been observed and their evolution, as consequence of the annealing treatment, is also consistent to that observed in previous research programs.

Shape Control in Wet Synthesis of Anisotropic Gold Nanoparticles

F. Testard¹, Z.C. Canbek¹; B. Fleury¹, N. Menguy², O. Tache¹, O. Spalla¹

¹CEA Saclay, DSM/IRAMIS/SIS2M/LIONS, UMR CEA/CNRS 3299, 91191 Gif sur Yvette, France ²Université Pierre et Marie Curie, IMPMC, UMR 7590 CNRS, Campus Jussieu, 75252 Paris Cedex

ABSTRACT

In the field of wet nanoparticles synthesis, the request for controlling shape and size is still very challenging. While size control can be achieved, the shape selection is more difficult to attain without further separation processes. This is particularly relevant for gold nanoparticles where direct synthesis of concentrated solution of desired anisotropic shape remains ambitious. To overcome this major drawback, there is still a need for a better understanding of the mechanism of the formation of anisotropic shape in metal nanoparticles. Some questions remains like the time scale at which the anisotropy develops and the reasons for transition between preformed isotropic seeds and final anisotropic shapes in FCC structures.

From experimental point of view, the kinetic measurements of important characteristics during the formation of the nanoparticles are a solid support to unravel the mechanism. In this talk, I will focus on the methodologies developed in our laboratory to explore the transition towards anisotropic shape of gold nanoparticles in solution. Key point of this transition can be obtained through combined time resolved SAXS, WAXS, XANES, UV-visible and static HRTEM and SANS.



Figure 1 : Nanorods/bipyramids or spheres: what is the driving orientation of final shape?

- 1. Canbek Z. C., Cortes Huerto R., Testard F., Spalla O., Moldovan S., Ersen O, Wisnet A., Wang G., Goniakowski J., Noguera C. and Menguy N., submitted (2014).
- Hubert F., Testard F., Thill A., Kong Q., Tache O., and Spalla O., *Cryst. Growth Des.* 12, 1548–1555 (2012)
 Han J.;Testard F.;Malloggi F.; Coulon P-E.; Menguy N., Spalla O., Langmuir, 28 15966–15974 (2012)
 Gomez-Grana, S; Hubert, F; Testard, F; Guerrero-Martinez, A; Grillo, I; Liz-Marzan, LM; Spalla, Langmuir 28 1453-1459 (2012)

Determination of Gold Nanoparticles Formation Step by *in situ* Time-resolved XANES in a Microfluidic Device

J.-S. Girardon¹, J.F. Paul¹, A. Tougerti¹, E. Fonda², S. Fazzini³

¹ Unité de Catalyse et de Chimie du Solide, Université Lille 1, 59655 Villeneuve d'Asq 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

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. Synchrotron radiation related techniques are useful to characterize such rapid NPs formation [1]. In order to access to a direct in situ time-resolved characterization, we build [2] 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 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 (see picture) and a detailed analysis of these spectral shapes supported by *ab inito* calculation and XANES spectra simulation data analysis, we were able to propose a step by step mechanism. 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. All the mechanism steps and the intermediate formed species will be highlighted during the talk

REFERENCES

J. Polte, T. T. Ahner, F. Delissen, S. Sokolov, F. Emmerling, A. F.Thünemann, R. Kraehnert, J. Am. Chem. Soc, 132 (2010) 1296J.
 Ftouni, M. Penhoat, A. Addad, E. Payen, C. Rolando, J.S. Girardon, Nanoscale 4 (2012) 4450

Self-assembly of CdSe Nanoplatelets

B. Abécassis,^a M. Tessier,^b P. Davidson, ^a B. Dubertret^b

^aLaboratoire de Physique des Solides, Univ. Paris-Sud, CNRS, UMR 8502, F-91405 Orsay Cedex (France) Laboratoire de Physique et d'Etude des Materiaux,CNRS,Université Pierre et Marie Curie, ESPCI, 10 rue Vauquelin, 75005Paris, France

ABSTRACT

Self organization of nanoparticles in hierarchical structures is an area of intense research due to the potential emergence of collective properties in assemblies of nanoparticles. Among the possible nanoparticle building blocks, 2D nanocrystals are currently under scrutiny since anisotropic interaction between them could yield original supra-structures. Recently, some of us have discovered a synthetic pathway to yield CdSe nanoplatelets with thicknesses controllable at the atomic level¹. In this talk i will show how tuning the solvant polarisability leads to the stacking of the nanoplatelets one on the top of each other into para-crystals exhibiting long-range lamellar order. Using high resolution synchrotron small angle X-ray scattering we describe in details the structure of these arrangements. Interestingly, this self-organisation has important consequences on the optical properties of the nanoplatelets since photoluminescence measurements at low temperature show that this stacking renders visible the longitudinal optical (LO) phonon replica of the band edge exciton. We propose a mechanism for the emergence of this new collective effect². In certain experimental conditions, the CdSe nanoplatelets self-assemble into micrometer scale long anisotropic needle-like superparticles³. Using a combination of techniques we will detail the structure of this arrangements and show that they are composed of around 10⁶ nanoplatelets organized in highly aligned columns. Within the super-particles, the nanoplatelets are stacked on each other to maximize the contact surface between the ligands. When deposited on a substrate, the planes of the platelets are oriented perpendicularly to its surface and the SPs exhibit polarized emission properties. Finally, i will discuss the formation mechanism of these superparticles.



- 1. Ithurria, S. et al. Colloidal nanoplatelets with two-dimensional electronic structure. Nature Materials 10, 1–6 (2011).
- 2. Tessier, M. D. et al. Phonon line emission revealed by self-assembly of colloidal nanoplatelets. ACS Nano 7, 3332–3340 (2013).
- Abécassis, B., Tessier, M. D., Davidson, P. & Dubertret, B. Self-assembly of CdSe nanoplatelets into giant micron-scale needles emitting polarized light. Nano Lett. in press. doi:10.1021/nl4039746

Assembly and Disassembly Kinetics of Virus-like Particles Probed by Time-resolved Small-angle X-ray Scattering

<u>D. Law-Hine</u>[†], M. Zeghal[†], V. Bailleux[†] S. Bressanelli[§], D. Constantin[†] and G. Tresset[†]

[†]Laboratoire de Physique des Solides, Université Paris-Sud, CNRS, 91400 Orsay, France [§]Institut de Biologie Intégrative de la Cellule (I2BC), CEA, CNRS, Université Paris-Sud, 91198 Gif-sur-Yvette, France

ABSTRACT

Viral particles are natural nanomaterials that can serve as excellent nano-building blocks for the fabrication of innovative nanostructured materials^{1,2}. Their ability to efficiently package and deliver genomic material also makes them attractive tools for the development of therapeutical strategies. However, there is still much to know about the mechanisms of kinetics of self-assembly of viral proteins simultaneously interacting with their genome.

State-of-the-art techniques such as Time-Resolved Small-Angle X-Ray Scattering (TR-SAXS) enable an in situ vizualisation of the early times of the self-assembly of viral proteins into spherical virus-like particles. Recent studies³ performed with a model of bovine norovirus have shown that this technique allows a reconstruction of intermediates that cooperatively interact to build up a capsid. Here, we present a plant viral system, the Cowpea Chlorotic

Mottle Virus (CCMV), where the same issue is addressed. CCMV is known to be able to efficiently incorporate organic or inorganic materials to make hybrid viruses^{1,4}. Our approach consists in finding the key intermediates that play a central role in the formation of empty capsids before investigating the formation of capsids packaging nanoparticles.

better $\overline{\widehat{A}}$ 105 We build models to provide а understanding of the processes governing the selfassembly in order to extract information about the nature of the intermediates, their structure and their typical lifetime. These models are based on global fitting with TR-SAXS data collected at synchrotron radiation facilities (SOLEIL and ESRF). We are also interested in the disassembly of capsids that proceeds in longer times and may follow or not the same kinetics pathway. About 30 min at 20°C are necessary for the disassembly to occur completely, while it takes less than 10s for the proteins to start





forming empty capsids depending on our experimental conditions. These findings may help to apprehend the mechanisms of self-assembly for a better control in diverse applications such as drug delivery or for other nanoengineering purpose.

REFERENCES

- 1. S. E. Aniagyei, C. J. Kennedy, B. Stein, D.A. Willits, T. Douglas, M.J. Young, M. De, V.M. Rotello, D. Srisathiyanarayanan, C.C Kao, B. Dragnea, , Nano Lett., 9, 393–398 (2009). Viruses and nanotechnology; Manchester, M., Steinmetz, N. F., Eds.; Springer: Heidelberg, Germany (2009).

4. Y. Hu, R. Zandi, A. Anavitarte, C. M. Knobler, and W. M. Gelbart, Biophys. J., 94, 1428 (2008).

^{3.} G. Tresset, C. Le Cœur, J.-F. Bryche, M. Tatou, M. Zeghal, A. Charpilienne, D. Poncet, D. Constantin, and S. Bressanelli, J. Am. Chem. Soc. 135, 15 373 (2013).

Controlling Self-assembly of Ferrofluids during Evaporation in PDMS

<u>C. Guibert^a</u>, J. Perez^b, V. Dupuis^a, V. Peyre^a, J. Fresnais^a

^a Laboratoire Physicochimie des Electrolytes et Nanosystèmes InterfaciauX (PHENIX) UMR 8234 Université Pierre et Marie Curie – CC 51, 4, place Jussieu, 75252 PARIS Cedex 05 – France

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

ABSTRACT

Making magnetic aggregates with controlled shapes and sizes by self-assembly is a challenging task that leads to new materials, which can be useful in microfluidics or microrheology. Such objects can indeed be manipulated with lower magnetic fields than their individual nanocomponents^[1].

In our work, we present an original method to produce a dispersion of spherical aggregates of magnetic nanoparticles (MNPs) in a silicon matrix made of polydimethylsiloxane (PDMS), based on the evaporation of water from a water-in-PDMS emulsion.

In order to get a better comprehension of the mechanisms that take place during the aggregation, we studied the role of different parameters such as the evaporation speed on the dispersion state by various techniques such as Small Angle X-ray Scattering (SAXS) experiments, TEM, and DLS^[2]. We investigated the role of the interparticular interactions by varying the MNPs functionalisation: bare and charged surface (electrostatic repulsion), coating with neutral polymer (steric repulsions) and with various polyelectrolytes (both kinds of repulsions)... Lastly, we will present a kinetics study of the evaporation followed by SAXS and a model that could describe it ^[3].



TEM pictures of different magnetic nanoparticles aggregates obtained in PDMS



Emulsion drying studied by SAXS : formation of aggregates in PDMS

- [1] J. le Digabel, N. Biais, J. Fresnais, J. F. Berret, P. Hersen, B. Ladoux, Lab. Chip 2011, 11, 2630.
- [2] M. Okada, H. Maeda, S. Fujii, Y. Nakamura, T. Furuzono, Langmuir 2012, 28, 9405.
- [3] M. H. Sorensen, J. T. Zhu, R. W. Corkery, R. C. Hayward, P. Č. A. Alberius, Microporous Mesoporous Mater. 2009, 120, 359.

PARALLEL SESSION

Cultural Heritage, Archaeology, Environment, Geosciences ECOLE POLYTECHNIQUE – MEETING ROOM N°16

Chairpersons: Stéphanie ROSSANO and Emmanuel GUILLON

IT-05	Actinide speciation in sea water and in a model biomarker <i>C. den Auwer</i>
OC-17	Sub-critical alkaline stabilization archaeological iron conservation: Transformation of akaganeite followed by in-situ XAS at the iron K-edge and completed by XRD analysis <i>M. Bayle</i>
IT-06	Complementarity of X-rays techniques for the conservation of iron cultural heritage materials <i>S. Reguer</i>
OC- 18	Interest of high resolution X-ray absorption spectroscopy in environmental sciences <i>I. Kieffer</i>
OC-19	Melting properties of the deep earth's mantle investigated by in situ measurements <i>D. Andrault</i>
OC-20	Precipitation in "old" duralumin used in airplanes A. Cochard
OC-21	PSICHE: In-situ imaging and tomography for materials science at SOLEIL. Presentation and perspectives. <i>A. King</i>

Actinide Speciation in Sea Water and in Sponge *A. Cavernicola*

M. Maloubier¹, H. Michel¹, M.-A. Tribalat¹, O. Thomas¹, C. Moulin², M.-Y. Dechraoui Bottein³, J.-L. Teyssie³, F.R. Oberhaensli³, <u>C. Den Auwer¹</u>

¹ Université Nice Sophia Antipolis Institut de Chimie de Nice (ICN) – UMR 7272 - France
 ² CEA, DAM, DIF F-91297 Arpajon, France
 ³ International Atomic Energy Agency - Environment Laboratories, MC-98000, Monaco

ABSTRACT

The fate of natural and anthropogenic radionuclides in the environment remains a major concern in our modern societies^[1]. Among the radionuclides of concern, actinides are the heaviest elements involved in nuclear activities. Surprisingly, very little is known about the speciation of actinides in seawater and their accumulation in marine organisms^[2]. Improving knowledge on the interaction between actinides and marine organisms is therefore essential to better understand the transfer mechanisms from the hydrosphere to the biosphere and to evaluate their global impact on the environment. Marine sponges have already been identified as hyper-accumulators of several trace elements and are proposed in this case as model biomonitor organisms. To address this question, we have focused on three actinide elements, uranyl(VI) {U(VI)O₂²⁺}, neptunyl(V) {Np(VI)O₂⁺} and americium(III). They are representatives of the actinide series but Pu(IV) who is the most sensitive to hydrolysis. Europium(III) (a stable lanthanide with chemical properties very close to that of americium) has been added to the list as a surrogate of the actinides at oxidation state +III.

As a first step, the speciation in seawater has been monitored in doped samples at cation concentrations of 5 10⁻⁵ M and 1 10⁻⁵ M by a combination of spectroscopies (TRLIF for Eu and U; EXAFS for Am, Eu, U and Np) together with speciation modelling using the BASSIST data base^[3]. In all cases, a carbonato species has been observed as the most likely form in sea water, although with significant differences in the speciation within the series, as expected^[4]. As a second step, the accumulation and speciation of {U(VI)O₂²⁺} and Eu(III) were investigated in the Mediterranean sponge *A. Cavernicola*. Yet because of the relatively high specific activity of americium, the chemical analogue europium was used. This sponge is commonly found along the coasts of southern France and previous laboratory studies have shown that it has a substantial capacity for metal accumulation^[5]. The amount of europium integrated in sponges exposed to the radiotracer ¹⁵²Eu was measured using a high-purity Ge gamma spectrometer system. Speciation has been investigated by a combination of the above specroscopic techniques and imaging using a STXM beam line.

REFERENCES

3. L. Bion, Radiochimica Acta, 91, 633-638 (2003)

^{1.} G. Le Petit, et al., Pure and Applied Geophysics, 171, 629-644 (2014)

^{2.} G. Choppin, and P. Wong, Aquatic Geochemistry, 4, 77-101 (1998)

^{4.} S. Maxwell, B. Culligan, J. Hutchison, R. Utsey, D. McAlister, J Radioanal Nucl Chem., 300, 1175-1189 (2014)

^{5.} G. Genta-Jouve, N. Cachet, F. Oberhänsli, C. Noyer, J-L Teyssié, O. P. Thomas, T. Lacoue-Labarthe, *Chemosphere* 89, 340-349 (2012)

Sub-critical Alkaline Stabilization Archaeological Iron Cnservation: Transformation of Akaganeite Followed by In-Situ XAS at the Iron K-edge and Completed by XRD Analysis

<u>M. Bayle^{1,2}</u>, P. de Viviés², J.-B. Memet², E. Foy¹, S. Reguer³, F. Mercier¹, N. Gonzalez-Pereyra⁴, D. Neff¹

¹ Laboratoire Archéomatériaux et Prévision de l'Altération, NIMBE LAPA CEA Saclay, CEA/CNRS 91191 Gif-sur-Yvette, France,

<u>marine.bayle@cea.fr</u>, <u>eddy.foy@cea.fr</u>, <u>florence.mercier@cea.fr</u>, <u>delphine.neff@cea.fr</u> ² A-CORROS Expertises, 23 chemin des moines, 13200 Arles, France,

devivies@a-corros.fr, jbmemet@a-corros.fr

³ Synchrotron SOLEIL, L'Orme des Merisiers – Saint Aubin – BP48 – 91192 Gif-sur-Yvette, France, <u>solenn.reguer@synchrotron-soleil.fr</u>

4 Clemson University Restoration Institute, Warren Lash Conservation Center, 1250 Supply Street, North Charleston, SC 29405, USA,

nestorg@clemson.edu

ABSTRACT

The excavation of iron archaeological artefacts corroded in chlorinated environments is difficult because of the presence of chlorides in the corrosion products that transform in contact with atmosphere and can lead to the complete degradation of the artefact.

To avoid that kind of damages, stabilization treatments are performed. The sub-critical process is an innovative treatment. It consists in immersing an artefact in an alkaline bath (NaOH 0.125M) pressurized until 30-35 bar and then heated to 180°C. In order to understand and improve this recently developed process, the transformation mechanisms of chlorinated phases under sub-critical conditions are studied. The chlorinated phase akaganeite (β -FeO_{1-x}(OH)_{1+x}Cl_x) is one of the Cl-containing phase responsible for severe damages inside the corrosion layers of iron artefacts.

Laboratory experiments have shown that akaganeite can transform in hematite (α -Fe₂O₃) under hydrothermal conditions but the presence of goethite can be also identified [1]. The objectives were to determine the dechlorination processes of akaganeite and to understand its transformation mechanisms by performing in-situ XAS measurements during the subcritical process (ESRF FAME beamline), and XRD measurements before and after the treatment (SOLEIL DiffAbs). Those experiments allow combining the local order information obtained by XAS, with the long range distance data from XRD to well characterise the process.

Two akaganeite were selected: one has been synthetized in laboratory and another one has been formed in natural conditions. The behaviour of archaeological powder is closer to real conditions of stabilization rather than synthetic samples. But the purity of the synthetized powder allows isolating the akaganeite transformation. Performing in-situ experiment allows obtaining information about the transformation kinetics and the reactivity variation of both archaeological and synthetic akaganeite.

^{1.} Drews, M., N.G. Gonzalez-Pereyra, and D. Cook. The transformation of iron oxides, oxyhydroxides and corrosion products by subcritical water treatment. in Interim meeting of the ICOM-CC Metal working group. 2013. Edinburgh.

The Complementarity of X-rays Techniques for the Conservation of Iron Cultural Heritage Materials

<u>S. Reguer¹</u>, J. Monnier², F. Kergourlay^{1,3}, E. Foy³, D. Neff³, F. Mirambet⁴, D. Vantelon¹, D. Testemale^{5,6}, M. Cotte⁶, JL. Hazemann^{5,6}, J. Susini⁶, E. Dooryhee^{5,6}, J.-L. Hodeau^{5,6}, P.Lagarde¹, P. Dillmann³

Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP48 91192 Gif/Yvette cedex, France
 ICMPE UMR 7182 CNRS/Univ. Paris-Est Créteil, 2-8 rue Henri Dunant, F-94320 Thiais, France
 LAPA, SIS2M/NIMBE UMR3299 CNRS, CEA Saclay, Bât. 637, F-91191 Gif/Yvette cedex, France
 C2RMF, Palais du Louvre, Porte des Lions, 14 Quai François Mitterrand, 75001 Paris, France
 Institut Néel, CNRS/Univ. Joseph Fourier, BP 166, F-38042 Grenoble Cedex 9, France

6- ESRF, 71 Avenue des Martyrs, CS40220, 38043 Grenoble Cedex 9, France

ABSTRACT

Iron is a component of many archaeological and ethnological objects but also of ancient monuments mechanically reinforced by metallic structures. The evaluation of the degradation state, the proposition of reliable corrosion diagnosis methods but also the development and improvement of conservation strategies, are of great interest to preserve such historical elements. For these reasons, the understanding of iron alteration on very long time and according to various environments is essential. It is of major importance to distinguish and locate the constitutive phases of the corrosion layers, because of their difference of reactivity in the corrosion processes. To this purpose, corroded samples from different archaeological earthy sites were carefully studied: wrought iron ingots founded on Gallo-Roman shipwrecks, Amiens cathedral reinforcement iron bars and also iron element from Indian built heritage.

The combination of different analytical investigation techniques, and among them XRD, XRF and XAS is crucial to reveal the morphology, elementary composition and phase structure of corrosion layers. μ XRD and μ -XAS experiments at Fe K edge allowed to refine the distribution of the predominant Fe oxidation state and to characterize the corresponding corrosion products revealing the iron corrosion system formed depending on the sample exposition (atmosphere, soil or marine environments). Moreover, the role of specific elements on phase's stability and the chemical form and distribution of these elements in the rust layer, especially S, P and CI, was investigated, using the combination of μ -XRF and μ -XANES at S, P and CI K edges. In addition, *in situ* experiments were realized in order to determine by XRD and XAS measurements (i) the iron corrosion processes (ii) the dechlorination processes, thanks to (electro-) chemical cells specifically designed.

This presentation will thus give an overview of the last 10 years of research about conservation of iron cultural heritage materials towards the experiments conducted on complementary beamlines.

REFERENCES

5. J. Monnier et al. Applied Physics A, 2010

^{1.} S. Reguer et al. Applied Physics A, 2006

S. Reguer et al. Corrosion Science, 2007
 P.Dillmann et al. Actualité Chimique, 2007

^{4.} S. Reguer et al. Corrosion Science, 2009

^{6.} J. Monnier et al. Corrosion Science, 2010

^{7.} J. Monnier et al. Actualité Chimique, 2011

^{8.} J. Monnier et al. JAAS, 2011

^{9.} J. Monnier et al. Corrosion Sciences, 2014

Applications of High Resolution X-ray Absorption Spectroscopy in Environmental Sciences

W. Del Net¹; I. Kieffer¹; E. Lahera¹; I. LLorens²; O. Proux¹; D. Testemale³; J.-L. Hazemann³

¹ OSUG, UMS 832 CNRS – Univ. J. Fourier, Grenoble;
 ² Institut de recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS – Univ. Lyon I;
 ³ Inst. Néel UPR 2940 CNRS, Grenoble

ABSTRACT

FAME (the French Absorption spectroscopy beamline in Material and Environmental sciences at the ESRF) is dedicated to X-ray Absorption Spectroscopy (XAS). The aim of this beamline is to cover a wide variety of common applications of XAS in materials science, biophysics, chemistry and mainly in geochemistry and geophysics sciences.

XAS allows to probe the speciation of a target chemical element (selected by the energy of its absorption edges), *i.e.* its electronic structure (the valence) and the structure of the coordination shells. One of the specificities of XAS measurements in the environmental sciences field is that the probed element (*e.g.* pollutant) is often diluted in the media, even in synthetic samples in order to be representative of the realistic concentration of these pollutants. XAS analysis currently performed on the FAME beamline with a solid state detector collecting the fluorescence signal shows a detection limit estimated around 50ppm¹. A way to improve significantly the detection limit in the case of complex or highly diluted samples is to use a crystal analyzer spectrometer (CAS)² and thus to get rid of the fluorescence and scattering contributions of the matrix.

Moreover, when the fluorescence signal is measured with a high energy resolution crystal analyzer (the one we developed on FAME has an energy resolution of about 1 to 5eV) instead of a classical fluorescence solid state detector ($\Delta E \sim 200-300$ eV), the experimental broadening is greatly reduced and sharp features in the XAS edge can be resolved. This enhanced sensitivity allows fine distinctions between similar samples.

Finally, having a crystal analyzer spectrometer offers the possibility to carry out x-ray emission spectroscopy (XES) and high energy resolution fluorescence detected XAS (HERFD XAS) in order to increase the selectivity of the method.

A 1m-bent 5-crystal spectrometer has been installed at the FAME beamline and is now open to users.

Examples coming from the environmental science community will be presented to illustrate those 3 different uses of high resolution XAS: detection limit lowering, energy resolution improvement and HERFD-XANES.

^{1.} Hazemann J.-L., Proux O., Nassif V., Palancher H., Lahera E. et al., J. Synchrotron Radiat. 16 283-292 (2009)

Melting Properties of the Deep Earth's Mantle Investigated by *in situ* Measurements

G. Pesce, <u>D. Andrault</u>, G. Manthilake, N. Bolfan-Casanova, J. Chantel, D. Novella, N. Guignot

Laboratoire Magmas et Volcans, Université Blaise Pascal, OPGC-CNRS-IRD, 5 rue Kessler, 63000 Clermont-Ferrand Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Gif-sur-Yvette

ABSTRACT

Studying the melting properties of the mantle is fundamental to understand the global dynamics of our planet. Already in the early stages of its history, Earth experienced extensive melting events leading to the formation of a magma ocean, due to the massive energy released by large-scale meteoritic impacts, radiogenic decay and core-mantle gravitational segregation. Partial melting however still plays a key role in today's mantle's dynamics. Seismic observations have in fact highlighted the presence of anomalies in the upper mantle, atop the 410 km discontinuity. These regions, called ultra-low velocity zones, show a significant reduction in shear wave velocity, compatible with the presence of partial melting [1].

We studied the melting properties of the mantle using *in situ* X-ray diffraction experiments and electrical conductivity measurements [2] at high pressure and high temperature. Both technics are very sensitive to the presence of liquid in the sample. They provide accurate information not only on the evolution with pressure of the solidus temperature, but also on the degree of partial melting with increasing temperature. Our samples consisted of a synthetic CI-chondrite glass, a "proxy" composition for the primitive mantle after core segregation. Pressures up to 25 GPa (the limit between upper and lower mantle at 670 km depth) were generated by the multi-anvil press.

Our results suggest that previous studies overestimated by ~300 K the solidus temperature (e.g. [3]), probably due to a lack of resolution in determining low degrees of partial melting in their experimental procedure, compared to the *in situ* experiments presented here. Our results imply that partial melting could happen more frequently than initially expected, particularly in mantle regions where incompatible elements and volatiles are concentrated.

- 2. T. Yoshino, G. Manthilake, T. Matsuzaki, and T. Katsura, Nature 451, 326-329 (2008).
- 3. K. Litasov and E. Ohtani, Physics of The Earth and Planetary Interiors 134, 105-127 (2002).

^{1.} D. A. Toffelmier and J. A. Tyburczy, Nature 447, 991-994 (2007).

Precipitation in "Old" Duralumin used in Airplanes

A. Cochard¹, S. Reguer², M.-H. Mathon³, N. Ratel-Ramond¹, P. Sciau¹

1: CEMES, CNRS, Université de Toulouse, 29 rue J.Marvig, 31055 Toulouse, France 2: DiffAbs beamline at SOLEIL Synchrotron, Saint-Aubin BP 48, 91192 Gif-sur-Yvette, France 3: Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif-sur-Yvette, France

ABSTRACT

Aluminum-copper alloys were widely used for aircraft from the World War I until now for structural applications due to their good strength-to-weight ratio. Then a precise knowledge of the nature of these alloys begins to interest the industrial heritage field. However, although these materials were processed less than a century ago and used in an industrial context, structural data are very limited. In many cases their structure was not investigated on the nanometer scale, which is fundamental to understand the mechanical properties [1] and the corrosion behavior of age-hardenable aluminum alloys. The link with archival documents from aircraft manufacturers is also complex for the alloys made before 1960-70, because the existing archival data of manufacturers are fragmentary [2]. The best way to highlight these "historical" alloys is obtained by crossing the available archive data and precise laboratory analyzes. The present study focuses on the Brequet 765 Saraha built in 1958. This doubledeck military aircraft was built during the post-Wold War II boost of the French aeronautical industry. It is currently in renovation by the association Ailes Anciennes Toulouse [3]. First laboratory analyses revealed that at least two different compositions were used for the rivets. the A-U3G and A-U4G alloys, as described in scientific literature by Tournaire and Renouard in 1956 [4]. The A-U3G alloy, easier to use, was developed to substitute the A-U4G alloy at the same time that the conception of the Brequet 765. The A-U4G1 was used for laminated pieces.

These structural hardening aluminum 2xxx type alloy, after a complex precipitation, contain a number of different precipitates with various compositions and morphologies, depending on the elaboration process, that play an important role in the mechanical properties of the alloy. To understand the differential ease of use of the two rivet aluminum alloys, they have been analyzed using a combination of techniques: neutron diffraction at LLB, X-ray diffraction and X-ray absorption spectroscopy at Cu K edge on DiffAbs beamline at SOLEIL Synchrotron. The aim of these experiments is to identify consistently the different precipitates according to different alloys: their composition, morphology (structure and size)and distribution. The nano-structure of these alloys are very different: the main precipitates of A-U4G rivets are composed of CuAl₂, Mg₁₇Al₁₂, Al₄MnSi_{0.7} and Al₁₇(Fe_{3.2}Mn_{0.8})Si₂, while for A-U3G precipitates, the main phase is Al₇Cu₂Fe. It should be noted that A-U3G composition, developed later, contains much less sub-micrometric (10-1000nm) and micrometric (1-10µm) precipitates.

^{1.} B. Dubost, P. Saintfort, Durcissement par précipitation des alliages d'aluminium, Dossier Techniques de l'ingénieur M240 (1991).

^{2.} M. Le Roux, L'entreprise et la recherche: un siècle de recherche industrielle à Pechiney, edited by Rive Droite, Histoire industrielle, Paris, 1998.

^{3.} D. Hartmann, Sauver Brigitte ou le sauvetage et la récupération du Breguet 765 « SAHARA » d'Evreux à Toulouse, (http://www.calameo.com/subscriptions/57493).

^{4.} M. Tournaire, M. Renouard, Alliages pour rivets de la famille du Duralumin, Revue de l'Aluminium 217 (1955).

PSICHE: In-situ Imaging and Tomography for Materials Science at SOLEIL. Presentation and Perspectives.

A. King, N. Guignot, P. Zerbino and J.-P. Itié

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

ABSTRACT

PSICHE is a high-energy synchrotron beam line for imaging and tomography at the French synchrotron SOLEIL. The imaging instrument has just been brought into service, with the first "friendly user" experiments successfully performed in September 2014. The tomograph is optimized for in-situ materials science experiments, with a high speed, high load capacity rotation stage and white beam compatible optics, but has already proven equally useful for life sciences and cultural heritage applications. The beam line also hosts high-pressure diffraction experiments, and this opens many possibilities for combining diffraction and imaging. This presentation will introduce the beam line to potential future users, and give examples of results that have been obtained so far. Future perspectives and plans will be presented, both for extending the scope of tomography measurements, but also for combining imaging and reciprocal space information with grain mapping or correlative tomography approaches for unique and innovative experiments.

PARALLEL SESSION

Diluted Matter

ECOLE POLYTECHNIQUE – SAUVY MEETING ROOM

Chairpersons: Vincent BOUDON and Francis PENENT

IT-07	Relaxation dynamics of atoms and molecules in the tender X-ray region <i>M. Simon</i>
OC-22	XUV induced fragmentation dynamics of 5-halouracils investigated in the time and energy domain <i>R. Cireasa</i>
OC-23	Understanding the internal torsion and bending motion of dimethyl ether via isotopic studies <i>P. Kutzer</i>
OC-24	Einstein–Bohr recoiling double-slit Gedanken experiment performed at the molecular level <i>M. Pattanen</i>
OC-25	Gas-phase ion-molecule chemistry: An experimental study of $CH_3^+ + CH_4$ A. Lopes
IT-08	Rotational doppler effect <i>F. Gel'mukhanov</i>
OC-26	New information on HC ₃ N ⁺ using Synchrotron- and laser-based photoelectron studies S. Boyé-Péronne
OC-27	Ultrafast dynamics and electronic state: Lifetime interferences in chlorine- containing molecules <i>G. Goldsztejn</i>
OC-28	X-ray photoionization of atomic oxygen ions <i>B.M. McLaughlin</i>
OC-29	High density THz frequency comb produced by coherent Synchrotron radiation S. Tammaro

Relaxation Dynamics of Atoms and Molecules in the Tender X-ray Region

M. Simon

Laboratoire de Chimie Physique-Matière et Rayonnement, CNRS&UPMC and SOLEIL, France

ABSTRACT

The interaction of tender x-rays (1-10 keV) with isolated atoms and molecules leads to interesting results like subfemtoseconds nuclear motion [1], huge PCI effects [2], electronic lifetime interferences [3], strong recoil effects [4], localization-delocalization of an inner shell core hole depending of the dissociation dynamics [5]...

Our group has recently developped an x-ray emission spectrometer [5], a vectorial correlation spectrometer (COLTRIMS) [6] and an HArd X-ray PhotoEmission Spectrometer (HAXPES) [7].

By selecting recent results, I will illustrate the research interest of our group in this energy region.

REFERENCES

[1] T. Marchenko, L. Journel, 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** , 144308 (2011)

[2] R. Guillemin, S. Sheinerman, C. Bomme, T. Marin, L. Journel, T. Marchenko, R. K. Kushawaha, N. Trcera, M. N. Piancastelli and M. Simon, Phys. Rev. Lett. 109, 013001 (2012)

[3] M. Kavčič, M. Žitnik, K. Bučar, and A. Mihelič, S. Carniato, L. Journel, R. Guillemin, and M. Simon, Phys. Rev. Lett. 105, 113004 (2010)

[4] M. Simon, R. Püttner, T. Marchenko, R. Guillemin, R. K. Kushawaha, L. Journel, G. Goldsztejn, M. N. Piancastelli, J. M. Ablett, J.-P. Rueff and D. Céolin, Nature Communications 5 4069 (2014)

[8] R. Guillemin, P. Decleva, M. Stener, C. Bomme, T. Marin, L. Journel, T. Marchenko, R.K. Kushawaha, K. Jänkälä, 6 N. Trcera, K.P. Bowen, D.W. Lindle, M.N. Piancastelli and M. Simon, Nature Communications accepted

[5] Loïc Journel, Lara El Khoury, Thierry Marin, Renaud Guillemin, Stéphane Carniato, Antoine Avila, Renaud Delaunay, Coryn F. Hague, and Marc Simon, Rev. Sci. Instrum. 80, 093105 (2009)

[6] C. Bomme, R. Guillemin, T. Marin, L. Journel, T. Marchenko, D. Dowek, N. Trcera, B. Pilette, A. Avila, H. Ringuenet, R. K. Kushawaha, and M. Simon, Rev. Sci. Instrum. 84, 103104 (2013)

[7] D. Céolin, J. M. Ablett, D. Prieur, T. Moreno, J.-P. Rueff, B. Pilette, T. Marchenko, L. Journel, T. Marin, R. Guillemin and M. Simon, J. Electron spectrosc. and Relat. Phenom. 190 188 (2013)

XUV Induced Fragmentation Dynamics of 5-halouracils Investigated in the Time and Energy Domain

<u>R. Cireasa</u>^{*1}, L. Avaldi⁴, V. Blanchet², P. Bolognesi⁴, F. Calegari⁵, P. Çarçabal¹, M. Castrovilli⁵, J.-P. Champeaux³, D. Dowek¹, Y. Mairesse², P. Moretto-Capelle³, M. Nisoli⁵, P. O'Keeffe⁴, A. Trabattoni⁵

¹ Institut des Sciences Moléculaires d'Orsay, Université Paris XI, Orsay, France
 ² Centre Lasers Intenses et Applications, Université de Bordeaux, Talence, France
 ³ Laboratoire Collisions Agrégats et Réactivité, Université Paul Sabatier, Toulouse, France
 ⁴ Istituto di Struttura della Materia, Area della Ricerca Roma 1, 00016, Monterotondo Scalo, Italy
 ⁵ Department of Physics, Politecnico di Milano,CNR-IFN, I-20133 Milan, Italy

ABSTRACT

5-Halouracils (5XU) are formed by substituting the H atom at position 5 of the uracil ring with a halogen atom. It was found out that the tumour cells are more sensitive to the lethal effects of the UV, X-ray, proton and γ radiation when their DNA is modified to replace the thymine with such molecules. 5FU is a drug routinely used in combined chemo- and radiotherapy treatments for its radio-sensitising properties.

In order to understand at the molecular level, the 5XU interaction with XUV radiation, we have investigated the ionisation and fragmentation of 5FU and 5BrU induced by high order harmonics, HH, (9-35 eV) and synchrotron radiation (9-26 eV, DESIRS beamline). The ensuing dynamics was detected by recording Time-of-Flight (TOF) spectra of the photofragments as a function of the delay between the XUV pump (harmonic fs pulse train or attosecond pulse) and the probe pulse (fs IR/UV) and as a function of the excitation energy. For the time-resolved measurements, the kinetic energy of the main fragments was recorded by velocity map imaging, while for the energy-resolved ones, both the fragment and the (correlated) photoelectron kinetic energies were measured by using the photoelectron-photoion coincidence 3D momentum imaging.

The mass spectra can be explained only by considering that the parent ionisation is followed by complex dynamics involving ring opening reactions, proton or hydrogen transfer, multichannel and sequential dissociations. Measuring at various photon energies in 9-26 eV range, the mass spectra and the photoemission spectra of the electrons coincident with the parent ion and with different fragment ions enabled us to identify the parent cation states involved in the fragmentation. In addition, the energy-resolved measurements reveal that most of the energy is taken by the photoelectron. All fragments bear very little kinetic energy, maximum 1 eV and typically, less than 0.5 eV. These results are consistent with those obtained in the fragmentation induced by HH. For all systems, we have recorded ultrafast dynamics (<10 fs) manifested as delayed signal appearances and sharp rising/decaying signals. An ultrafast decay of about 40 fs was observed for the signal from the fragment 43 (HNCO or FCCH) and the complementary rising behaviour on the same timescale was observed for fragment 44, which can be only formed by H/H⁺ transfer, most probably via tautomerisation. Similar behaviours, although slower, were measured for the fragments 31 (FC) and 32 and for BrU fragments. These dynamics may be associated with H or proton transfer processes where the difference in timescale is determined by the initial and final sites of the H/proton transfer and, in particular, to the involvement of the halogen atom.

Understanding the Internal Torsion and Bending Motion of Dimethyl Ether via Isotopic Studies

P. Kutzer¹, O. Pirali², P. Rov² and T. F. Giesen¹

¹University of Kassel, Institute of Physics, Heinrich-Plett-Str. 40, 34132 Kassel, Germany ²Société civile Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin – BP 48, 91192 Gif Sur Yvette Cedex, France

ABSTRACT

Dimethyl ether (DME) is well suited to study the large amplitude internal motion of molecules. The internal torsion of both methyl groups exhibits strong coupling effects of both rotors and also with the C-O-C in plane bending mode.Furthermore DME is of astrophysical interest as the main isotopologue as well as the singly ¹³C substituted species have been detected in the interstellar medium [1, 2].



The molecule is well-studied by means of high resolution spectroscopy, although there are still some important open questions left, especially for the ¹³C substituted species [3, 4]. Calculated band centre frequencies of the torsional motion obtained from high level ab initio calculations still deviate from experimental values, and comparison to ¹³C substituted species has so far been restricted to a few measurements of pure rotational transitions [4].

Recently, we recorded first high resolution broadband spectra of pure samples of singly and doubly ¹³C substituted DME in the region of 70 cm⁻¹ to 500 cm⁻¹ with a resolution of 30 MHz using the FT-IR spectrometer at the AILES beam-line of the SOLEIL synchrotron. We also recorded spectra of the ¹³C substituted species between 800 cm⁻¹ and 10000 cm⁻¹ at a lower resolution at Kassel.

Here we present our first analysis of the C-O-C bending mode of all three isotopologues and preliminary results for the first torsionally excited states. For the C-O-C bending mode the recorded spectra are well described by a standard Watsonian set of molecular parameters. We will also compare our experimental derived vibrational energies of band centres for different excited modes of DME isotopologues with our calculated values.

Our measurements and analyses will help to foster quantum chemical modelling of large amplitude motion, and improve assignments of astrophysical observations at the confusion limit.

- [1] [2] S. E. Bisschop, et al: A&A 552, A112 (2013)
 - L. E. Snyder, et al, Astrophys. J. **191** L79_L82 (1974) C. P. Endres, et al, A & A **504**, 635-640 (2009)
- [3]
- [4] [5] M. Koerber, et al, A&A 558, A112 (2013)
- M. Carvajal, et al, J. Mol. Spectr. 279 3-11 (2012)

Einstein–Bohr Recoiling Double-slit Gedanken Experiment Performed at the Molecular Level

X.-J. Liu¹, Q. Miao^{2,3}, F. Gel'mukhanov^{1,2}, <u>M.Patanen¹</u>, O. Travnikova¹, C. Nicolas¹, H. Ågren², K. Ueda⁴, and C. Miron^{1,5}

¹Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France ²Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden

³College of Electronics, Communication and Physics, Shandong University of Science and Technology, Qingdao, 266590 Shandong, China

⁴Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

⁵Extreme Light Infrastructure – Nuclear Physics (ELI-NP), 'Horia Hulubei' National Institute for Physics and Nuclear Engineering, 30 Reactorului Street, RO-077125 Măgurele, Jud. Ilfov, Romania

ABSTRACT

A double-slit experiment reveals the dual nature of electrons : when they are shot trough closely spaced narrow slits, they form an interference pattern to a detector behind the slits as if they would have travelled through both slits i.e. behaved like waves [1]. However, if there is information available of which slit the electron has traversed, the interference pattern disappears. The essence of Einstein-Bohr's debate about wave-particle duality was whether a momentum transfer between a particle and a slit could give the « which-path » infromation, and thus destroy the interference pattern [2]. However, in order to measure the recoil of a slit, the slits should move independently. This recoiling double-slit experiment has been realized at PLEIADES beamline by resonant X-ray photoemission from molecular oxygen [3]. Oxygen molecule offers a unique « quantum workbench » to materialize this gedanken experiment with two different scenarios : geometries near equilibrium internuclear distance of O atoms (coupled slits) and in a dissociative state far away from equilibrium internuclear distance (decoupled slits). Interference between emitted resonant Auger electrons is observed in the former case, while the electron momentum transfer to independently moving O atoms quenches the interference in the latter case. Momentum transfer is seen in our experiment as Doppler labelling of the counter-propagating atomic slits, and the survival and the disappearance of the interference pattern is in full agreement with Bohr's complementarity.

- 1. C. Jönsson Z. Phys. 161, 454–74 (1961).
- 2. N. Bohr in *Quantum Theory and Measurement*, edited by J. A. Wheeler and W. H. Zurek, Princeton : Princeton University Press, 1983, pp. 9–49.
- X.-J. Liu, Q. Miao, F. Gel'mukhanov, M. Patanen, O. Travnikova, C. Nicolas, H. Ågren, K. Ueda, and C. Miron, *Nature Photonics (2014) doi:10.1038/nphoton.2014.289.*

Gas-phase Ion-molecule Chemistry: An Experimental Study of CH₃⁺ + CH₄

<u>A. Lopes¹</u>, C. Romanzin¹, B. Cunha de Miranda¹, J. Žabka², M. Polášek², D. Ascenzi³, A. Cernuto³, C. Alcaraz^{1,4}

¹LCP, UMR8000 du CNRS, Université Paris-Sud, Orsay- France
 ²J. Heyrovski Institute of Physical Chemistry of the ASCR, Prague- Czech Republic
 ³Atomic & Molecular Physics Lab., University of Trento- Italy
 ⁴Synchrotron SOLEIL, L'Orme des merisiers, St Aubin, France

ABSTRACT

The methyl carbocation is a reactive species which has been detected in a lot of gaseous environments fed by high energy sources such as the interstellar medium, planetary ionospheres as well as laboratory plasmas for methane conversion into higher hydrocarbons for instance. His reactivity with several hydrocarbons is well-known for the ground state [1-3], whereas only few data about the reactivity of excited CH_3^+ ions are available in the literature although excited species are common in planetary atmospheres and plasmas. Here we report on experiments where CH_3^+ ions are generated via direct photoionization of the methyl radical, formed in a supersonic beam by pyrolysis of CH_3NO_2 , thus allowing the production of CH_3^+ with a controlled degree of internal excitation when the photon energy is tuned between 9.8 and 12.5 eV.

Branching ratios and absolute reaction cross-sections have been obtained for the $CH_3^+ + CH_4$ reactive system. Reaction dynamics and dependence on the vibrational excitation of the parent ion will be discussed on the basis of the CH_3^+ cation's excitation distributions measured for photon energies between 10 and 13.25 eV by the PEPICO (Photoelectron Photoion Coincidence) method using the DELICIOUS III spectrometer of the SAPHIRS experiment. In this experiment, we collect all the photoelectrons and measure their kinetic energy in order to derive the distribution of internal energy of the parent ion CH_3^+ by the following equation: $hv - IP = E_c(e^-) + E_{int}(CH_3^+)$. We found that, regardless on the photon energy, a ground state population of CH_3^+ is produced and that, by increasing the photon energy, an additional population of very excited CH_3^+ ion is formed.

The results obtained on the SAPHIRS experiment confirmed the conclusions derived from the reactivity studies on CERISES at SOLEIL and LCP. At the LCP, parent cations CH_3^+ are formed by electron impact on two precursors, CH_4 or CH_3CI . We discovered that two different populations of CH_3^+ are formed depending on the choice of the precursor. When CH_4 is used, the reactivity observed corresponds to CH_3^+ parent ions merely at its ground state, close to what we observe at SOLEIL at 10 eV photon energy, whereas if CH_3CI is used, an additional component of the reactivity is observed stemming from excited CH_3^+ parent ions close to what we observe for 12 eV photon energy. For future reactive studies of CH_3^+ with other hydrocarbons targets at SOLEIL, this will allow us to prepare the experiments at LCP by searching what products would appear in the reaction of excited CH_3^+ cations, saving a considerable amount of time during the runs at SOLEIL.

Roger P. Clow, J.H.F., Ion-cyclotron resonance study of the kinetic energy dependance of ion-molecule reactions rates. Int. J. Mass Spec. Ion Phys., 1970. 4: p. 165-179.

^{2.} Fred P. Abramson, J.H.F., Ion-Molecule Reactions of Methane. J. Chem. Phys, 1966. 45(6): p. 1925-1931.

^{3.} Z. Herman, P.H., A. Lee, R. Wolfgang, *Direct mechanism of reaction* $CH_3^+ + CH_4 = C_2H_5^+ + H_2$. J. Chem. Phys., 1969. **51**: p. 454-455.

Rotational Doppler Effect

F. Gel'mukhanov

Royal Institute of Technology, School of Biotechnology, Division of Theoretical Chemistry & Biology, Roslagstullsbacken 15 S-106 91 Stockholm, Sweden

ABSTRACT

X-ray spectroscopy being one of the main tools to study electronic structure was recognized also as an powerful technique which shed light on nuclear dynamics. It was found recently that the rotational Doppler effect [1] in X-ray spectroscopy being natural fingerprint of nuclear motion gives deep insight in molecular nuclear dynamics [2] in bound and dissociative states. The Doppler labeling of the fragments of the dissociation together with the frequency controlled duration of X-ray scattering provides direct and detailed information about the potentials and dynamics in repulsive states. Recently discovered the rotational Doppler effect [1,2,3,4] in X-ray ionization gives site selective information about the valence molecular orbitals[3]. The Doppler splitting of X-ray resonances [5] gives also an inique tool to study the nonequibrium distributions over translational and rotational degrees of freedom [6,7]. The Doppler control of the amount of which path information allowed us recently to attack the background problem of the wave particle duality in Young's double slit experiment [4]. We demontrate at first time the rotational Doppler effect in high energy Auger spectra of CO and show the quantum correlation of rotational and translational degrees of freedom [7].

- 1. Y.-P. Sun, C.-K. Wang, and F. Gel'mukhanov, Phys. Rev. A 82 052506 (2010).
- T.D. Thomas, E. Kukk, K. Ueda, T. Ouchi, K. Sakai, T.X. Carroll, C. Nicolas, O. Travnikova, and C. Miron, Phys. Rev. Lett. 106, 193009 (2011)
- C. Miron, Q. Miao, C. Nicolas, J D. Bozek, W. Andralojc, M. Patanen, G. Simoes, O. Travnikova, H. Ågren and F. Gel'mukhanov, Nat. Communi., 8, 3816 (2014)
- 4. Q. Miao, O. Travnikova, F. Gel'mukhanov, V. Kimberg, Y.-P. Sun, T. D. Thomas, C. Nicolas, M. Patanen, and C. Miron, Phys. Rev. Lett., submitted.
- 5. S. Gavrilyuk,, Y.-P. Sun, S. Levin, H. Agren and F. Gelmukhanov, Phys. Rev. A 81, 035401 (2010).
- M. Simon, R. Puttner, T. Marchenko, R. Guillemin, R. K. Kushawaha, L. Journel, G. Goldsztejn, M. N. Piancastelli, J. M. Ablett and J.-P. Rueff and D. Ceolin, Nat. Commun. 5, 4069 (2014).
- 7. D. Ceolin, J.-C. Liu, V. Vaz da Cruz, H. Agren, J. Pascal Rueff, R. Puttner, T. Marchenko, R. Guillemin, R. K. Kushawaha, L. Journel' M. N. Piancastelli, M. Simon, and F. Gel'mukhanov (in manuscript)

New Information on HC₃N⁺ using Synchrotron and Laser-based Photoelectron Studies

S. Boyé-Péronne

Institut des Sciences Moléculaires d'Orsay CNRS & Université Paris-Sud, 91405 Orsay Cédex

ABSTRACT

Cyanoacetylene, HC_3N , is the first member of the cyanopolyyne family which exhibits two triple bonds of different nature (C=C and C=N). It presents a fundamental interest for the electronic structure of linear and extended π systems such as polyynes C_{2n}H₂ and cyanopolyynes HC_{2n+1}N. This molecule has been identified in the interstellar medium, in comets, and it is an important constituent of Titan's atmosphere. It can be photoionized in the upper atmosphere of this satellite where its cation contributes to the ionospheric chemistry. Few spectroscopic studies have been performed on the cation electronic structure up to now^{1,2,3} since this compound is not commercial and needs to be synthesized prior to any experiments.

To improve the spectroscopic knowledge of this important cation, high-resolution photoelectron studies have been performed using two vacuum ultraviolet (VUV) radiation sources. Threshold-PhotoElectron Spectroscopy experiments have been carried out between 93000 and 175000 cm⁻¹ with the CERISES set-up on the DESIRS beamline of SOLEIL. New information has been assessed on the vibronic structure of HC3¹⁴N⁺ cation and its ¹⁵N isotopologue with a typical resolution of 20 cm⁻¹, allowing to resolve for the first time the complex pattern of the $B^{+2}\Pi$ electronic state⁴.

Different fragmentation channels consecutive to dissociative ionization have been observed and the corresponding apparition thresholds have been measured.

Complementary experiments have been performed with the VUV lasers of the CLUPS laser plateform of Paris-Sud University on two selected electronic states, $X^{+2}\Pi$ and $B^{+2}\Pi$. Pulsed-Field Ionization Zero-Kinetic-Energy (PFI-ZEKE) photoelectron spectra have been recorded for the ¹⁴N and ¹⁵N isotopologues with a typical resolution of 2 cm⁻¹. Accurate values of the adiabatic ionization potential, of the spin orbit coupling constant and of vibrational mode energies of the $X^{+2}\Pi$ ground state have been determined⁵.

All of these results are supported by complete active space second order perturbation theory calculations (CASPT2) to describe the multiconfigurational character of the excited electronic structure of HC_3N^+ .

- 1. C. Baker and D.W. Turner, Proceeding of the Royal Society A. 308, 19-37 (1968).
- S. Leach *et al.*, *J. Chem. Phys.* **140**, 174305 (2014).
 H. Okabe and V.H. Dibeler, *J. Chem. Phys.* **59**, 2430-2435 (1973).
- 4. A. Desrier et al., J. Phys. Chem. A. to be submitted (2015).
- 5. B. Gans et al., J. Phys. Chem. A. to be submitted (2015).

Ultrafast Dynamics and Electronic State - Lifetime Interferences in Chlorine-containing Molecules

<u>G. Goldsztejn^{1,2}</u>, T. Marchenko^{1,2}, R. Guillemin^{1,2}, L. Journel^{1,2}, R.K. Kushawaha^{1,2}, R. Püttner³, D. Céolin⁴, M.N. Piancastelli^{1,2,5} and M. Simon^{1,2,4}

¹ CNRS, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, F-75005, Paris, France

² Sorbonne Universités, UPMC Univ Paris 06, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, F-75005, Paris, France

³Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
 ⁴ Synchrotron SOLEIL, l'Orme des Merisiers, F-91192, Gif-sur-Yvette Cedex, France
 ⁵ Department of Physics and Astronomy, Uppsala University, SE-75120, Uppsala, Sweden

ABSTRACT

Ultra-fast photodissociation in chlorine-containing molecules has been known for more than twenty years [1,2].

While the first observations were made after photoexcitation of the CI L shell, the study of nuclear motion in these molecules has been recently extended to deep shells by means of Resonant Inelastic X-ray Scattering (RIXS) in the tender x-ray region (2–12 keV) [3,4,5].

A new experimental station [6] dedicated to HArd X-ray PhotoElectron Spectroscopy (HAXPES), has been mounted on the GALAXIES beamline of the synchrotron SOLEIL.

Using this setup, we have studied the electronic relaxation of HCl and CH₃Cl [7] after Cl 1s excitation under resonant Raman conditions, i.e. with total instrumental resolution below the natural line width of the decay features.

In particular, we were able to observe nuclear dynamics on the 1-femtosecond time scale using the 'core-hole clock approach' [8].

These measurements also allowed us to unravel subtle phenomena as electronic statelifetime interferences, which were also observed in RIXS [9] and in Argon using HAXPES [10]. We present a 'simple model' simulation, based on a theoretical model [11], which reproduces well the electronic state-lifetime interferences in both HCl and CH_3CI .

- 1. H. Aksela, et al., Phys. Rev. A., 41 (1990), 11, pp. 6000-6005.
- 2. O. Bjorneholm et al., Phys. Rev. Lett., 79 (1997), 17, pp. 3150-3153.
- M. Simon, L. Journel, R. Guillemin, W. C. Stolte, I. Minkov, F. Gel'mukhanov, P. Salek, H. Ågren, S. Carniato, R. Taïeb, A.C. Hudson, and D.W. Lindle, *Phys. Rev. A*, 73(2006),020706.
- 4. T. Marchenko *et al*, *J. Chem. Phys.*, **134** (2011), 144308
- L. El Khoury et al., J. Chem. Phys, **136** (2012), 024319.
 D. Céolin et al., J. of Elect. Spectro. and Rel. Ph., **190** (2013) 188.
- 7. M. N. Piancastelli, G. Goldsztejn, T. Marchenko, R. Guillemin, R. K. Kushawaha, L. Journel, S. Carniato, J-P. Rueff, D. Céolin and M. Simon, J. Phys. B, 47 (2014), 124031.
- 8. F. Gel'mukhanov and H. Ågren, Phys. Rep., 312(1999), 87.
- 9. M. Kavčič, M. Žitnik, K. Bučar, A. Mihelič, S. Carniato, L. Journel, R. Guillemin, and M. Simon, Phys. Rev. Lett., 105 (2010), 113004
- 10. D. Céolin et al., Submitted (2014).
- 11. G. B. Armen, J. C. Levin and I. A. Sellin, Phys. Rev. A., 53 (1996), 2,pp. 772-784.

X-ray Photoionization of Atomic Oxygen lons

<u>B. M. McLaughlin^{1, 2}, J. M. Bizau^{3, 4}, D. Cubaynes^{3, 4}, S. Guilbaud³, C. Blancard⁵, M. M. Al Shorman³, I. Q. Ababneh⁶ and M. F. Gharaibeh³</u>

¹Centre for Theoretical Atomic, Molecular and Optical Physics (CTAMOP)

School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, UK

²Institute for Theoretical Atomic and Molecular Physics (ITAMP)

Harvard Smithsonian Center for Astrophysics, MS-14 Cambridge, MA 02138, USA

³Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS UMR 8214

Université Paris-Sud, Bat. 350, F-91405 Orsay cedex, France

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

⁵CEA-DAM-DIF, Bruyères-le-Châtel, F-91297 Arpajon Cedex, France

⁶Department of Physics, Jordan University of Science and Technology, Irbid 22110, Jordan

ABSTRACT

Synchrotron light sources are presently producing detailed absolute cross section measurements on highly charged ions in the K-shell region, as previously only theoretical results were available in this x-ray region. An overview will be given of the symbiotic and synergistic relationship between theory and experiment for support of the ongoing experimental effort at the SOLEIL light source with special emphasis on the atomic oxygen iso-nuclear sequence in the x-ray region [1,2]. Fundamentally this species is one of the most important astrophysical atomic iso-nuclear sequences and widely used to calibrate a wealth of x-ray spectra taken by current satellites such as Chandra and XMM-Newton. This work is a follow-up to our most recent successful study of the atomic nitrogen iso-nuclear sequence [3,4,5], another extremely important astrophysical species, in the x-ray region. Detailed cross-section comparisons will be presented at the workshop between theory and experiment for the atomic oxygen iso-nuclear sequence and several other important astrophysical ions will be discussed.

- 1. B. M. McLaughlin, J. M. Bizau, D. Cubaynes, M. M. Al Shorman, S. Guilband, I. Sakho, C. Blancard, and M. F. Gharaibeh, J. Phys. B: At. Mol. Opt. Phys. 47 115201 (2014)
- 2. B. M. McLaughlin, J. M. Bizau, D. Cubaynes, M. M. Al Shorman, S. Guilband, C. Blancard, M. M. Al Shorman, I Q Ababneh and M. F. Gharaibeh, J. Phys. B: At. Mol. Opt. Phys. in preparation
- 3. M. F. Gharaibeh et al J. Phys. B: At. Mol. Opt. Phys. 44 175208 (2011)
- 4. M. M. Al Shorman et al J. Phys. B: At. Mol. Opt. Phys. 46 195701 (2013)
- 5. M. F. Gharaibeh et al J. Phys. B: At. Mol. Opt. Phys. 47 065201 (2014)

High Density THz Frequency Comb Produced by Coherent Synchrotron Radiation

<u>S. Tammaro^{a,b}</u>, O. Pirali^{a,c}, P. Roy^a, J.-F. Lampin^d, G. Ducournau^d, A. Cuisset^b, F. Hindle^b, G. Mouret^b

^aSynchrotron SOLEIL, L'Orme des Merisiers, St-Aubin BP48, 91192 Gif-sur-Yvette, France ^bLPCA, 189A Avenue Maurice Schumann, 59140 Dunkerque, France ^cISMO, CNRS-Université Paris-Sud, 91405 Orsay, France ^dIEMN, Avenue Poincaré-Cité Scientifique, 59652 Villeneuve D'Ascq, France

ABSTRACT

The AILES beamline at synchrotron SOLEIL has been designed to provide a light source covering the complete infrared (IR) range with an extension in the **THz domain**.

We have performed the **first heterodyne study** which consists of mixing (on Schottky diode mixer) the broadband synchrotron source with a well-defined electronic signal (harmonics of a local oscillator) and detecting the intermediate frequency (IF) in the low frequency range using a spectrum analyser. Preliminary tests in the 200 GHz and 400 GHz band have demonstrated that a greatly improved spectral resolution (typically down to few KHz) can be achieved. We extended the study in the 600 GHz band for Low-Alpha, 8-bunches and single-bunch mode using a fast bolometer for both: mixing the synchrotron source with the local oscillator in the heterodyne experimental setup, and for a direct detection of synchrotron radiation without the mixer.

This experiment allowed us to **characterize the synchrotron beam** with a resolution never achieved before. We show that for all storage modes cited above, the so-called "continuum" synchrotron radiation is actually composed of several discrete features having ultra-fine structures composing a well-defined, high spectral density THz frequency comb.

The heterodyne detection technique has also been applied to high resolution gas phase spectroscopy. Several pure rotational lines of acetonitrile (CH₃CN) around 200 GHz have been recorded and compared to a 30 MHz convoluted spectrum.

REFERENCES

[1] Barros et al. , Review Scientific Instruments (RSI), 84,033102, (2013)

PARALLEL SESSION

Electronic & Magnetic Property of Matter, Surfaces and Interfaces

ECOLE POLYTECHNIQUE – AUDITORIUM BECQUEREL

Chairpersons: Antonio TEJEDA and Matteo d'ASTUTO

IT-09	Infrared near-field imaging and spectroscopy with broadband sources <i>Y. De Wilde</i>
OC-30	One dimensional π -conjugated band dispersion in ordered polymeric chains Y. Fagot-Revurat
OC-31	Coexistence of metallic and semiconducting nanoribbons on a continuous graphene layer <i>A. Celis</i>
OC-32	Orientational tuning of the two-dimensional electron gases at the low-index surfaces of $SrTiO_3$ <i>T.C. Rödel</i>
OC-33	In depth atomic structure of the pentacene/Cu(110) interface in the monolayer coverage regime: Theory and X-ray diffraction results <i>M. Sauvage</i>
IT-10	Magnetic cooling at molecular level: Two case studies by XAS and XAMCD investigation <i>M. Affronte</i>
OC-34	Direct determination of the chemical ordering of Co1.5Fe1.5Ge epitaxial thin films <i>A. Bataille</i>
OC-35	Laser induced dynamics in FeRh <i>F. Pressacco</i>
OC-36	Investigation of the magnetic spin structure with X-ray absorption spectroscopy in transmission mode <i>K. Chen</i>
OC-37	XMCD at Co and Fe L2,3 edges of photomagnetic Co/Fe dinuclear complex <i>F. Sadaf</i>

Infrared Near-field Imaging and Spectroscopy with Broadband Sources

Y. De Wilde

Institut Langevin, ESPCI-ParisTech and CNRS, 1, rue Jussieu, 75238 Paris Cedex 05, France yannick.dewilde@espci.fr

ABSTRACT

Scattering type near-field scanning optical microscopy (s-NSOM) can typically measure superresolved images of the sample at a single wavelength. To generalize the concept, we have developed a versatile infrared s-NSOM which operates with broadband sources, allowing one to perform imaging and Fourier transform infrared (FTIR) spectroscopy in the near-field. Two configurations will be discussed in our presentation.

The first one, is based on the thermal emission produced by the sample itself, which is scattered in the near-field with a tip, in a configuration called thermal radiation scanning optical microscopy (TRSTM). We have recorded images and FTIR spectra of materials which support surface phonon polaritons [1,2]. We show that the TRSTM probes both the spatial and frequency dependence of the electromagnetic local density of states (LDOS), and that the thermal emission is in this case quasi-monochromatic in the near-field, in striking contrast with blackbody-like far-field thermal emission spectra.

The second configuration utilizes the high brightness infrared source of AILES beamline at the synchrotron SOLEIL, which is focused on the scattering tip while it scans the surface of the sample, or when a FTIR spectrum is recorded at a fixed position. The probe has allowed one to record super-resolved images and spectra at infrared wavelengths [3]. Preliminary results have also been obtained in the terahertz range, which are sufficient to clearly demonstrate that super-resolution is also accessible in this spectral range using our approach.

REFERENCES

[2] Babuty, A., Joulain, K., Chapuis, P.-O., Greffet, J.-J., De Wilde, Y., "Blackbody Spectrum Revisited in the Near Field", Physical Review Letters **110**, 146103 (2013).

[3] Peragut, F., Brubach, J.B., Roy, P., De Wilde, Y.

^[1] De Wilde, Y., Formanek, F., Carminati, R., Gralak, B., Lemoine, P.-A., Mulet, J.-P., Joulain, K., Chen, Y., Greffet, J.-J., "Thermal radiation scanning tunnelling microscopy", Nature **444**, 740 (2006).

[&]quot;Infrared near-field imaging and spectroscopy based on thermal or synchrotron radiation"

Applied Physics Letters 104, 251118 (2014).

One Dimensional π-Conjugated Band Dispersion in Ordered Polymeric Chains

G.Vasseur¹, <u>Y. Fagot-Revurat¹</u>, M. Sicot¹, B. Kierren¹, D.Malterre¹,
G. Galeotti², J. Lipton-Duffin², L. Cardenas², F.Rosei²,
M. Di Giovannantonio³, G. Contini³, P. Lefevre⁴, F. Bertran⁴,
V. Meunier⁵, D. Perepichka⁶

 ¹Institut Jean Lamour, Université de Lorraine - CNRS, Vandoeuvre-les-Nancy, France
 ²Institut National de la Recherche Scientifique, Varennes, Canada ;
 ³Istituto di Struttura della Materia, CNR, Roma, Italy ;
 ⁴Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Gif sur Yvette, France ;
 ⁵Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, New York, United States;
 ⁶Department of Chemistry and Centre for Self-Assembled Chemical Structures, McGill University, Montreal, Canada.

ABSTRACT

Graphene-like 2D organic materials can be grown and confined onto suitable surfaces depositing and activating selected molecules with different strategies in order to be employed as active media in organic electronics devices. In this respect, the surface-confined polymerization is a very promising bottom-up approach that allows the creation of layers with desired architectures and tunable optical or electronic properties. The most successful method used to obtain ordered polymers on surfaces in ultra-high vacuum is based on the Ullmann coupling reaction, producing covalently linked networks starting from aryl halide precursor molecules [1,2]. A surface-catalyzed dehalogenative polymerization has been recently evidenced for the (1,4)-dibromobenzene (DBB)/Cu(110) interface coupling structural and spectroscopic measurements [3]. In the submonolayer range, an organometallic phase is obtained for room-T deposition evolving into planar one dimensional polymeric structures of poly-para-phenylene (PPP) above 200°C. Therefore, we have investigated the structural and electronic properties of (DBB,DIB)/Cu(110) interfaces in the submonolayer range combining LEED, STM/STS, HR-XPS and ARPES measurements on the CASSIOPEE beamline. On the one hand, ARPES intensity maps allowed us to identify a quasi-one dimensional graphene-like π- band as a consequence of the polymerization process with a direct HOMO-LUMO band gap of 1.15 eV and a metallic character [4]. On the other hand, STS conductance maps evidence confinement of LUMO states above the Fermi level for short oligomers decreasing below the Fermi level for the "long" polymers in perfect agreement with ARPES data. The metallic character is shown to originate from a substantial substrate/polymer interaction well described by our DFT calculations. These results will be discussed in the general context of inorganic/organic interfaces and molecular nanoelectronics.

- [1] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M.V. Peters and S. Hecht, Nature Nanotech. 2, 687-691 (2012);
- [2] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A.P. Seitsonen, M. Saleh, X. Feng, K. Mullen and R. Fasel, Nature 466, 470-473 (2010);
- [3] M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas, Y. Fagot Revurat, A. Cossaro, A. Verdini, D.F. Perepichka, F. Rosei and G. Contini, ACS Nano 7, 8190 (2013); ACS Nano 8, 1969 (2014);
- [4] G. Vasseur et al., in preparation (2014).

Coexistence of Metallic and Semiconducting Nanoribbons on a Continuous Graphene Layer

<u>A. Celis</u>^{1,2}, I. Palacio², N. Maya², A. Gloter², A. Zobelli², M. Sicot⁴, D. Malterre⁴, M. S. Nevius³, C. Berger³, W. de Heer³, E.H. Conrad³, A. Taleb-Ibrahimi², A. Tejeda^{1,2}

¹Laboratoire de Physique des Solides, UMR CNRS 8502, Université Paris Sud. 91405 Orsay, France
 ²Synchrotron SOLEIL, Saint-Aubin, 91192 Gif-sur-Yvette, France
 ³ School of Physics, The Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA
 ⁴Institut Jean Lamour, BP 70239, F-54506 Vandoeuvre-lès-Nancy, France

ABSTRACT

Graphene nanoribbons (GNRs) with armchair edges are expected to display tunable bandgaps, a property required in order to build electronic devices. This gap strongly depends on the fine control of ribbon width and thus by the edge regularity of the ribbon at an atomic level, which cannot be attained even by state-of-the-art lithography. By combining lithography and annealing, artificial facets are obtained on a SiC(0001) surface; subsequently by confined controlled sublimation, nanoribbons with well-defined edges can be produced on these artificial facets^{1,2}. A deep study of these GNRs structure was necessary to relate its atomic and electronic properties. In this work we present a thorough morphological characterization of these ribbons by Scanning Tunneling Microscopy (STM), High Resolution cross-sectional Transmission Electron Microscopy (HR-XTEM) and correlate it to Angle Resolved Photoemission Spectroscopy (ARPES)^{3,4}. Our results indicate the presence of both metallic and semiconducting behavior on a continuous graphene layer whose electronic properties depend directly on their atomic structure, and are in agreement with our DFT numerical simulations⁴.

- 1. M. Sprinkle et al. Nature Nanotech. 5, 727 (2010)
- 2. W. de Heer et al. Proceedings of the National Academy of Sciences of the United States of America, 108, 41 (2011)
- 3. J. Hicks et al. Nature Physics. Vol. 9, 49 (2013)
- 4. I. Palacio et al. (submitted).

Orientational Tuning of the Two-dimensional Electron Gases at the Low-index Surfaces of SrTiO₃

<u>T.C. Rödel</u>^{1,2}, C. Bareille¹, F. Fortuna¹, F. Bertran², P. Le Fèvre², T. Maroutian³, P. Lecoeur³, M. Gabay⁴, M.J. Rozenberg^{4,5}, A. Santander-Syro¹

¹CSNSM. Université Paris-Sud and CNRS/IN2P3. Bâtiments 104 et 108. 91405 Orsav cedex. France ²Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP48, 91192 Gif-sur-Yvette, France ³Institut d'Electronique Fondamentale, Université Paris-Sud and CNRS, Bâtiment 220, 91405 Orsay, France ⁴Laboratoire de Physique des Solides, Université Paris-Sud and CNRS, Bâtiment 510, 91405 Orsay, France ^bDepartamento de Física–IFIBA Conicet, FCEN, UBA, Ciudad Universitaria P.1, 1428, Buenos Aires, Argentina

ABSTRACT

Two-dimensional electron gases (2DEGs) in SrTiO₃ have been studied extensively in the last decade after its discovery at the LaAlO₃/SrTiO₃ interface by Ohtomo & Hwang¹. This heterostructure displays many fundamentally interesting properties, such as field-effect induced insulator-to-superconductor transitions², magnetism³ and the coexistence of magnetism and superconductivity⁴.

clarify the microcopic electronic structure of the То 2DEG. we conducted angle resolved-photoemission spectroscopy (ARPES) experiments of a closely related system: the 2DEG at the surface of SrTiO₃. Our group studied the 2DEGs at various different surface orientations of SrTiO₃ (as well as KTaO₃) at the Cassiopée beamline at Synchrotron Soleil.^{5,6,7,8}

Recent results⁸ demonstrate that the electronic structure of the 2DEG at the surface of SrTiO₃ (Fermi surfaces, subband masses and orbital ordering) can be tuned by confining the electrons at different surface orientations. This occurs because the crystallographic symmetries of the surface and subsurface planes and the effective electron masses along the confinement direction influence the symmetry of the electronic structure and the orbital ordering of the t_{2g} manifold. Remarkably, our analysis of the data also reveals that the carrier concentration and thickness are similar for all three surface orientations, despite their different polarities. The orientational tuning of the microscopic properties of two-dimensional electron states at the surface of SrTiO₃ echoes the tailoring of macroscopic (e.g., transport) properties reported recently in LaAIO₃/SrTiO₃ (110) and (111) interfaces, and is promising for searching new types of two-dimensional electronic states in correlated-electron oxides.

- 1. A. Ohtomo and H.Y. Hwang, Nature 427, 6 (2004)
- 2. A.D. Caviglia et al., Nature 456, 624 (2008)
- 3. A. Brinkman et al., Nature Mater. 6, 493 (2007)
- 4. D.A. Dikin et al., Phys. Rev. Lett. 107, 056802 (2011) 5. A.F. Santander-Syro et al., Nature 469, 189 (2011)
- 6. A.F. Santander-Syro et al., Phys. Rev. B 86, 121107 (2012)
- 7. C. Bareille *et al.*, *Sci. Rep.* **4**, 3586 (2014) 8. T.C. Rödel *et al.*, *Phys. Rev. Applied* **1**, 051002 (2014)

In Depth Atomic Structure of the Pentacene/Cu(110) Interface in the Monolayer Coverage Regime: Theory and X-ray Diffraction Results

<u>M. Sauvage-Simkin^a</u>, A. Coati^b, Y. Garreau^{c,b}, A. Vlad^b, K. Müller^d, A. Bendounan^b and A. Kara^e

a) Synchrotron SOLEIL and UR1-CNRS, Saint Aubin BP 48, 91192 Gif-sur-Yvette Cedex, France, associate to IOM-CNR

b) Synchrotron SOLEIL, Saint Aubin BP 48, 91192 Gif-sur-Yvette Cedex, France,

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

d) Surfaces and Thin Films group Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands,

e) Department of Physics, University of Central Florida, Orlando, Florida 32816, United States

ABSTRACT

The interfaces between π -conjugated molecules and noble metal substrates have been the subject of many experimental and theoretical studies. For the pentacene (Pn)/copper couple, long-range ordered molecular arrays have been observed on Cu(110)^{1,2} by Low Energy Electron Diffraction and Scanning Tunneling Microscopy. Ab-initio calculations have confirmed the changes in the electron density occurring in Pn/Cu(110)³ and distortions in the molecule and substrate upper layers have been proposed, however, no direct determination of the actual atomic displacements had been attempted. In the present study, the atomic structure of the Pn/Cu(110) interface for coverages at and just below one monolayer has been determined by in-situ Grazing Incidence X-ray Diffraction (GIXD), performed on the ultra-high vacuum diffractometer of beamline SixS (Soleil Synchrotron) and supported by state-of-the-art DFT calculations⁴ (fig. 1). The in-depth sensitivity of GIXD allows to track the adsorption induced distortions down to the fifth substrate layer. The magnitude of the atomic displacements, found equivalent for the two coverages under investigation, is a signature of the strength of the molecule/substrate interaction with significant charge transfer.



Fig.1: (left) top an side view of the molecule adsorption geometry from DFT calculations; (right) rod 0 2 L: clean surface (black squares), 0.6MLPn/Cu (red squares),1MLPn/Cu (blue circles), fit with refined DFT model (blue line)

REFERENCES

1 S. Söhnchen, S. Lukas, G. Witte, J. Chem. Phys. 121 (2004) 525

2 K. Müller, A. Kara, et al. Phys. Rev. B 79 (2009) 245421

K. Müller et al. J. Phys. Chem. C, 116 (2012) 23465
 M. Sauvage-Simkin, A. Coati, Y. Garreau, A. Vlad, K. Müller, A. Bendounan, A. Kara, J. Phys. Chem. C, in press
Magnetic Cooling at Moleclar Level: Two Case Studies by XAS and XAMCD Investigation

V. Corradini¹, A. Ghirri¹, A. Candini¹, R. Biagi^{1,2}, U. del Pennino^{1,2}, V. De Renzi^{1,2}, E. Otero³, P. Ohresser³, T. N. Hooper⁵, R. Inglis⁴, E. K. Brechin⁴, E. McInnes⁵ and <u>M. Affronte^{1,2}</u>

¹S3 Centre, Institute Nanoscience - CNR, via G. Campi 213/A, 41125 Modena (I).
 ²Dipartimento di Fisica, Università di Modena e Reggio Emilia via G. Campi 213/A, 41125 Modena (I).
 ³Synchrotron SOLEIL, L'Orme des Merisiers, 91120 Saint-Aubin (F).
 ⁴School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, EH93JJ, UK
 ⁵School of Chemistry and Photon Science Institute, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

ABSTRACT

Proving the preservation of functionality at the molecular scale is still a major challenge, both for the choice of suitable derivatives and protocols and for the employed experimental tools and methods. By using a combined scanning probe (AFM and STM) and spectroscopic methodology (XPS, XAS and XMCD) we show that two families of molecules, namely Fe14 and Gd₄M₈ derivatives (with $M=Zn^{2+}$, Ni²⁺) are robust molecular units which preserve their electronic, magnetic and thermodynamic properties when deposited on a metallic surface. Namely we measured entropy variation DeltaS=[S(6T)-S(0T)] exceeding 8R (20 J kg⁻¹ K⁻¹) at 4K in isolated Gd₄N₈ molecules dispersed on Au(111) surface and show a viable route to exploit large magnetocaloric effect at single molecule level.



REFERENCES

 V. Corradini, A. Ghirri, A. Candini, R. Biagi, U. del Pennino, G. Dotti, E. Otero, F. Choueikani, R. J. Blagg, E. J.L. McInnes, M. Affronte Advanced Materials 25, 2816–2820 (2013), DOI: 10.1002/adma.201205257
 V.Corradini, A.Ghirri, A. Candini, R. Biagi, U. del Pennino, V. De Renzi, G. Dotti, E. Otero, T. N. Hooper, R. Inglis, E. K. Brechin and M.

V.Corradini, A.Ghirri, A. Candini, R. Biagi, U. del Pennino, V. De Renzi, G. Dotti, E. Otero, T. N. Hooper, R. Inglis, E. K. Brechin and M. Affronte Adv. Funct.Mat <u>24, 30, p</u>. 4782–4788, 2014 doi: **10.1002/adfm.201400460** (2014).

Direct Determination of the Chemical Ordering of Co_{1.5}Fe_{1.5}Ge Epitaxial Thin Films

A. Neggache^{1,2}, <u>A.M. Bataille³</u>, F. Porcher³, A. Vlad², A. Coati², Y. Garreau², F. Bertran², P. Lefevre², T. Hauet¹ and S. Andrieu¹

1 Département P2M, Institut Jean-Lamour, Nancy, France 2 Synchrotron Soleil, Saint-Aubin, France 3 Laboratoire Léon Brillouin, CEA Saclay, France

ABSTRACT

One of the main issue in spintronics is to finalize the concept of non-volatile memory. While the storing and reading functions can be satisfactorily achieved using trilayers made of two magnetic layers separated by a non-magnetic one (either metallic or insulating), the writing function requires more efficient ways of manipulating the layer magnetizations than the conventional ones based on magnetic fields. This can be done using the spin transfer torque phenomenon¹, which consists in switching the magnetization by flowing a spinpolarized current through the memory element. The first experimental realizations were obtained more than a decade ago², but the critical currents were much too high to allow integration in realistic devices. Several routes can be envisioned³ to lower the critical current: increasing the spin-polarization of the current, lowering the magnetic damping, switching the magnetic anisotropy from in-plane to perpendicular⁴. A key point is thus to find materials which fulfill all these requirements at once. A class of materials looks particularly promising: the Heusler alloys⁵, of which a fair number has been theoretically predicted as half metallic, i.e. fully spin polarized at the Fermi level.

We focus here on one of these materials, Co_{1.5}Fe_{1.5}Ge (CFG). We have epitaxially grown CFG thin films onto MgO substrates by MBE, and thoroughly characterized them, notably by directly measuring their spin polarization by spin-resolved photoemission. Together with magneto-transport experiments, these measurements evidence that our films are not half metallic, the spin polarization being only 25 %. The question is now whether this property is intrinsic or only observed in our samples, which may deviate from the ideal material. In particular, chemical ordering is expected to have a dramatic influence on spin polarization. To determine it precisely, we performed anomalous X-ray diffraction measurements on the SIXS beamline, which 2+2 axes setup suppress the need for geometrical corrections. Using standard crystallographic procedures, we were able to refine the occupancy of each of the 3 crystallographic sites with a precision of 2% and to unambiguously conclude that our epitaxial CFG films exhibit the nominal Heusler crystallographic atomic distribution, making the low spin-polarization an intrinsic property of the material. By demonstrating that high quality crystallographic data can also be obtained on thin films, and used to perform full structure determination, this work also opens new opportunities for X-ray diffractometry.

REFERENCES

5 T. Graf, C. Felser, S. S. P. Parkin, Progress in Solid State Chemistry 39, 1 (2011)

¹ J.C. Slonczewski. J. Mag. Mag. Mat. 159, L1 (1996) 2 J.A. Katine & al, Phys. Rev. let. 84, 3149 (2000)

³ M.D. Stiles, A Zangwill, Phys. Rev. B 66 (1), 014407

⁴ S. Mangin, D. Ravelosona, J.A. Katine, M.J. Carey, B.D. Terris, E.E. Fullerton, Nat. Mater. 5, 210 (2006)

⁶ A. Neggache, T. Hauet, F. Bertran, P. Le Fèvre, S. Petit-Watelot, T. Devolder, P. Ohresser, P. Boulet, C. Mewes, S.Maat, J. R. Childress, and S. Andrieu, Appl. Phys. Lett 104 252412 (2014)

Laser Induced Dynamics in FeRh

F. Pressacco¹, V. Uhlir², A. Nicolaou¹, F.Sirotti¹

¹Synchrotron SOLEIL, BP 48, Saint-Aubin, F91192 Gif sur Yvette, FRANCE ²University of California San Diego, California, USA

ABSTRACT

The FeRh system shows a first order transition from an Anti-ferromagnetic (AFM) phase at room temperature to a Ferromagnetic phase above 400 K. The change in the magnetic order results in a net change of the magnetization from zero to 1.2 kA/m[1]. This is an uncommon behavior for a magnetic system in which a decrease of the magnetization is observed upon heating.

We investigate the changes induced by the phase transition in the valence band by means of angle-resolved photo-electron spectroscopy (ARPES) [2]. We were able to isolate a clear signature in the valence band of the magnetic phase and to use it to follow the evolution of the magnetization dynamics in an IR pump- SR probe experiment performed at TEMPO beamline.

REFERENCES

1. S. O. Mariager, F. Pressacco, et Al Phys. Rev. Lett., 108(1):087201 (2012)

2. A. X. Gray, D. W. Cooke, et Al Phys. Rev. Lett., 108:257208 (2012)

Investigation of the Magnetic Spin Structure with X-ray Absorption Spectroscopy in Transmission Mode

K. Chen

Synchrotron SOLEIL, L'orme des Merisiers, Saint Aubin – BP48, 91192 Gif-sur-Yvette Cedex

ABSTRACT

Magnetic spin structures are often investigated with STXM, PEEM and scattering. Is it possible to investigate the magnetic spin structures using x-ray absorption spectroscopy (XAS), or can we get the information of the spin structures from the shape of the XAS? Here from simulation and experimental results of DyCo3 and DyCo4 alloy film, we show the possibility to get extra information of magnetic structures from XAS in transmission mode. By comparing the experimental and simulation results of transmission and absorption cross section, different domain structures ((a): randomly, (b) parallel connection and (c) series connection) are determined as shown below. This method is applied to determine the real spin structures in DyCo3 and DyCo4 at different temperatures.



XMCD at Co and Fe L_{2.3} edges of Photomagnetic Co/Fe Dinuclear Complex

<u>F. Sadaf¹</u>, M.-A. Arrio¹, A. Juhin¹, E. Koumousi^{2,3}, C. Mathonière², R. Clérac³, E. Otero⁴, P.Ohresser⁴, 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 Sadaf.fatima@impmc.upmc.fr

ABSTRACT

The nanoscale magnetic materials are potential candidates for energy efficient, photoswitchable molecule-based information storage [1]. Recently, a dinuclear molecule, labelled (1) in the following, has been synthesized [2]. It is built from Fe(III) cyanides and Co(II) ions and it can be seen as the elementary motif of the Co-Fe Prussian Blue Analogues (PBA). The molecule (1) is the first dinuclear complex to exhibit thermal and photomagnetic bistablility. In this talk, we present XMCD results obtained on (1) as well as on the Fe and Co precursors that are the building blocks for (1).

We have performed X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at Fe and Co L_{2.3} edges on the DEIMOS beamline at SOLEIL. The photomagnetic transition in Co-Fe Prussian Blue analogues (PBA) is a complex phenomenon that has been observed in 3D systems and other low dimensional systems. It has never been measured on systems as small as (1). The main question behind this work is to determine how the photomagnetic transition is governed by either the local electronic structure of the individual ions or by the metal-to-metal electron transfer in Fe-CN-Co linkages. XMCD at Fe and Co L_{2.3} edges was measured as a function of temperature ranging from 300K to 4K to follow the thermally induced charge transfer between Fe(III)-Co(II) paramagnetic pair and the Fe(II)-Co(III) diamagnetic pair. At 4K, (1) is irradiated by a 660 nm laser and switches to the Fe(III)-Co(II) paramagnetic pair. The reversibility of the charge-transfer has been measured by warming (1) to 300 K. The detailed interpretation of the XAS and XMCD data was achieved using Ligand Field Multiplet calculations. Fe^{III} and Co^{III} ions were found to possess large orbital magnetic moments compared to the spin magnetic moments. These exceptionally large orbital magnetic moments are crucial in the charge transfer mechanism and in its coupling to the crystal structure.

REFERENCES

6. J. Kim, S. Han, In-Ku Cho, K. Y. Choi, M. Heu, S. Yoon, B. J. Suh, Polyhedron, 2004, 23, 1333-1339.

^{1.} O. Sato, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2004, 5, 3, 2013-223.

^{2.} E. S. Koumousi, I. R. Jeon, Q. Gao, P. Dechambenoit, D. N. Woodruff, P. Merzeau, L. Buisson, X. Jia, D. Li, F. Volatron, C. Mathonière, J. Am. Chem. Soc. 2014, 136, 15461-15464.

D. Li, R. Clérac, O. Roubeau, E. Harte, C. Mathonière, R. Le Bris, and S.M. Holmes, J. Am. Chem. Soc, 2008, 130, 252-258.
 Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière, and S. M. Holmes, Angew Chem., 2010, 49, 3752-3756.
 D. Siretanu, D. Li, L. Buisson, D. M. Bassani, S. M. Holmes, C. Mathonière, and R. Clérac, Chem. Eur. J., 2011, 17, 11704-11708.

PARALLEL SESSION

Matter & Material Properties: Structure, Organization, Characterization, Elaboration ECOLE POLYTECHNIQUE – AUDITORIUM GAY-LUSSAC

Chairpersons: Judith MONNIER and Sandra NINET

IT-11	About nuclear fuels on MARS <i>P. Martin</i>
OC-38	The local environment of substitutional Al ³⁺ in goethite probed by XANES and first-principles calculations <i>M</i> .Ducher
OC-39	Tracking the chemical composition of embedded magnetic nanowires by X- ray absorption spectroscopy <i>A. Novikova</i>
OC-40	In situ anomalous X-ray scattering: chemical order in Ag-M nanoparticles during growth and annealing <i>A. Lemoine</i>
OC-41	The new RICS-MCD end-station at GALAXIES: A photon-in, photon-out tool to probe magnetism under extreme conditions using hard X-rays <i>J.M. Ablett</i>
IT-12	Anomalous single crystal diffraction technique: The ideal tools to investigate the Cu/Zn disorder in kesterite photovoltaic compound <i>A. Lafond</i>
OC-42	Laue diffraction microscopy on French CRG-IF BM32 at ESRF J.S. Micha
OC-43	In situ combined synchrotron X-ray diffraction and wafer curvature measurements on chalcogenide films <i>T. Ouled-Khachroum</i>
OC-44	Mechanical study of metallic thin films under controlled biaxial deformation <i>R. Guillou</i>
OC-45	Ammonia monohydrate at high pressure <i>J.A. Queyroux</i>

IT-11

About Nuclear Fuels on MARS

P. Martin¹, R. Bès^{1,4}, E. Geiger¹, V. Pennisi¹, P. Matheron¹, Y. Pontillon¹, B. Arab-Chapelet², M. Rivenet³, P.-L. Solari⁴, S. Schultig⁴, C. Martial¹, M. Strach¹, R. Belin¹, D. Prieur⁵

1CEA, DEN, DEC, Centre d'études nucléaires de Cadarache, Saint Paul Lez Durance, 13108, France 2 CEA, DEN, DRCP, Centre d'études nucléaires de Marcoule, Bagnols-sur-Cèze, 30207, France 3 Univ. Lille Nord de France, Unité de Catalyse et de Chimie du Solide, UCCS, UMR CNRS 8181, ENSCL-USTL, BP 90108, 59652 Villeneuve d'Ascq Cedex, France

4 Synchrotron SOLEIL, Ligne de lumière MARS, L'Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

5 European Commission, Joint Research Centre, ITU, P.O. Box 2340, 76125 Karlsruhe, Germany

ABSTRACT

This talk aims to show through 3 recent experiments performed on MARS beamline¹, how XAS is a powerful tool to enhance the understanding of processes encountered in nuclear fuels. The first study was carried out in the framework of the development of advanced UO_2 nuclear fuels. Currently, the most efficient use of the UO₂ fuel in reactor is mainly limited by the evolution of its microstructure and the behavior of volatile fission (Cs, Te, I) products during irradiation. Recent experimental studies have shown that the temperature and oxygen potential (P₀₂) conditions for Pressurized Water Reactors may stabilize some gaseous species of iodine (like Tel_{2(g)}) which are quite corrosive towards the cladding. One solution would be to use an oxygen-buffered UO₂ fuel, functioning in a P_{O2} range where the corrosive specie $Tel_{2(a)}$ is destabilized in favor of the non-corrosive specie $Csl_{x(a)}$. The redox couples of niobium [(Nb₂O₅/NbO₂) and (NbO₂/NbO)] seem quite promising but their efficiency are directly linked to the composition of the micrometer size precipitates present in the fuel after fabrication. Thanks to µ-XAS measurements performed at the Nb K-edge, the ratio between the different Nb redox phases present in the precipitates as a function of different manufacturing conditions were obtained as well as the chemical form of niobium in solution in the UO₂ matrix. A solubility model of niobium in UO₂ is currently built from the crossinterpretation of the µ-XANES data and the electronic µ-probe measurements performed on the same samples.

In the second illustration, HERFD^2 measurements performed at Th, U, Pu and Am L₃ edges in binary and ternary mixed oxides compounds using the crystal analyzer spectrometer (CAS) will be detailed. The improvement in resolution obtained using CAS has been notably used to obtain accurate evaluation of mixed valence state ratio in the framework of fundamental actinide chemistry and in the more applied context of the development of U-Pu-O type nuclear fuels with high contents of plutonium for the IVth generation nuclear reactors.

The third study deals with the understanding of the fission products (FP) behaviours and release mechanisms during a severe accident occurring in a Nuclear Power Plant. Among the FP created, molybdenum is one of the most important as its oxygen potential during irradiation is very close to the UO₂ fuel. μ -EXAFS results obtained at Mo K-edge allowed us to follow as a function of annealing conditions (reproducing a severe accident scenario) the Mo chemical state in both the precipitates and the UO₂ matrix. These measurements were performed on a UO₂ fuel doped with 11 stable FP during fabrication³ to prepare future experiments on irradiated fuels.

^{1.} I. LLorens et al., Radiochimica acta 102, 957-972, (2014).

^{2.} High Energy Resolution Fluorescence Detection

^{3.} Details about these samples are available in E. Geiger abstract submitted to SUM2015.

The Local Environment of Substitutional Al³⁺ in Goethite Probed by XANES and First-principles Calculations

M. Ducher¹, D. Cabaret¹, M. Blanchard¹, R. Nemausat¹, D. Vantelon²

¹ IMPMC, UPMC, UMR 7590, case 115, 4 place Jussieu, 75005 Paris ² Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint-Aubin

ABSTRACT

X-ray absorption near edge structure (XANES) spectroscopy is a technique of choice to obtain qualitative information on the local structure/environment. However, experimental data, often, require simulations to be interpreted.

Previous study [1] on aluminous goethite, which is an Al-bearing iron oxyhydroxide known to substitute Fe with Al up to 33 mol % [2], showed differences in the edge region of the spectra as the concentration of Al changed. A lack of resolution did not allow studying the pre-edge region. The work suggested that numerical simulations could explain the spectral features.

We present new Al K-edge XANES spectra of aluminous goethites and diaspore, which is the aluminium end-member of the partial solid solution goethite/diaspore, at the LUCIA beamline at synchrotron SOLEIL (Figure 1). The experimental spectra display a change in absorption peaks intensity at both the pre-edge and the edge region. First principles calculations done with the XSpectra code [3], based on density functional theory (DFT) in a

pseudopotential plane wave framework [4], allow gaining insights on the local environment of Al when the Al concentration changes.

The comparison between theoretical and experimental spectra and the investigation of the structure give information about the AI distribution. Furthermore, the calculated spectra reproduce successfully the experimental trends. Therefore, the structural modifications can be linked to the spectral differences. In particular, the larger A-B peak spacing in diaspore, compared to AI-bearing goethites, is found to be related to the first cation neighbours around the absorbing AI atom. The decrease of the B/A intensity ratio with increasing AI concentration is due to smaller cation-cation distances and the distortion of the



Figure 1: Experimental AI *K*-edge XANES spectra of aluminous goethites and diaspore.

 $AIO_3(OH)_3$ octahedron. Finally, the decrease in intensity of the pre-edge features with increasing AI concentration are compared with partial density of states (PDOS) calculations and is unambiguously related to the decrease in the number of Fe atoms.

This study illustrates the advantages of combining numerical simulations and experimental measurements to extract information about the local structure from the spectra that goes beyond the usual speciation information extracted from XANES.

- 1. P. Ildefonse and D. Cabaret and P. Sainctavit, Physics and Chemistry of Minerals 25, 112-121 (1998).
- 2. R. W. Fitzpatrick and U. Schwertmann, Geoderma 27, 334-347 (1982)
- 3. C. Gougoussis and M. Calandra, A. P. Seitsonen and F. Mauri, Physics Review B 80, 075102 (2009)
- 4. P. Giannozzi et al., Journal of Physics: Condensed Matter 21, 395502 (2009)

Tracking the Chemical Composition of Embedded Magnetic Nanowires by X-ray Absorption Spectroscopy

A. Novikova^{1, 3}, F. Vidal², Y. Zheng², D. Demaille², Y. Dumont³, E. Fonda¹

 Synchrotron Soleil, L'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette
 INSP, UPMC, CNRS UMR7588, 4 place Jussieu, 75005 Paris
 Groupe d'Etude de la Matière Condensée,(GEMaC), Université de Versailles Saint-Quentin en Yvelines-CNRS UMR8635, 78035 Versailles

ABSTRACT

Study of objects smaller than 10 nm with new properties becomes more and more common and reported. Atomic resolution can be obtained with scanning tunnelling or transmission electron microscopy¹. This does not mean that all pertinent information on a system may be obtained by microscopy even in the best cases. We present here an example of how x-ray absorption spectroscopy (XAS) easily helps in determining the chemical composition of elements constituting the nano objects, including objects too small or disordered to be studied by X-ray diffraction or other scattering techniques.

Embedded magnetic nanowires of Co, Ni and Co_xNi_{1-x} alloys, with diameters in the 3-6 nm range, have been produced by self-assembling in CeO₂ and SrTiO₃ matrices and their growth by Pulsed Laser Deposition has been already described^{2,3}. While Ni crystallizes in the fcc lattice in both CeO₂ and SrTiO₃, Co presents a mixture of hcp and fcc unless the fcc phase is stabilized by alloying with Ni². The Co structures in CeO₂ exhibit also a certain reversibility upon oxidation and reduction that has been followed in situ revealing the presence of a four-fold coordinated Co(II) nano oxide phase⁴, surprisingly, conversion of hcp into fcc or vice-versa does not occur during the thermal cycles.



Finally, we will present some recent results on the Fe:SrTiO₃ system, illustrating how XAS can provide useful feedback in the elaboration of original nano-systems. It will be shown that we can span from diluted Fe in SrTiO₃ to mixtures of Fe(II) oxide and Fe bcc, depending on the growth conditions. Such finding may help to rationalize recent puzzling results published in the literature.

REFERENCES

1. A. W. Robertson, and J. H. Warner, Nanoscale 5, 4079 (2013).

- 2. F.J. Bonilla, A. Novikova, F. Vidal, Y. Zheng, E. Fonda, D. Demaille, V. Schuler, A. Coati, A. Vlad, Y. Garreau, M. Sauvage-Simkin, Y. Dumont, S. Hidki and V.H. Etgens, ACS Nano 7, 4022 (2013).
- 3. F. Vidal, Y. Zheng, J. Milano, D. Demaille, P. Schio, E. Fonda, Vodungbo, B., Applied Physics Letters 95,152510 (2009).
- 4. A. Novikova et al., to be submitted to J. Appl. Phys.

In–situ Anomalous X-ray Scattering: Chemical Order in Ag-M Nanoparticles during Growth and Annealing

<u>A. Lemoine^{1, 2*}</u>, Z. Kataya¹, P. Andreazza¹, C. Andreazza-Vignolle¹, Y. Garreau^{2, 3}, A. Coati², J. Creuze⁴, B. Legrand⁵

1 Centre de Recherche sur la Matière Divisée, Univ. Orléans, CNRS, 45071 Orléans 2 Synchrotron Soleil, L'Orme de Merisiers, Saint Aubin, 91192 Gif-sur-Yvette 3 Laboratoire Matériaux et Phénomènes Quantiques, Univ. Paris Diderot-Paris 7, CNRS, 75205 Paris 4 SP2M, ICMMO, Univ. Paris-Sud , 91405 Orsay Cedex 5 SRMP/DMN, SRMP-DMN, CEA Saclay, 91191 Gif-sur-Yvette Cedex * asseline.lemoine @cnrs-orleans.fr

ABSTRACT

Nanoalloys are investigated for their promising physico-chemical properties, which are governed by the nanoparticles (NPs) size, morphology, structure, and also by the chemical order. In the case of bi-metallic systems, several chemical orders as alloyed, core-shell, or Janus (etc...) particles can be achieved, allowing to tune the NPs properties [1]. Therefore, it is essential to develop experimental methods that provide morphological and structural information with a chemical selectivity, in order to access to the degrees of mixing or segregation of the metals in the NPs.

Anomalous X-ray scattering is a non-destructive technique that can be used to study insitu and in real-time the morphological and structural evolutions of nanoalloys. This method exploits the variations of the contribution of one element to the scattering as a function of the energy close to an absorption edge. Thus, combining Anomalous Small and Wide Angles Xray Scattering in Grazing Incidence (A-GISAXS [2] and A-GIWAXS [3]), the chemical order in supported nanoalloys can be investigated.

This experimental work focuses on systems whose phase diagrams present immiscibility gap (AgCo, AgPt). Supported bi-metallic NPs, smaller than 3nm, are prepared by UHV deposits on an amorphous substrate. Thanks to this method, the NPs composition can be controlled, and the metals can be deposited simultaneously or sequentially [4]. The aim of this work is to investigate the stability of the NPs and their equilibrium configurations during their growth and annealing, in order to determine the impact of the competition between the thermodynamic principles and experimental kinetic parameters.

In situ A-GISAXS and A-GIWAXS measurements were performed on the SixS beamline at synchrotron SOLEIL. The experimental setup allows achieving a significant anomalous effect despite the weak amount of matter involved.

The AgCo NPs exhibit a core-shell configuration after deposition at RT, with a Co core and an Ag shell, that tends to a metals segregation towards Janus NPs during annealing.

The AgPt NPs have the tendency to a more or less homogeneous mixing (which is favoured by annealing) as a function of the composition and the deposition mode. In particular, the $Ag_{0.5}Pt_{0.5}$ NPs of 3nm are close to an ordered nanoalloy at 400°C.

REFERENCES

3. T. U. Schülli, et al., Phys. Rev. B, 71, 035326 (2005)

I. R. Ferrando, J. Jellinek, R. L. Johnston, Chemical Reviews, 108, 3, (2008)

^{2.} P. Andreazza, H. Khelfane, O. Lyon, C. Andreazza-Vignolle, A. Ramos, and M. Samah, Eur. Phys. J., 218, 231-244 (2012)

^{4.} Z. Kataya, Thèse de Doctorat de l'Université d'Orléans (2013)

The New RIXS-MCD End-station at GALAXIES: A Photon-*in*, Photon-*out* Tool to Probe Magnetism under Extreme Conditions using Hard X-rays

<u>J.M Ablett¹, </u>A. Juhin,² N. Mas,^{1,2} N. Daffé, ^{1,2} Ph. Sainctavit,² A. Shukla, P. Ohresser^{1,2} J.-P. Rueff ^{1,3}

 ¹ Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint Aubin, France.
 ² Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, CNRS & Université Pierre et Marie Curie, 75005 Paris, France
 ³ Laboratoire de Chimie Physique – Matière et Rayonnement, CNRS & Université Pierre et Marie Curie, 75005 Paris, France

ABSTRACT

XMCD is a powerful and 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 the $L_{2,3}$ edges of 3d ions), it enables the determination of the spin and orbital magnetic moments by means of sum rules. Magnetic moments of 3d transition metal ions are generally studied at the metal $L_{2,3}$ absorption edges using soft X-rays. Nevertheless, the short penetration depth is not compatible with demanding sample environments such as high pressure or liquid cells. At the metal *K* edge, the weak XMCD signal and the absence of spin-orbit split edges do not llow, for now, a detailed quantitative interpretation. Recently, a novel approach, which consists in coupling XMCD and RIXS spectroscopies at the *K* edge of 3d ions, has been proposed.¹ It consists in combining XMCD and 1s2p RIXS at the *K* pre-edge (i.e., $1s^2 2p^6 3d^N 1s^1 2p^6 3d^{N+1} 1s^2 2p^5 3d^{N+1}$), using one photon *in* and one photon *out*.

A RIXS-MCD experiment has been set up on the GALAXIES beamline using a quarter wave plate to obtain circular polarized light. We have successfully measured the bidimensional RIXS-MCD map at the Fe *K* pre-edge in magnetite. Technical aspects of the experiment will be presented together with the first results. Possible applications offered by the combination of RIXS and XMCD in the hard x-ray range will then be discussed.

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)

Figs: Left: RIXS-XMCD Set-up at the GALAXIES beamline. Right: RIXS 2D difference polarisation map highlighting the dichroic nature of the pre-edge (1s→3d) peak in magnetite (Fe3O4) in a magnetic field of ~0.5 Tesla.





Anomalous Single Crystal Diffraction Technique: The Ideal Tools to Investigate the Cu/Zn Disorder in Kesterite Photovoltaic Compound

A. Lafond

Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France

ABSTRACT

Global environmental concerns and the continuous increase of the demand for energy urge to develop renewable energy technologies. Solar energy is the most abundant, inexhaustible and clean of all the renewable energy. Harvesting less than 0.05% of the solar energy coming on the earth in one year will be enough to cover the annual energy consumption. Photovoltaic (PV) conversion, which is the direct conversion of sunlight into electricity, is the finest ways to harness the solar energy.

According to all analysts, silicon-based PV panels will continue to own the biggest part of the market share [1], but there is also room for thin-film solar cells which can save both materials and energy during the fabrication process. The development of the two mature thin film technologies is questionable because of the scarcity and/or the toxicity of the involved chemical elements, such as In, Ga, Cd and Te. In that context, Cu₂ZnSnS₄ derivative materials (CZTS) have been proposed as earth-abundant and non toxic thin-film solar cell absorbers. Energy conversion efficiencies up to 12.6 % have already been reported [2]. For further improvement, detailed insight into the crystal structure is crucial.

After a controversy period about the real structure of Cu_2ZnSnS_4 it has recently been demonstrated by several groups that this compound adopts the kesterite structure (space group *I*-4) and not the stannite one [3]. This structure derives from the cubic sphalerite-ZnS structure-type and corresponds to the alternating sequence of two cationic planes along the c-axis: Cu/Sn located at z=0 and z=1/2 (2a and 2b Wyckoff positions, respectively) and Cu/Zn at z=1/4 and z=3/4 (2c and 2d sites). Nevertheless, some *ab-initio* calculations [4] as well as experimental results [5] indicate the possibility of a Cu/Zn disorder. Unfortunately, Cu and Zn cannot be distinguished by conventional laboratory X-ray diffraction because they have very close atomic scattering factors.

The single crystal resonant diffraction technique (Cristal line at Soleil) has been used to overcome this issue. From a quenched sample such diffraction experiments have demonstrate the occurrence of a full disorder of Cu and Zn in the z = 1/4 and z = 3/4 atomic planes, i.e. a random distribution of Cu⁺ and Zn²⁺ on the 2c and 2d crystallographic sites [6]. The structure, namely disordered kesterite, is then described in the *I*-42*m* space group. In addition, very recent experiments have shown that very long time annealed crystals still present a large level of Cu/Zn disorder.

REFERENCES

- 2 W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, et al., Adv. Energy Mater. 4 1301465 (2014).
- 3 S. Schorr, Sol. Energy Mater. Sol. Cells. 95 1482–1488. (2011).
- 4 S. Chen, J.H. Yang, X.G. Gong, A. Walsh, S.H. Wei, Phys Rev B. 81 245204 (2010).
- 5 X. Fontané, V. Izquierdo-Roca, E. Saucedo, S. Schorr, V.O. Yukhymchuk, et al., J. Alloys Compd. 539 190–194 (2012).

6 A. Lafond, L. Choubrac, C. Guillot-Deudon, P. Fertey, M. Evain, S. Jobic, Acta Crystallographica Section B. 70 390–394 (2014).

¹ D.M. Bagnall, M. Boreland, Energy Policy. 36 4390–4396 (2008).

Laue Diffraction Microscopy on French CRG-IF BM32 at ESRF

<u>J.-S. Micha^{1,4}</u>, O. Robach^{2,4} O. Ulrich^{2,4}, O. Geaymond^{3,4} and F. Rieutord^{2,4}

1 Université Grenoble Alpes/CEA-INAC/ UMR SprAM 5819 CNRS-CEA, F-38000 Grenoble 2 Université Grenoble Alpes/CEA-INAC/ SP2M, F-38000 Grenoble 3 Université Grenoble Alpes/CNRS-Institut Néel, F-38000 Grenoble 4 CRG-IF BM32 at European Synchrotron Radiation Facility, F-38000, Grenoble

ABSTRACT

X-ray scattering experiments on polycrystals at micrometer scale shed new lights on structure and mechanical behavior of unique or assembly of small objects in microelectronics, metallurgy, and fundamental mechanics... Scattering on single crystal is a powerful and advanced structural technique but is generally a tedious task when measuring several Bragg reflections needing time-consuming detector and sample rotations. Applied on micrometric crystals for which orientation is unknown such technique using monochromatic x-ray beam is therefore no longer suitable. Laue diffraction corresponding to the scattering of a white (polychromatic) beam overcomes these limitations. A large number of Bragg reflections is then collected on a 2D detector from a single x-ray shot. After the calibration of the detector position with respect to the sample position, the Laue pattern analysis proceeds with the indexation (Miller indices assignment to each Laue spot) and unit cell refinement (angular distortions only). Laue Diffraction Microscopy allows a fast 2D mapping of grain to grain orientation and strain with a submicrometric spatial resolution (beamsize: 300nmX300nm²). Only few beamlines on 3rd generation synchrotron facilities offer an intense white micro-sized beam dedicated to materials science investigation ex or in situ. On french CRG-IF beamline located at the exit of ESRF's BM32 a Laue Microscope installation performs routinely orientation mapping leading directly to grain shape, phase mapping and localization of orientation/strain gradients (defects) [1]. Depending on the degree of disorder, intragrain local elastic strain variation can be also assessed. Two extensions of the Laue technique are also under development to determine the local full strain tensor [2] (by measuring the energy of Laue spots ranging in 5-22 keV) and the localization of x-ray scattering sources in sample depth (by following the Differential Aperture X-ray Microscopy method [3]).

- O. Robach et al, A tunable multicolour `rainbow' filter for improved stress and dislocation density field mapping in polycrystals using X-ray Laue microdiffraction, Acta Crysta. A 69, 164 (2013)
- 3. B.C. Larson et al, Three-dimensional X-ray structural microscopy with submicrometre resolution, Nature 415, 887 (2002)

^{1.} O. Ulrich et al, A new white beam x-ray microdiffraction setup on the BM32 beamline at the European Synchrotron Radiation Facility, Rev. Sci. Instr. 82, 033908 (2011)

In Situ Combined Synchrotron X-ray Diffraction and Wafer Curvature Measurements on Chalcogenide Films

<u>T. Ouled-Khachroum¹</u>, M.-I. Richard^{1,2}, P. Noé³, C. Guichet¹, C. Mocuta⁴, F. Hippert⁵, O. Thomas¹

 ¹Aix-Marseille Université, CNRS, IM2NP UMR 7334, F-13397 Marseille France
 ²ID01/ESRF, The European Synchrotron, CS 40220, F-38043 Grenoble Cedex 9, France
 ³Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin – BP 48, 91192 Gif-sur-Yvette Cedex, France
 ⁴CEA-LETI, MINATEC campus, 17 rue des Martyrs, F 38054 Grenoble, France
 ⁵LNCMI (CNRS, UJF, UPS, INSA), 25 rue des Martyrs, F 38042 Grenoble Cedex 9, France

ABSTRACT

Phase change memory technology is considered to be one of the most promising alternative technologies for non-volatile embedded resistive memories [1]. Chalcogenide phase change materials (PCM), such as GeTe and Ge₂Sb₂Te₅ (GST), are able to quickly and reversibly switch between an amorphous and a crystalline state with very different optical and electrical properties. The amorphous phase is characterized by a high resistivity and low optical reflectivity and the crystalline phase by a much lower resistivity and higher reflectivity. These properties allowed the integration of such chalcogenide materials in optical storage devices (DVD-RAM) and more recently in non-volatile memory technology (NVM).

Recently, we have followed by mean of *in situ* X-ray diffraction, fast three-dimensional (3D) pole figure [2] and optical curvature measurements [3] the crystallization of amorphous asdeposited thin and ultra-thin (from 100 to 5 nm) chalcogenide (GST) films at the DiffAbs beamline, synchrotron SOLEIL. A newly designed furnace has been developed to allow annealing of the samples, while combining X-ray and optical measurements. The combination of these techniques permits to obtain important insights on the stress buildup and relaxation mechanisms of the thin chalcogenide films as well as an in-depth understanding of the mechanics involved in the amorphous-to-crystal transition.

^{1.} A. Fantini et al., 2010 IEEE International Electron Devices Meeting (IEDM), 2010, pp. 29.21.21-29.21.24.

^{2.} C. Mocuta, M.-I. Richard, J. Fouet, S. Stanescu, A. Barbier, C. Guichet, O. Thomas, S. Hustache, A. Zozulya, and D. Thiaudière, J. Appl. Crystallogr. 46, 1842 (2013).

^{3.} M.-I. Richard, J. Fouet, C. Guichet, C. Mocuta, and O. Thomas, Thin Solid Films 530, 100 (2013).

Mechanical Study of Metallic Thin Films under Controlled Biaxial Deformation

<u>R. Guillou¹</u>, E. Le Bourhis¹, P. Goudeau¹, P.-O. Renault¹, P. Godard¹, D. Faurie², G. Geandier³, C. Mocuta⁴, D. Thiaudière⁴

¹Institut PPRIME – CNRS/Université de Poitiers, Futuroscope, France ²LSPM – Université Paris 13, Villetaneuse, France ³IJL – CNRS/Université de Lorraine, Nancy, France ⁴Synchrotron SOLEIL, DiffAbs, Gif sur Yvette, France

ABSTRACT

Thin film technology is pervasive in microelectronics, optics, magnetic, micro-mechanics. However, the mechanical stability of such nanoscale structure is crucial for applications since it is related to device lifetime. Synchrotron X-ray diffraction (XRD) is a powerful tool to analyse the mechanical behavior of multiphase materials due to its selectivity. Using a biaxial tensile setup developed during an ANR project on the DiffAbs beamline at synchrotron SOLEIL (Figure 1) [1], we performed controlled biaxial deformation tests on composite such as metallic thin films deposited on polyimide substrate (Kapton). Strains analysis of both phases of a W/Cu thin multilayer and of Au thin films have been performed during a biaxial loading using the so-called sin² ψ method. During deformation, the sublayers' Bragg peak shifts are monitored thanks to a 2D detector. The shifts of Bragg peaks are analysed to obtain the lattice strains which are plotted as a function of the macroscopic in-plane strains measured thanks to Digital Image Correlation (DIC). Digital images of the specimen surface were captured with an optical camera fixed under the tensile device. This approach allows for scrutinizing film behavior at elastic-inelastic transition [2].



Figure 1: biaxial tensile setup



Figure 2: Biaxial tensile device set on the goniometer of the DiffAbs beamline at the synchrotron SOLEIL

REFERENCES

 Geandier, G., Thiaudière, D., Randriamazaoro, R. N., Chiron, R., Djaziri, S., Lamongie, B., Diot, Y., Le Bourhis, E., Renault, P. O., Goudeau, P., Bouaffad, A., Castelnau, O., Faurie, D., Hild, F., Rev. Sci. Instrum, 81(2010) 103903
 Djaziri, S., Faurie, D., Renault, P. O., Le Bourhis, E., Goudeau, P., Geandier, G., Thiaudière, D., Acta Mater., 61 (2013) 5067-5077

Ammonia Monohydrate at High Pressure

C. Liu^{1,2}, <u>J.-A. Queyroux</u>¹, K. Beneut¹, G. Le Marchand¹, S. Ninet¹ and F. Datchi¹

 ¹ Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Université Pierre et Marie Curie – Paris 6, CNRS UMR 7590, Paris, France
 ² Institute of Atomic and Molecular Physics, Jilin University, Changchun, 130012, China

ABSTRACT

Knowing the properties of H_2O , NH_3 and their mixtures under high pressure and temperature is important for planetary science because these H-bonded ices are present in Jovian planets and their satellites under a wide range of pressure (P) and temperature (T) conditions. The high P-T properties of the pure ice compounds have been the focus of many investigations, which have revealed a rich polymorphism. In particular, our group has recently shown the existence of superionic and ionic phases of ammonia^{1,2}, which had been previously predicted by first principles calculations^{3,4}. In these phases, proton transfers between molecules give rises to ionic species NH^{4+} and NH^{2-} , which may be relevant to explain the magnetic fields of Neptune or Uranus. By contrast with the pure components, the properties of (H_2O , NH_3) mixtures under extreme P-T conditions have been much less explored although these systems are possibly more relevant for planetary physics.

This presentation will focus on the properties of the ammonia monohydrate (AMH) solid compound, with stoechiometry 1 NH₃:1 H₂O. Experimental high-pressure studies on these systems have been mostly limited to P < 10 GPa and T < 300 K and reveal a rich polymorphism as at least 6 phases are reported. The known phases are all molecular and present heteronuclear O...H-N and N-H...O hydrogen bonds, as encountered in more complex macromolecules such as DNA. Nevertheless, a recent theoretical study⁵ has suggested that AMH transforms into an ionic solid composed of NH⁴⁺ and OH⁻ ions, in a similar fashion as the self-ionization observed in pure ammonia², but at much lower pressures (10 GPa instead of 150 GPa), thus much easier to reach in experiments. To check this surprising prediction, we have performed the first infrared absorption studies of AMH up to 40 GPa at 300 K and 100 K on SMIS beamline and X-ray diffraction experiments over a wide range of pressure and temperature on PSICHE beamline and on ID 27 at ESRF. The molecular/ionic phase transition is indeed observed, as evidenced by the appearance of vibrational modes from NH⁴⁺ and OH⁻ species, but the observed structure is not compatible with the predicted one. We will discuss our results in this presentation.

REFERENCES

4, Chris J Pickard and RJ Needs. "Highly compressed ammonia forms an ionic crystal". In: Nature materials 7.10 (2008), pp. 775–779.

^{1,} S. Ninet, F. Datchi, and A. Saitta. "Proton Disorder and Superionicity in Hot Dense Ammonia Ice". In: *Phys. Rev. Lett.* 108 (16 2012), p. 165702.

^{2,} S. Ninet et al. "Experimental and theoretical evidence for an ionic crystal of ammonia at high pressure". In : Phys. Rev. B 89 (17 2014), p, 174103

^{3,} C. Cavazzoni et al. "Superionic and Metallic States of Water and Ammonia at Giant Planet Conditions". In: Science 283.5398 (1999), pp. 44–46.

^{5,} Gareth I.G. Griffiths et al. "High pressure ionic and molecular crystals of ammonia monohydrate within density functional theory". In: *The Journal of Chemical Physics* 137.6, 064506 (2012).

POSTERS SESSION

List of Student Posters

PO-BH-01	Relation structure-fonction d'une Protéine Périplasmique d'Agrobacterium Tumefaciens Impliquée dans la Virulence <i>A. El Sahili</i>
PO-BH-02	Crystal Stucture of RNaseZ ^L in Saccharomyces cerevisiae <i>M. Ma</i>
PO-BH-03	Structural Study of the Sub-telomeric Tbf1 Protein and its Functional Synergy with Telomeric Rap1 Protein <i>W. Messaoud</i>
PO-BH-04	Regulation of the S. <i>pneumoniae</i> Competence State: Structural Analysis of the ComD-ComE two-component System <i>D. Sanchez</i>
PO-CP-05	Controlling Self-assembly of Ferrofluids during Evaporation in PDMS <i>C. Guibert</i>
PO-CP-06	Study of the Reduction of TiO ₂ Supported Molybdenum Oxide Catalysts by Combining in-situ XANES Spectroscopy at $L_{2,3}$ Edge and DFT Calculation <i>H. Hu</i>
PO-CP-07	Assembly and Disassembly Kinetics of Virus-like Particles Probed by Time-resolved Small-angle X-ray Scattering <i>D. Law-Hine</i>
PO-CP-08	The Torsional Spectrum of Doubly Deuterated Methanol CD ₂ HOH <i>M. Ndao</i>
PO-DM-09	High-resolution Analysis of the v_3 Band of 36 SF $_6$ and New Global Fit of 32 SF $_6$ Parameters Including New $3v_3$ Band Data <i>M. Faye</i>
PO-DM-10	Synchrotron Based High Resolution Study of Protonated Rare Gases in the Far- and Mid-infrared Regions – Dunham Analysis of ArH ⁺ , KrH ⁺ and XeH ⁺ S. Gruet
PO-DM-11	Direct and Dissociative Photoionization Studies of Methylcyanoacetylene (CH $_3C_3N)$ N. Lamarre
PO-EM-12	Investigation of Liquid Ferrofluids with XMCD: Instrumentation and Experiments <i>N. Daffé</i>
PO-EM-13	Combining Mn L- and O K-edge Resonant Inelastic X-ray Scattering for the Study of Orbital Excitations in Multiferroic $TbMnO_3$ J. Feng
PO-EM-14	Ferromagnetic/Organic Interfaces <i>C. Fourmental</i>
PO-EM-15	Unveiling the Magnetic State of Iron in the Superconducting Pressure Region <i>B. Lebert</i>

PO-EM-16	Ab Initio Calculation of K-edge XMCD Spectra <i>N. Mas</i>
PO-EM-17	Orientational Tuning of the Two-dimensional Electron Gases at the Low-index Surfaces of ${\rm SrTiO_3}$ T.C. Rödel
PO-EM-18	XMCD at Co and Fe $L_{2,3}$ edges of Photomagnetic Co/Fe Dinuclear Complex F. Sadaf
PO-EM-19	First Electrical Measurements of MgO-based MTJs with Versatile Variable Temperature Insert <i>M. Studniarek</i>
PO-MM-20	Structure des Aluminosilicates de Plomb Vitreux et Fondus <i>I. Ben Kacem</i>
PO-MM-21	XANES Study of Thermoelectric Skutterudites $Yb_yCo_4Sb_{12}$ (y = 0.10, 0.15, 0.20) <i>M. Benyahia</i>
PO-MM-22	In situ X-ray Study of the Formation of Oxide-supported Gold Nanoparticles using Micelle Nanolithography <i>V. Dhanasekaran</i>
РО-ММ-23	The Local Environment of Substitutional Al ³⁺ In Goethite Probed by XANES and First-principles Calculations <i>M. Ducher</i>
PO-MM-24	Mechanical Study of Multilayered Thin Films under Continuous Controlled Biaxial Deformation <i>R. Guillou</i>
РО-ММ-25	Ammonia Monohydrate at High Pressure J.A. Queyroux
PO-MM-26	Strain State in Ultrathin Metallic Nanowires Vertically Epitaxied In Oxide Matrix V. Schuler
PO-MM-27	Bond Stretching Phonon Softening and Kinks in the Angle-resolved Photoemission Spectra of under Doped $La_{2-x}Ba_xCuO_{4+\delta}$ Superconductors <i>Z. Zhang</i>

Relation structure-fonction d'une Protéine Périplasmique d'Agrobacterium Tumefaciens Impliquée dans la Virulence.

<u>A. El Sahili</u>^{1,2}, M. Ahmar³, C. Virus⁴, S. Planamente^{2,1}, A. Vigouroux¹, B. Guimaraes⁵, M. Aumont-Nicaise⁶, G. Li³, J. Reader⁴, Y. Queneau³, D. Faure² et S. Moréra¹.

1-Laboratoire d'Enzymologie et Biochimie Structurales (LEBS), CNRS, avenue de la terrasse, 91198-Gif-sur-Yvette, France

2-Institut des Sciences du Végétal (ISV), CNRS, avenue de la terrasse, 91198-Gif-sur-Yvette, France 3-Institut de Chimie et de Biochimie Moléculaires et Supramoléculaires, ICBMS, INSA Lyon, UMR 5246, CNRS, Université Lyon 1, INSA Lyon, CPE-Lyon; Bât J. Verne, 20 av A. Einstein, 69621 Villeurbanne, France
4-Department of Cell Biology and Physiology, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA
5-Synchrotron SOLEIL, 91192 Gif sur Yvette, France
6-Institut de Biochimie et de Biophysique Moléculaire et Cellulaire, UMR8619, CNRS, Université Paris-Sud, 91405-Orsay, France

ABSTRACT

Proteine périplamsique AccA d'Agrobacterium tumefaciens

Agrobacterium tumefaciens est une bactérie pathogène de plante qui provoque une maladie dite de la galle du collet caractérisée par la formation de tumeurs au niveau du site d'infection. Seules les bactéries possédant le plasmide Ti, dit de virulence sont pathogènes. Le cycle d'infection est composé de 3 étapes : i) La plante blessée sécrète des composés qui attirent A. tumefaciens et activent des protéines de virulences. ii) Ces protéines vir transfèrent un morceau du pTi appelé T-DNA de la cellule bactérienne vers la cellule de la plante. iii) Les gènes portés par le T-DNA sont exprimés. Ils codent pour des enzymes de biosynthèse d'hormones végétales qui sont à l'origine de la formation de tumeurs qui sont colonisées par les bactéries. Les gènes du T-DNA codent aussi pour des enzymes de biosynthèses de petites molécules appelées opines qui sont utilisées comme nutriments par les bactéries.

Dans le cas de la souche C58 d'*A. tumefaciens*, une opine particulière, l'Agrocinopine A initie la production de signaux quorum sensing qui mènent à la propagation des gènes de virulence. Cette opine diffuse dans le périplasme de la bactérie pathogène. Elle y est reconnue par la protéine périplasmique AccA qui l'amène à un transporteur de type ABC qui l'importe dans la cellule ou elle est utilisée comme source de carbone et de phosphate et déclenche la propagation des gènes de virulence.

Cependant, une autre bactérie, non pathogène, *Agrobacterium radiobacter* K84, produit un antibiotique appelé Agrocine 84. Cette toxine est létale pour A. tumefaciens C58. Elle entre dans la cellule bactérienne via la protéine AccA.

L'objectif a donc été de combiner la détermination structurale de complexes AccA/ligand et étude biochimique de ces interactions pour comprendre la spécificité de la protéine AccA pour ces deux molécules qui ont des structures chimiques très différentes et des activités antagonistes.

Crystal Stucture of RNaseZ^L in Saccharomyces cerevisiae

<u>M. Ma^a</u>, I. Gallay^a, N. Lazar^a, C.Condon^b and H. van Tilbeurgh^a

^aDepartment de Biochimie Biophysique et Biologie Structurale, Institut de Biologie Intégrative de la Cellule, Bât 430,Université de Paris-Sud,91405 ORSAY CEDEX ^bInstitut de Biologie Physico-Chimique, CNRS FRE3630, 75005 PARIS

ABSTRACT

Pre-tRNA requires a process of maturation. While 5'- processing is ubiquitously executed by RNaseP, the RNases that responsibe for the 3'-processing differ from domain to domain even organism. For CCA non-coding tRNAs (and CCA-coding tRNA in Thermo.), RNaseZ crops the 3'-tail after the "Discriminator" nucleotide, then CCA-triples is added to the 3'-end of tRNA by the tRNA nucleotidyl-transferase, then the tRNAs are recognized for subsequently amino-acids transfer.¹²

RNase Z belongs to the β -lactomase superfamily, exist in two forms: RNase Z short expressed in both protokaryotes and eukaryotes, while RNase Z Long express only in eukaryotes. RNaseZs, there is the conserved Histitine motif which contribute to the catalytic center with Zn, and a flexible arm which essential to tRNA binding. The dimer crystal structure of RNaseZs in Bacilus Subtilis shows that the tRNA is catalysed by one of the molecule, but the T-arm is clamped by the other molecule.^{3 4}

RNase Z^{L} is considered to be derived from RNase Z^{s} . Our study shows the crystal structure of the RNase Z^{L} in *Saccharomyces cerevisiae*. The whole the structure contains N-terminal portion and C-terminal portion, each portion contains an obvious β -lactomase core which consists of repeated (anti)parallel β -sheets with inserted α -helix. Flexible arm exist only in Cterminal portion but not in N-terminal, coherent with the primary sequence alignment. Based on this we propose a model of RNaseZ^L/tRNA complex. Instead of processing two tRNA molecules at the same time in RNase Zs dimer, one RNase ZL molecule processes only one tRNA. The tRNA 3'-end insert into the catalytic center of the C-terminal portion exactly. ELAC2, the homolog of RNaseZ in human, is reported to be a susceptible gene to prostate cancer. The structure of RNase Z^L provides a structural basis for drug design.

- 1. Hartmann RK, Gössringer M, Späth B, Fischer S, Marchfelder A. The making of tRNAs and more RNase P and tRNase Z. *Prog Mol Biol Transl Sci.* 2009;85(08):319–68. doi:10.1016/S0079-6603(08)00808-8.
- 2. Redko Y, Li de la Sierra-Gallay I, Condon C. When all's zed and done: the structure and function of RNase Z in prokaryotes. *Nat Rev Microbiol.* 2007;5(4):278–86. doi:10.1038/nrmicro1622.
- 3. Li de la Sierra-Gallay I, Mathy N, Pellegrini O, Condon C. Structure of the ubiquitous 3' processing enzyme RNase Z bound to transfer RNA. *Nat Struct Mol Biol.* 2006;13(4):376–7. doi:10.1038/nsmb1066.
- 4. Li de la Sierra-Gallay I, Pellegrini O, Condon C, Sierra-Gallay I de la, Jeffrey PD. Structural basis for substrate binding, cleavage and allostery in the tRNA maturase RNase Z. *Nature*. 2005;433(February):1–5. doi:10.1038/nature03234.1.

Structural Study of the Sub-telomeric Tbf1 Protein and its Functional Synergy with Telomeric Rap1 Protein

W. Messaoud, S. Miron & M.-H. Le Du

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

ABSTRACT

Telomeres are nucleo-protein structures that constitute the end of eukoryotes linear chromosomes and are crucial for genome integrity [1]. In human, telomeres dysfunctions are associated to cancers and ageing pathologies.

In the yeast Saccharomyces cerevisiae, telomeric DNA is constituted by degenerated TG_{1-3} repeats. **Rap1** protein directly binds the double strand region of these DNA repeats to form telomere first shell assembly (Figure 1), and interacts with protein partners Rif1, Rif2, Sir3 and Sir4 involved in telomeres protection, and negative regulation of lengthening [1]. Telomeres naturally shorten upon cell divisions, and the ultimate barrier against DNA repair machineries involves a functional synergy between Rap1 and the sub-telomeric protein **Tbf1** [2].

Tbf1 is related to TRF1 and TRF2 telomeric proteins from higher eukaryotes, and recognizes DNA sequence T_2AG_3 typical from higher eukaryotes telomeres or yeast sub-telomeric regions. At short telomeres, TG_{1-3} repeats adjoin sub-telomeric T_2AG_3 and Rap1 and Tbf1 come closer.

It has been recently shown that Tbf1 is involved in:

1/ protection of short telomeres against some double strand break repair mechanisms [2];

2/ negative regulation of long telomeres lengthening [3].

Our previous studies of Rap1 architecture allowed us building a first shell telomere assembly (Figure 1) [4,5]. On this basis and using similar approaches, we are now seeking at understanding the structural behaviour of Tbf1 upon its interaction with DNA, how it may interact with Rap1, and how telomere shortening could favour these interactions.

REFERENCES

[1] Giraud-Panis M-J, Pisano S, Benarroch-Popivker D, Pei B, Le Du M-H and Gilson E. (2013) Front. Oncol., 2013, 3, 48. Revue

^[2] Fukunaga K, Hirano Y, Sugimoto K. (2012) Mol Biol Cell. Jan;23(2):347-59.

^[3] Arneric, M., and Lingner, J. (2007) EMBO Rep 8(11), 1080-1085

^[4] Matot B, Le Bihan YV, Lescasse R, Pérez J, Miron S, David G, Castaing B, Weber P, Raynal B, Zinn-Justin S, Gasparini S, and Le Du M-H. (2012) Nucleic Acids Research, 40, 3197-3207.

^[5] Le Bihan Y-V, Matot B, Pietrement O, Giraud-Panis M-J, Gasparini S, Le Cam E, Gilson E, Sclavi B, Miron S, and Le Du M-H. (2013) Acta Cryst., D69, 409-419

Regulation of the S. pneumoniae Competence State: Structural Analysis of the ComD-ComE Two-component System

M. Boudes, <u>D. Sanchez</u>, M. Graille, H. van Tilbeurgh, D. Durand and S. Quevillon-Cheruel

Institut de Biochimie et Biophysique Moléculaire et Cellulaire. Bât 430 -Université de Paris-Sud 11 91405 ORSAY

ABSTRACT

Natural transformation allows genetic exchanges between bacteria and is involved in the evolution and maintenance of their genome. In *Streptococcus pneumonia*, the competence state is transient and requires the expression of dedicated genes. Its regulation depends on the two-component system ComD-ComE. We have addressed the activation pathway of ComE by a structural study combining X-ray and SAXS.

The two domains of ComE, the regulatory REC domain which contain the phosphorylatable D58 and the LytTR effector domain which binds the comcde promoter region, are connected by a flexible linker[1]. We have mimicked the active and non-active forms of ComE by generating the phosphorylated mimetic ComE^{D58E} and the nonphosphorylatable ComE^{D58A} mutants respectively. Full-length ComE^{D58A} crystallized as an atypical dimer via its REC domain which is also seen with the isolated REC^{D58A} and REC^{D58E}. The LytTR domain adopts a tandem arrangement consistent with the two direct repeats of comcde. On the opposite SAXS data showed that ComE^{D58A} is monomeric in solution while ComE^{D58E} dimerizes via the REC domains. The interplay between ComD, ComE and comcde was also investigated. SAXS data analysis on the reconstituted ComD-ComE^{D58A} complex revealed an elongated shaped envelop fitting a dimer of ComD associated with two monomers of ComE. Complexes between LytTR, ComE^{D58A} or ComE^{D58E} and *comcde* are both containing two monomers of protein per DNA duplex. Model deduced from SAXS data suggested that *comcde*-bound ComE^{D58E} forms a compact dimer comparible to the crystal structure of ComE^{D58A} alone while *comcde*-bound ComE^{D58A} adopts different conformations with or without dimer contact. The binding of ComE^{D58E} on *comcde* induces an increased bending angle of the DNA molecule compared to ComE^{D58A} or LytTR.

We propose a mechanistic scenario where the phosphorylated ComE dimer induces an extra bending of *comcde* DNA region allowing the activation of the *com* operon transcription. The shut-off of the competence could be caused by the disruption of ComE dimer.

Boudes, M., Sanchez, D., Graille, M., van Tilbeurgh, H., Durand, D., & Quevillon-Cheruel, S. (2014). Structural insights into the dimerization of the response regulator ComE from *Streptococcus pneumoniae*. *Nucleic Acids Research*, 42(8), 5302– 5313.

Controlling Self-assembly of Ferrofluids during Evaporation in PDMS

<u>C. Guibert^a</u>, J. Perez^b, V. Dupuis^a, V. Peyre^a, J. Fresnais^a

^a Laboratoire Physicochimie des Electrolytes et Nanosystèmes InterfaciauX (PHENIX) UMR 8234 Université Pierre et Marie Curie – CC 51, 4, place Jussieu, 75252 PARIS Cedex 05 – France

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

ABSTRACT

Making magnetic aggregates with controlled shapes and sizes by self-assembly is a challenging task that leads to new materials, which can be useful in microfluidics or microrheology. Such objects can indeed be manipulated with lower magnetic fields than their individual nanocomponents^[1].

In our work, we present an original method to produce a dispersion of spherical aggregates of magnetic nanoparticles (MNPs) in a silicon matrix made of polydimethylsiloxane (PDMS), based on the evaporation of water from a water-in-PDMS emulsion.

In order to get a better comprehension of the mechanisms that take place during the aggregation, we studied the role of different parameters such as the evaporation speed on the dispersion state by various techniques such as Small Angle X-ray Scattering (SAXS) experiments, TEM, and DLS^[2]. We investigated the role of the interparticular interactions by varying the MNPs functionalisation: bare and charged surface (electrostatic repulsion), coating with neutral polymer (steric repulsions) and with various polyelectrolytes (both kinds of repulsions)... Lastly, we will present a kinetics study of the evaporation followed by SAXS and a model that could describe it ^[3].



TEM pictures of different magnetic nanoparticles aggregates obtained in PDMS



Emulsion drying studied by SAXS : formation of aggregates in PDMS

- [1] J. le Digabel, N. Biais, J. Fresnais, J. F. Berret, P. Hersen, B. Ladoux, Lab. Chip 2011, 11, 2630.
- [2] M. Okada, H. Maeda, S. Fujii, Y. Nakamura, T. Furuzono, Langmuir 2012, 28, 9405.
- [3] M. H. Sorensen, J. T. Zhu, R. W. Corkery, R. C. Hayward, P. Č. A. Alberius, Microporous Mesoporous Mater. 2009, 120, 359.

Study of the Reduction of TiO₂ Supported Molybdenum Oxide Catalysts by Combining *in-situ* XANES Spectroscopy at L_{2,3} Edge and DFT Calculation

<u>H. Hu</u>[†], A. Tougerti[†], J.-C. Morin[†], B. Lassalle[‡], D. Vantelon[‡], V.Briois[‡] and S. Cristol^{†,*}

[†]Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Université Lille 1, France [‡]Synchrotron SOLEIL L'Orme des Merisiers, Saint-Aubin - BP 48 91192 Gif-sur-Yvette Cedex, France

ABSTRACT

Supported Molybdenum catalysts are extensively investigated as they are actives for numerous reactions like olefin metathesis and selective oxidation reactions. Furthermore this system (after sulfidation) is also widely used in the hydrotreating industrial processes, which represent 10% of the total world market for catalysts. Hence the improvement of the performance of this class of catalysts is of paramount economic and environmental importance. In recent works, with the combination of XANES spectra (Mo K edge), DFT calculation and modeling XANES spectra using multiple scattering (MS) theory, we were able to draw a clear picture of the structure of the activated catalyst¹. However, electronic and geometric structure adopted by this catalyst during the catalytic reaction is still unknown. Indeed, drastic changes were observed upon reduction of the catalyst with methanol and it was rather complex to distinguish the changes in electronic structure and the changes in the geometry. In order to get more insights on the electronic structure of the system under operando conditions, the reducibility of this catalyst is studied by in-situ XANES at Mo L₂₃ edge (spectra are recorded at LUCIA beamline), Mo K edge (spectra are recorded at SAMBA beamline) and DFT modeling(using VASP code). DFT calculation shows that certain oxygen sites are more likely to be affected during the reaction. Spin density induced by the reduction of the system is localized on Molybdenum atoms (Figure 1). We are also modelling XANES spectra by using multiplet theory (CTM4XAS software) and comparing them to DFT results in order to get more insights into the electronic structure of the reduced Mo species.



Figure 1 Spins density introduced by H₂ adsorption 1. Side view (left) 2. Top view (right), the positions of added hydrogens are indicated by arrows

REFERENCES

1. Tougerti *et al.* "Synergy between XANES Spectroscopy and DFT to Elucidate the Amorphous Structure of Heterogeneous Catalysts: TiO₂-Supported Molybdenum Oxide Catalysts." Angewandte Chemie International Edition 52.25 (2013): 6440-6444.

Assembly and Disassembly Kinetics of Virus-like Particles Probed by Time-resolved **Small-angle X-ray Scattering**

<u>D. Law-Hine</u>[†], M. Zeghal[†], V. Bailleux[†] S. Bressanelli[§], D. Constantin[†] and G. Tresset[†]

[†]Laboratoire de Physique des Solides, Université Paris-Sud, CNRS, 91400 Orsay, France [§]Institut de Biologie Intégrative de la Cellule (I2BC), CEA, CNRS, Université Paris-Sud, 91198 Gif-sur-Yvette. France

ABSTRACT

Viral particles are natural nanomaterials that can serve as excellent nano-building blocks for the fabrication of innovative nanostructured materials^{1,2}. Their ability to efficiently package and deliver genomic material also makes them attractive tools for the development of therapeutical strategies. However, there is still much to know about the mechanisms of kinetics of self-assembly of viral proteins simultaneously interacting with their genome.

State-of-the-art techniques such as Time-Resolved Small-Angle X-Ray Scattering (TR-SAXS) enable an in situ vizualisation of the early times of the self-assembly of viral proteins into spherical virus-like particles. Recent studies³ performed with a model of bovine norovirus have shown that this technique allows a reconstruction of intermediates that cooperatively interact to build up a capsid. Here, we present a plant viral system, the Cowpea Chlorotic

Mottle Virus (CCMV), where the same issue is addressed. CCMV is known to be able to efficiently incorporate organic or inorganic materials to make hybrid viruses^{1,4}. Our approach consists in finding the key intermediates that play a central role in the formation of empty capsids before investigating the formation of capsids packaging nanoparticles.

better $\overline{\widehat{A}}$ 105 We build models to provide а understanding of the processes governing the selfassembly in order to extract information about the nature of the intermediates, their structure and their typical lifetime. These models are based on global fitting with TR-SAXS data collected at synchrotron radiation facilities (SOLEIL and ESRF). We are also interested in the disassembly of capsids that proceeds in longer times and may follow or not the same kinetics pathway. About 30 min at 20°C are necessary for the disassembly to occur completely, while it takes less than 10s for the proteins to start



Fig. 1: TR-SAXS patterns of self-assembling CCMV capsid proteins.

forming empty capsids depending on our experimental conditions. These findings may help to apprehend the mechanisms of self-assembly for a better control in diverse applications such as drug delivery or for other nanoengineering purpose.

REFERENCES

- 1. S. E. Aniagyei, C. J. Kennedy, B. Stein, D.A. Willits, T. Douglas, M.J. Young, M. De, V.M. Rotello, D. Srisathiyanarayanan, C.C Kao, B. Dragnea, , Nano Lett., 9, 393–398 (2009). Viruses and nanotechnology; Manchester, M., Steinmetz, N. F., Eds.; Springer: Heidelberg, Germany (2009).

4. Y. Hu, R. Zandi, A. Anavitarte, C. M. Knobler, and W. M. Gelbart, Biophys. J., 94, 1428 (2008).

^{3.} G. Tresset, C. Le Cœur, J.-F. Bryche, M. Tatou, M. Zeghal, A. Charpilienne, D. Poncet, D. Constantin, and S. Bressanelli, J. Am. Chem. Soc. 135, 15 373 (2013).

The Torsional Spectrum of Doubly Deuterated Methanol CD2HOH

<u>M. Ndao</u>,¹ L. H. Coudert,¹ F. K. Tchanna,¹ L. Margulès,² L. Manceron,³ and P. Roy³

¹ LISA, UMR 7583, CNRS, Université Paris Est Créteil et Paris Diderot, Créteil, France
 ² Laboratoire PhLAM, UMR 8523, CNRS-Université de Lille 1, Villeneuve d'Ascq, France
 ³ Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France

ABSTRACT

Although the torsional spectrum of several isotopic species of methanol with a symmetrical CH3 or CD3 was analyzed some time ago, it is recently [1], and only for the monodeuterated species, that such an analysis was extended to the case of an asymmetrical methyl group.

In this poster, based on a Fourier transform high-resolution spectrum recorded in the 20 to 670 cm⁻¹ region, the first analysis of the torsional spectrum of doubly deuterated methanol CD₂HOH will be presented. The *Q* branch of many torsional subbands could be observed and their assignment was initiated using a theoretical torsion-rotation spectrum computed with an approach accounting for the torsion-rotation Coriolis coupling and for the dependence of the generalized inertia tensor on the angle of internal rotation [2]. 46 torsional subbands were thus assigned. For 28 of them, their rotational structure could be assigned and fitted using an effective Hamiltonian expressed as a J(J + 1) expansion; and for 2 of them microwave transitions within the lower torsional level could also be included in the analysis [3]. In several cases these analysis revealed that the torsional levels are strongly perturbed [4].

In the poster, the torsional parameters retrieved in the analysis of the torsional subband centers will be discussed. The results of the analysis of the rotational structure of the torsional subbands will be presented and we will also try to understand the nature of the perturbations. At last, preliminary results about the analysis of the microwave spectrum will be presented.

REFERENCES

[2] Lauvergnat, Coudert, Klee, and Smirnov, J. Mol. Spectrosc. 256 (2009) 204.

^[1] El Hilali, Coudert, Konov, and Klee, J. Chem. Phys. 135 (2011) 194309.

^[3] Quade, Lui, Mukhopadhyay, and Su, J. Mol. Spectrosc. **192** (1998) 378.

^[4] Pearson, Yu, and Drouin, J. Mol. Spectrosc. 280 (2012) 119.

High-resolution Analysis of the v₃ Band of ³⁶ SF₆ and New Global Fit of ³² SF₆ Parameters Including New 3v₃ Band Data

M. Faye¹, V. Boudon¹, L. Manceron² and F. Kwabia Tchana³

1. Laboratoire Interdisciplinaire Carnot de Bourgogne - UMR 6303 CNRS–Université de Bourgogne, 9, av. Alain Savary, B.P. 47870, F-21078 Dijon Cedex, France

2. Ligne AILES- Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette Cedex, France. and MONARIS, UMR8233, CNRS-UPMC, 4 place Jussieu, F-75005, Paris.

3. Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris-Est Créteil et Université Paris-Diderot, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France

ABSTRACT

Aiming at a better modeling of the atmospheric absorption of sulfur hexafluoride (SF₆), we recently performed new measurements at the AILES beam line of the SOLEIL synchrotron facility near Paris. Using the IFS125HR interferometer coupled with a cryogenic multiple pass cell [1] containing the SF₆ gas, new spectra have been recorded in the 100–3200 cm⁻¹ wave number range. The optical path length of the light beam was adjusted to 93 m and the SF₆ sample was cooled down to 153 K. The pressure was 1.25 mbar. We could record 17 rovibrational bands of SF₆ in this region with a resolution of 0.0025 cm⁻¹.

These results allowed us to perform the detailed analysis of several bands. Thereby, for the first time, the weak v_3 band of the 36 SF₆ isotopologue (with 0.02% of natural abundance) has been assigned and fitted. We also analyzed in detail the $3v_3$ third stretching overtone of the 32 SF₆ main isotopologue. Including these new parameters of $3v_3$ in the XTDS model [2], we substantially improved the previous global fit [3] of SF₆ parameters. This enables complete modeling of two hot bands $v_3+v_2-v_2$ and $v_3+v_1-v_1$ in the strong absorption region of SF₆ (around the v_3 mode). Other band analyses are also under progress.

REFERENCES

[1] F. K. Tchana, F. Willaert, X. Landsheere, J-M. Flaud, L. Lago, M. Chapuis, Ch. Herbeaux, P. Roy and L. Manceron, "A new, low temperature long-pass cell for mid-infrared to terahertz spectroscopy and synchrotron radiation use", Review ofScientific Instruments, 84, 093101 (2013).

[2] Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov and J-P. Champion, "XTDS and SPVIEW : Graphical tools for the analysis and simulation of high-resolution molecular spectra", Journal of Molecular Spectroscopy 251, 102-113 (2008).
 [3] M. Faye, A. Le Ven, V. Boudon, L. Manceron, P. Asselin, P. Soulard, F. Kwabia Tchana and P. Roy, "High-resolution spectroscopy of

[3] M. Faye, A. Le Ven, V. Boudon, L. Manceron, P. Asselin, P. Soulard, F. Kwabia Tchana and P. Roy, "High-resolution spectroscopy of difference and combination bands of SF₆ to elucidate the v₃ +v₁ -v₁ and v₃ +v₂ -v₂ hot band structures in the v₃ region", Molecular Physics, (2014).

Synchrotron Based High Resolution Study of Protonated Rare Gases in the Far- and Mid-infrared Regions – Dunham Analysis of ArH⁺, KrH⁺ and XeH⁺

<u>S. Gruet^{1,2}</u> and O. Pirali^{1,2}

¹Ligne AILES - Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette Cedex, France. ²Institut des Sciences Moléculaires d'Orsay, UMR 8214, CNRS Université Paris-Sud, F-91405 Orsay, France.

ABSTRACT

Protonated rare gases constitute a unique group of transient molecules which are of importance in ion-molecule reactions studies as well as astrophysical purposes. This has been illustrated by the recent detection of ³⁶ArH⁺ [1] using the Herschel satellite. In contrast the detection of HeH⁺ (having a high importance in the chemistry of the early universe) is still lacking.[2,3] HeH⁺, NeH⁺, ArH⁺, KrH⁺, and XeH⁺ including their isotopic species have been extensively investigated in the millimeter and infrared domains.[4-12] These species are produced in a hollow cathode discharge cell and most of the data from the literature have been obtained thanks to tunable far-infrared techniques (for recording pure rotation transitions in the ground state) and to emission Fourier transform techniques (for studying the rovibrational excited states). On the AILES beamline of SOLEIL we have developed a liquid nitrogen cooled hollow cathode discharge cell to record absorption spectra of reactive species. This new experimental device, coupled with the AILES beamline Fourier transform spectrometer is a powerful tool to record broadband high resolution spectra of molecular ions in the far-infrared. [13] This technique appears to be very complementary to tunable farinfrared laser techniques possessing a higher sensibility but in a much narrower spectral range. In this poster, we will show experimental results and analysis of three protonated rare gases (ArH⁺, KrH⁺ and XeH⁺, including several isotopic species) that we have obtained in the far-infrared (pure rotation) and in the mid-infrared regions (rovibration). The analysis and fits include our new measurements in addition with the literature data. The observation of numerous isotopologues spectra allowed to determine the mass-independent Dunham parameters of the molecule describing the rotational energy levels of each isotopic species with a single set of parameters.[14]

- 1. M. J. Barlow et al. Science, 2013, 342, 1343
- 2. S. Bovino et al. A&A, 2011, 529, A140
- 3. Zinchenko et al. MNRAS, 2011, 415 L78
- 4. P. Bernath and T. Amano, Phys. Rev. Lett. 1982, 48, 20
- 5. M. Wong et al. J. Chem. Phys. 1982, 77, 693
- 6. M. Cueto et al. Aptrophys. J. Lett. 2014, 783, L5
- 7. J. W. Brault and S. P. Davis, Physica Scripta, 1982, 25, 268
- 8. J. W. C. Johns, J. Mol. Spectrosc. 1984, 106 124
- 9. W. C. Bowman et al. J. Chem. Phys. 1983, 79, 4
- 10. Y. Ohtaki et al. J. Mol. Spectrosc. 2001, 210, 271
- 11. S. A. Rogers et al. J. Chem. Phys. 1987, 87, 159
- 12. H. Odashima et al. J. Mol. Spectrosc. 1998, 190 107
- 13. S. Gruet et al. Canadian Journal of Physics, 2013, 91, 937
- 14. R. J. Le Roy, J. Mol. Spectrosc. 1999, 194, 189

Direct and Dissociative Photoionization Studies of Methylcyanoacetylene (CH₃C₃N)

<u>N. Lamarre¹</u>, B. Gans¹, C. Alcaraz^{2,3}, C. Romanzin^{2,3}, B.K. Cunha de Miranda², C. Falvo¹, S. Douin¹, J.-C. Guillemin⁴ and S. Boyé-Péronne¹

 Institut des Sciences Moléculaires d'Orsay, Université Paris-Sud, Orsay
 Laboratoire de Chimie Physique, Université Paris-Sud, Orsay
 Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin
 Institut des Sciences Chimiques de Rennes, Ecole Nationale Supérieure de Chimie de Rennes, Rennes

ABSTRACT

Methylcyanoacetylene (CH₃C₃N) is an astrophysical-relevant molecule detected in molecular clouds [1] and in the atmosphere of Titan [2], the largest Saturn's moon. The interaction of this molecule with the galactic or solar vacuum-ultraviolet radiation leads to direct and dissociative ionization and the resulting cation $CH_3C_3N^+$ and its ionic fragments can participate to the complex carbon chemistry in these media [2]. In order to study the state-specific reactivity of $CH_3C_3N^+$ in the gas-phase, a good understanding of its vibronic structure is required. Prior to the present work, the spectroscopic knowledge of the cation was limited to very few studies, some of them performed in matrices environments: low resolution measurements of the ionization energies had been performed by photoelectron spectroscopy for the first excited electronic states [3,4,5] and some vibrational mode frequencies had been extracted [3,6].

Using the TPES (Threshold-PhotoElectron Spectroscopy) technique and the CERISES experimental setup of the VUV beamline DESIRS at SOLEIL synchrotron, we have recorded for the first time the TPES spectra of the X⁺ ²E \leftarrow X ²A₁, A⁺ ²A₁ \leftarrow X ²A₁ and B⁺ ²E \leftarrow X ²A₁ transitions. In the direct ionization excitation range, the electronic energies of the first three electronic states X⁺ ²E, A⁺ ²A₁ and B⁺ ²E and the vibrational frequency values for several modes have been determined more accurately. In addition, in the higher excitation energy range (>12.4 eV), ion yields for dissociative ionization fragments have been derived. All of these results are supported by *ab initio* calculations.

REFERENCES

3. G. Bieri. et al., "Electronic states of substituted haloacetylene and cyanoacetylene radical cations", Chemical Physics 36, 1979, pp.1-14.

^{1.} N. W. Broten al., "The detection of interstellar methylcyanoacetylene", The Astrophysical Journal 276, 1984, pp. L25-L29

^{2.} V. Vuitton et al., "Ion chemistry and N-containing molecules in Titan's upper atmosphere", Icarus 191, 2007, pp. 722-742

L. Asbrink et al., "0.4 nm He(II) photoelectron spectra of organic molecules Part II. Aza-compounds (C, H, N)", Journal of Electron Spectroscopy and Related Phenomena 21, 1980, pp. 93-101.

R. Kuhn *et al.*, "Photoelectron-photon coincidence studies of the A and B excited electronic states of X-C≡C-C≡N⁺, X = CH₃, CD₃, CI, Br, I", *Journal of Electron Spectroscopy and Related Phenomena* 34, 1984, pp. 253-260.
 J. Fulara *et al.*, "Electronic absorption spectra of N≡C-C≡N⁺, H-C≡C-C≡N⁺ and CH₃-C≡C-C≡N⁺ in Neon matrices", *Journal of*

J. Fulara *et al.*, "Electronic absorption spectra of N≡C−C≡N⁺, H−C≡C−C≡N⁺ and CH₃−C≡C−C≡N⁺ in Neon matrices", *Journal of Physical Chemistry* 89, 1985, pp. 3190-3193.

Investigation of Liquid Ferrofluids with XMCD: Instrumentation and Experiments

<u>N. Daffé^{1,2,3}</u>, A. Juhin¹, M. Rovezzi⁴, N. Mas^{1,2}, M. Sikora⁵, Ph. Sainctavit^{1,2}, F. Choueikani², V. Gravilov-Isaac³, S. Neveu³, V. Dupuis³, P. Glatzel⁴.

¹IMPMC, UMR CNRS 7590, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France. ²Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint Aubin, France ³PHENIX, UMR 8234, Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France .4 ESRF, BP220, 38043 Grenoble Cedex, France.5 AGH University of Science and Technology, 30-059 Kraków, Poland

ABSTRACT

Ferrofluids are colloidal suspensions of magnetic nanoparticles embedded in a carrier liquid. They are well-known for their numerous applications from medicine [1], optical waveguides [2] to engineering [3]. In the liquid phase at 300K, nanoparticles magnetization fluctuates while in the frozen liquid, below the blocking temperature, the anisotropy energy overcome the thermal activation energy. In the present study, investigation of magnetic properties was made in these two thermodynamic states of ferrofluids. Among these magnetic liquids, Binary Ferrofluids are constituted of two different types of magnetic nanoparticles. Binary Ferrofluids exhibit magnetic behaviors that do not correspond to the simple combination of each constituent properties but includes inter-particle interactions. For this reason, investigation of magnetic properties in Binary Ferrofluids requires measurements in the liquid phase. Soft X-ray Magnetic Circular Dichroism (XMCD) measurements at the $L_{2,3}$ edges of 3d transitions metals is a powerful method to measure element specific magnetic moments. However, working in liquid phase remains a big challenge when using soft X-rays spectroscopies. We have started the conception of a liquid cell on the DEIMOS beamline at SOLEIL. The setup, which is still under development, aims at being compatible with the short penetration depth of soft X-rays, ultra-high vacuum, and low temperatures. Compared to Soft X-ray MCD, using hard X-ray MCD at the K edge with large penetration depth allows direct investigation of magnetic liquid samples but does not provide direct information on the magnetic moments carried by the 3d orbitals. In this context Hard X-ray RIXS-MCD spectroscopy [4] is a very valuable alternative to soft X-rays MCD at K-edge of 3d elements when liquid cell sample environments are required. In particular we focus here on the K preedge of 3d elements $(1s^2 2p^6 3d^N \rightarrow 1s^1 2p^6 3d^{N+1} \rightarrow 1s^2 2p^5 3d^{N+1})$ [5]. The experiments were performed on ID26 beamline at the ESRF via the development of a static liquid cell. The setup was built to endure high magnetic field and low temperatures. We performed a complete measurement of RIXS-MCD 2D spectra and element specific magnetization curves at Mn and Co K-edge of Binary Ferrofluids mixing cobalt ferrite CoFe₂O₄ with manganese ferrite MnFe₂O₄. The liquid cell combined to the RIXS-MCD measurements offer a good reliability of the measurements and the experiment can be extended to other magnetic liquid systems.

REFERENCES

[2]F. Choueikani, F. Royer, D. Jamon, A. Siblini, J. J. Rousseau, S. Neveu, J. Charara, App. Phys. Lett. 94, 051113 (2009).

[3]S. Engelmann, A. Nethe, Th. Scholz, H.-D. Stahlmann, J. Magn. Magn. Mater. 272, 2345-2347(2004).
[4]M. Sikora, A. Juhin, T.-S. Weng, Ph. Sainctavit, C. Detlefs, F. M. F. De Groot, P. Glatzel, Phys. Rev. Lett. 105, 037202(2010).

^[1]R. Hiergeist, W. Andrä, N. buske, R. Hergt, I. Hilger, U. Richter, W. Kaiser, J. Magn. Magn. Mater. 201, 420-422 (1999).

^[5]A. Juhin, M. Sikora, M. Estrader, S. Estradé, F. Peiro, M.D.Barlo, Ph. Sainctavit, P. Glatzel, J. Nogués, Nanoscale 6, 11911-11920(2014).

Combining Mn L- and O K-edge Resonant Inelastic X-ray Scattering for the Study of Orbital Excitations in Multiferroic TbMnO₃

<u>J. Feng</u>,^a C.F. Hague,^{a,b} N. Jaouen,^b H. Zhou,^c J.-M. Mariot,^a S.G. Chiuzbaian^{a,b}

 ^a Laboratoire de Chimie Physique-Matière et Rayonnement, Sorbonne Universités, UPMC Univ Paris 06 / CNRS, UMR 7614, 11 rue Pierre et Marie Curie, F-75005 Paris, France
 ^b Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, B.P. 48, F-91192 Gif-sur-Yvette, France
 ^c National High Magnetic Field Laboratory, 1800 E. Paul Dirac Dr., Tallahassee, Florida 32310, USA

ABSTRACT

The understanding of simultaneous ferroelectric and magnetic long-range orders in TbMnO₃ hinge on the fine details of the electronic structure. We report on the first resonant inelastic x-ray scattering (RIXS) study performed at the manganese L (2p-3d) and oxygen K (1s-2p) resonances. Using the AERHA spectrometer¹ installed on the SEXTANTS beamline² of Synchrotron SOLEIL it was possible to probe both resonances in a single high-throughput



experiment.

We explored the presence of spectral weight at 2.9 eV transferred energy in the Mn L spectra, as indicated in a previous RIXS study at the Mn K resonance (1s-3d).³ The latter was attributed to coexisting on-site and inter-site orbital excitations predominantly involving Mn 3d states.³ Its non-local character is clearly reflected in our O K data as fluorescence-like behavior. Therefore our approach allows disentangling local and non-local contributions: the large potential of the 2p core-hole on Mn site grants access to local excitations while the O K data are known to shed light on delocalized excitations. We reveal the presence of a local d-d

excitation at 2.4 eV in both Mn L and O K data, while another orbital excitation at 1.5 eV is present only in the Mn L spectra. The results are interpreted in a local crystal-field framework allowing describing the local environment of the Mn ions in unprecedented detail.

Sorin G. Chiuzbaian, Coryn F. Hague, Antoine Avila, Renaud Delaunay, Nicolas Jaouen, Maurizio Sacchi, François Polack, Muriel Thomasset, Bruno Lagarde, Alessandro Nicolaou, Stefania Brignolo, Cédric Baumier, Jan Lüning, and Jean-Michel Mariot, Review of Scientific Instruments 85, 043108 (2014).

M. Sacchi, N. Jaouen, H. Popescu, R. Gaudemer, J.-M. Tonnerre, S.G. Chiuzbaian, C.F. Hague, A. Delmotte, J.-M. Dubuisson, G. Cauchon, B Lagarde, and F Polack, Journal of Physics: Conference Series 425, 072018 (2013).

J.M. Chen, J.M. Lee, S.W. Huang, K.T. Lu, H.T. Jeng, C.K. Chen, S.C. Haw, T.L. Chou, S.A. Chen, N. Hiraoka, H. Ishii, K.D. Tsuei, and T.J. Yang, Physical Review B 82, 094442 (2010).

Ferromagnetic/Organic Interfaces

C. Fourmental^{1,2}, Y. Garreau^{1,2}, A. Coati¹, V. Repain² & A. Bellec²

¹Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint-Aubin, France ²Laboratoire MPQ, Bâtiment Condorcet, 10 rue A. Domon et L. Duquet, 75205 Paris 13, France

ABSTRACT

Due to their low spin-orbit interaction and the possibility to functionalize them at will, the use of organic materials is a promising way for the development of new spintronic applications, especially for the realization of vertical spin valves in which the non-magnetic spacer is made of an organic film. Promising results have already been obtained on C_{60} based spin-valve presenting a magneto-resistance at room temperature¹. The results on LSMO/Alq3/Co nano-junctions which exhibiting large magneto-resistance values at low temperature clearly underline the importance of controlling the interface between the organic molecules and the ferromagnetic electrodes². It is crucial to understand the structural properties of organic/ferromagnetic interfaces. By X-ray-diffraction important results have been obtained on the adsorption of thiols³ or C60 molecules^{4,5} on metallic surfaces, but none on ferromagnetic surfaces.

Cobalt on Platinum is a system, which presents a Spin Reorientation Transition (SRT), occuring when a thin film (some monolayers) of Cobalt is deposited on Platinum. By MOKE (Magneto-Optic Kerr Effect) measurements, we have observed that the SRT can be modified by evaporating some C_{60} layers on the Cobalt on Platinum; this is really surprisingly, if one notice that C_{60} is a non-magnetic molecule. The direct study of the structure of this system (C_{60} on Cobalt on Platinum) by GIXD (Grazing-Incidence X-ray Diffraction) is hard because of the number of parameters involved. For this the reason, we start the study of such a system by deposit of C_{60} on a Co(0001) substrate.

The first result we obtained by LEED shows that C_{60} is well-organized on the Cobalt surface, presenting a perfect (4x4) surface reconstruction, which has been confirmed by our first GIXD measurements. We collected a set of structure factors along the reciprocal space surface diffracted rods. The measurements are sensitive to bulk relaxations after the deposit of C_{60} and in principle allow to identify the atomic structure and orientation of C_{60} molecules at the surface, as shown by R. Felici et al.⁴ in the similar case of C_{60} deposited on Pt, which proved the formation of Pt vacancies behind the C_{60} layer.

- 1. M. Gobbi et al., Adv. Mater., 23, 1609-1613 (2011)
- 2. C. Barraud et al., *Nat. Phys.*, **6**, 615-620 (2010)
- 3. X. Torrelles et al., J. Phys. Chem. B, 110, 5586 (2006)
- 4. R. Felici et al, *Nat Mater*, **4**, 688- 692 (2005)
- 5. X. Torrelles et al, Phys. Rev. B, 86,075461 (2012)

Unveiling the Magnetic State of Iron in the Superconducting Pressure Region

J. Ablett¹, M. d'Astuto², F. Baudelet¹, M. Casula², A. Juhin², G. Le Marchand², <u>B. Lebert^{1,2}</u>, P. Munsch², A. Polian², J.-P. Rueff¹, Z. Zhang^{1,2}

 Synchrotron SOLEIL, L'Orme des Merisiers, BP 48, Saint Aubin, 91192 Gif sur Yvette, France
 Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), UMR CNRS 7590, Université Pierre et Marie Curie - case 115, 4 place Jussieu, 75252 Paris cedex 05, France

ABSTRACT

Iron has been a well-known material since antiquity for its unique magnetic properties. Despite its abundance on Earth, geophysical relevance, and numerous technological applications; iron's rich electronic and magnetic properties are far from being understood from both a theoretical and experimental point of view.

Iron undergoes a martensitic transition at 13 GPa and room temperature from α -iron (bcc) to ε -iron (hcp)¹, which is concomitant with a magnetic collapse from a ferromagnetic to an apparently nonmagnetic state^{2,3}. As well, the ε -iron phase exhibits superconductivity between 15 GPa and 30 GPa, with a T_C of 2K⁴. Nonetheless, the exact nature of the ε -iron phase is still disputed. Mossbauer spectroscopy⁵ finds an upper limit on the magnetic moment of 0.05 μ_B and preliminary neutron scattering⁶ data failed to find any magnetic order. On the other hand, Raman spectroscopy⁷, x-ray emission spectroscopy⁸ (XES), and transport measurements⁹ show indications of a local moment. Furthermore, theoretical calculations predict an anti-ferromagnetic phase¹⁰, possibly linked to iron's low temperature superconductivity.

Using K β XES, we mapped out the superconducting pressure region of iron from 3 to 50 GPa and 4 to 583 K. We performed XES with unprecedented statistics in order to directly study the K β ' satellite's form and position. The satellite's shape and position is stable in α -iron and then exhibits a sharp and discontinuous decrease in intensity, increase in width, and shift in energy at 15 GPa, coinciding with the onset of superconductivity. The satellite intensity then decreases linearly towards zero around 30 GPa. These results suggest a new magnetic state which is linked to superconductivity.

- 1. D. Bancroft, E. L. Peterson, and S. Minshall, J. Appl. Phys. 27, 291 (1956).
- 2. O. Mathon, F. Baudelet, J. Itié, a. Polian, M. d'Astuto, J. Chervin, and S. Pascarelli, Phys. Rev. Lett. 93, 255503 (2004).
- 3. M. d'Astuto et al.: Magnetism under Pressure with Synchrotron Radiation, Lect. Notes Phys. 697, 375-399 (2006)
- 4. K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, and K. Amaya, Nature 412, 316 (2001).
- 5. S. Nasu, T. Sasaki, T. Kawakami, T. Tsutsui, and S. Endo, J. Phys. Condens. Matter 14, 11167 (2002).
- 6. S. Klotz, ILL Exp. Report 5-31-1676 (2007)
- 7. S. Merkel, A. Goncharov, H. Mao, P. Gillet, and R. Hemley, Science 288, 1626 (2000).
- 8. A. Monza, A. Meffre, F. Baudelet, J.-P. Rueff, M. D'Astuto, P. Munsch, S. Huotari, S. Lachaize, B. Chaudret, and A. Shukla, *Phys. Rev. Lett.* **106**, 247201 (2011).
- 9. S. Gilder and J. Glen, Science 279, 72 (1998).
- 10. G. Steinle-Neumann, L. Stixrude, and R. E. Cohen, Proc. Natl. Acad. Sci. U. S. A. 101, 33 (2004).

Ab Initio Calculation of K-edge XMCD Spectra

<u>N. Mas</u>^{1,2}, A. Juhin¹, Ph. Sainctavit¹, Ch. Brouder¹, M. Calandra¹ and F. Baudelet ²

 ¹ Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, CNRS & UPMC, 75005 Paris, France
 ² Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint Aubin, France

ABSTRACT

X-ray Magnetic Circular Dichroism (XMCD) is a powerful tool for the elementspecific study of the magnetic structure of complex systems. For 3*d* transition ions, measurements at the $L_{2,3}$ absorption edges (i.e. with a 2*p* core hole in the final state) provide information on the spin and orbital contributions to the magnetic moment through well-established sum rules. Nevertheless, the short penetration depth of soft X-rays makes them incompatible with demanding sample environments such as high pressure anvils or liquid cells. In such environments, XAS and XMCD spectroscopies can still be employed at the K-edge (i.e. with a 1*s* core hole in the final state) using hard X-rays. For example, on the dispersive beamline ODE at SOLEIL, XAS and XMCD measurements can be performed upon simultaneous application of high pressure, low temperature and magnetic field.

The understanding of the experimental results, as well as the connection between the dichroic signal and magnetic properties, require the crucial support of theoretical interpretations. However, the quantitative analysis of K-edge XMCD spectra is far from straightforward. We are addressing this issue and propose a renewed approach to interpret K edge XMCD.

Taking advantage of the simple structure of the electronic Coulomb repulsion between the 1s core-hole and the 3d or 4p orbitals, we intend to use a monoelectronic formalism based on the Density Functional Theory [1] to calculate ab initio K-edge XMCD spectra. We will present this approach that aims at including in a single computational code [2] all the different terms of the relativistic cross section with the ability to consider the core hole and to use a non muffin-tin potential. Based on the first results obtained for simple metallic systems, we will examine in detail the weight of each term of the cross section (most important multipole and spin-orbit contributions). We will also discuss the role of spinorbit coupling and the influence of the magnetic state of the neighbours of the absorbing atom.

We plan to apply this formalism to calculate XAS and XMCD spectra of 3*d* transition metals in various spinels and intermetallic systems, which will allow to probe the influence of delocalized and non-delocalized magnetic orbitals on the XMCD signal. This work is partially supported by a grant from the LabEx MATISSE.

REFERENCES

1. C. Gougoussis, M. Calandra, A. P. Seitsonen, and F. Mauri Phys. Rev. B 80, 075102 (2009)

2. C. Gougoussis et al., in preparation

Orientational Tuning of the Two-dimensional Electron Gases at the Low-index Surfaces of SrTiO₃

<u>T.C. Rödel^{1,2}</u>, C. Bareille¹, F. Fortuna¹, F. Bertran², P. Le Fèvre², T. Maroutian³, P. Lecoeur³, M. Gabay⁴, M.J. Rozenberg^{4,5}, A. Santander-Syro¹

¹CSNSM, Université Paris-Sud and CNRS/IN2P3, Bâtiments 104 et 108, 91405 Orsay cedex, France
 ²Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP48, 91192 Gif-sur-Yvette, France
 ³Institut d'Electronique Fondamentale, Université Paris-Sud and CNRS, Bâtiment 220, 91405 Orsay, France
 ⁴Laboratoire de Physique des Solides, Université Paris-Sud and CNRS, Bâtiment 510, 91405 Orsay, France
 ⁵Departamento de Física–IFIBA Conicet, FCEN, UBA, Ciudad Universitaria P.1, 1428, Buenos Aires, Argentina

ABSTRACT

Two-dimensional electron gases (2DEGs) in $SrTiO_3$ have been studied extensively in the last decade after its discovery at the LaAlO₃/SrTiO₃ interface by Ohtomo & Hwang¹. This heterostructure displays many fundamentally interesting properties, such as field-effect induced insulator-to-superconductor transitions², magnetism³ and the coexistence of magnetism and superconductivity⁴.

To clarify the microcopic electronic structure of the 2DEG, we conducted angle resolved-photoemission spectroscopy (ARPES) experiments of a closely related system: the 2DEG at the surface of $SrTiO_3$. Our group studied the 2DEGs at various different surface orientations of $SrTiO_3$ (as well as $KTaO_3$) at the Cassiopée beamline at Synchrotron Soleil.^{5,6,7,8}

Recent results⁸ demonstrate that the electronic structure of the 2DEG at the surface of SrTiO₃ (Fermi surfaces, subband masses and orbital ordering) can be tuned by confining the electrons at different surface orientations. This occurs because the crystallographic symmetries of the surface and subsurface planes and the effective electron masses along the confinement direction influence the symmetry of the electronic structure and the orbital ordering of the t_{2g} manifold. Remarkably, our analysis of the data also reveals that the carrier concentration and thickness are similar for all three surface orientations, despite their different polarities. The orientational tuning of the microscopic properties of two-dimensional electron states at the surface of SrTiO₃ (110) and (111) interfaces, and is promising for searching new types of two-dimensional electronic states in correlated-electron oxides.

- 1. A. Ohtomo and H.Y. Hwang, Nature 427, 6 (2004)
- 2. A.D. Caviglia et al., Nature 456, 624 (2008)
- 3. A. Brinkman et al., Nature Mater. 6, 493 (2007)
- 4. D.A. Dikin *et al.*, *Phys. Rev. Lett.* **107**, 056802 (2011)
- 5. A.F. Santander-Syro *et al.*, *Nature* **469**, 189 (2011) 6. A.F. Santander-Syro *et al.*, *Phys. Rev. B* **86**, 121107 (2012)
- 7. C. Bareille *et al.*, *Sci. Rep.* **4**, 3586 (2014)
- 8. T.C. Rödel et al., Phys. Rev. Applied 1, 051002 (2014)
XMCD at Co and Fe L_{2,3} edges of Photomagnetic Co/Fe Dinuclear Complex

<u>F. Sadaf¹</u>, M.-A. Arrio¹, A. Juhin¹, E. Koumousi^{2,3}, C. Mathonière², R. Clérac³, E. Otero⁴, P. Ohresser⁴, P. Sainctavit^{1,4}

IMPMC, CNRS UMR 7590, UPMC, France
 ICMCB, CNRS UPR 9048, France
 CRPP, CNRS UPR 8641, France
 Synchrotron SOLEIL, Saint-Aubin, France

Sadaf.fatima@impmc.upmc.fr

ABSTRACT

The nanoscale magnetic materials are potential candidates for energy efficient, photoswitchable molecule-based information storage [1]. Recently, a dinuclear molecule, labelled (1) in the following, has been synthesized [2]. It is built from Fe(III) cyanides and Co(II) ions and it can be seen as the elementary motif of the Co-Fe Prussian Blue Analogues (PBA). The molecule (1) is the first dinuclear complex to exhibit thermal and photomagnetic bistablility. In this talk, we present XMCD results obtained on (1) as well as on the Fe and Co precursors that are the building blocks for (1).

We have performed X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at Fe and Co $L_{2,3}$ edges on the DEIMOS beamline at SOLEIL. The photomagnetic transition in Co-Fe Prussian Blue analogues (PBA) is a complex phenomenon that has been observed in 3D systems and other low dimensional systems. It has never been measured on systems as small as (1). The main question behind this work is to determine how the photomagnetic transition is governed by either the local electronic structure of the individual ions or by the metal-to-metal electron transfer in Fe-CN-Co linkages. XMCD at Fe and Co $L_{2,3}$ edges was measured as a function of temperature ranging from 300K to 4K to follow the thermally induced charge transfer between Fe(III)-Co(II) paramagnetic pair and the Fe(II)-Co(II) paramagnetic pair. At 4K, (1) is irradiated by a 660 nm laser and switches to the Fe(III)-Co(II) paramagnetic pair. The reversibility of the charge-transfer has been measured by warming (1) to 300 K. The detailed interpretation of the XAS and XMCD data was achieved using Ligand Field Multiplet calculations. Fe^{III} and Co^{II} ions were found to possess large orbital magnetic moments are crucial in the charge transfer mechanism and in its coupling to the crystal structure.

- 1. O. Sato, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2004, 5, 3, 2013-223.
- 2. E. S. Koumousi, I. R. Jeon, Q. Gao, P. Dechambenoit, D. N. Woodruff, P. Merzeau, L. Buisson, X. Jia, D. Li, F. Volatron, C.
- Mathonière and R. Clérac, J. Am. Chem. Soc. 2014, 136, 15461-15464.
- 3. D. Li, R. Clérac, O. Roubeau, E. Harte, C. Mathonière, R. Le Bris, and S.M. Holmes, J. Am. Chem. Soc, 2008, 130, 252-258.
- 4. Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière, and S. M. Holmes, Angew Chem., 2010, 49, 3752-3756.
- 5. D. Siretanu, D. Li, L. Buisson, D. M. Bassani, S. M. Holmes, C. Mathonière, and R. Clérac, Chem. Eur. J., 2011, 17, 11704-11708.
- 6. J. Kim, S. Han, In-Ku Cho, K. Y. Choi, M. Heu, S. Yoon, B. J. Suh, Polyhedron, 2004, 23, 1333-1339.

First Electrical Measurements of MgO-based MTJs with Versatile Variable Temperature Insert

<u>M. Studniarek</u>, L. Joly, F. Scheurer, W. Weber, M. Bowen, S. Boukari, B. Muller, E. Sternitzky, F. Schleicher, E. Beaurepaire, P. Ohresser

Institut de Physique et Chimie des Matériaux de Strasbourg, 23 Rue du Loess, 67035 Strasbourg Synchrotron SOLEIL, L'Orme des Mersiers, Saint-Aubin, 91192 Gif-Sur-Yvette

ABSTRACT

Magnetic tunnel junctions (MTJ), with its most popular MgO dielectric barrier, have been intensively studied for the last two decades¹. Despite this body of research, subtle nuances of solid-state tunneling within the picture of spin and symmetry conservation have not been yet fully understood. Recent years brought into light many interesting details about defect-mediated transport through ultrathin MgO barrier² but also raised new questions.

New possibilities arise thanks to a recently installed Versatile Variable Temperature Insert (V²TI) on beamline DEIMOS. The V²TI device, which was conceived/designed by IPCMS and DEIMOS scientists/engineers, was manufactured at the IPCMS. This device is an alternative insert to the end station with a separate temperature control system. Its novel feature is the possibility to conduct UHV electrical transport measurements (or deliver electrical stimulation) under the x-ray beam with precise control over the temperature. Its 12 wires allow bonding up to 5 devices in 4-point measurement mode (or 10 in 2-point) on a dedicated chip that is then mounted and transferred directly in UHV. We performed the first scientific V²TI combined mission mode using with in expert а home designed multiplexing/measurement station (IPCMS mobile Fert bench) in June 2014. We will present preliminary spintronic results that confirm the full operation of V^2TI .

CoFeB/Mgo/CoFeB MTJs were processed via photolithography from stacks grown at IJL, Nancy³. Using wedge bonding, we connected 5 devices in 4-point mode to a V²TI chip at the ICPMS, and brought samples to Soleil within an antistatic protection environment. We used 45° geometry (surface to beam angle) to allow fluorescence mode of XAS detection. To optically address the appropriate micrometer-size MTJ, we used end station motors to obtain XAS intensity maps. This enables fine positioning with a resolution down to 20µm. In this way and thanks to electrical multiplexing provided by the IPCMS's Mobile Fert bench, we achieve concurrent electrical/optical multiplexing. The large number of wires here allowed us to overcome issues of junction breakdown during UHV transfer, and to increase beam time efficiency by not having to exit UHV to switch to another device. Our successful measurements of R(H) and I(V) curves confirm the big potential for the V²TI toward electrically/optical multiplexed, efficient electrical measurements within the wide parameter space (bias voltage, temperature, magnetic field, photon energy, light polarity) provided by beamline DEIMOS.

- 1. Miao, G.-X., et al., Reports Prog. Phys. 74, 036501 (2011).
- 2. Schleicher, F. et al., Nat. Commun., 5, 4547 (2014).
- 3. Bernos, J. et al. Phys., Rev. B 82, 060405(R) (2010).

Structure des Aluminosilicates de Plomb Vitreux et Fondus

I. Ben Kacem^{1,2}, L. Gautron¹, D. Neuville²

1: Laboratoire Géomatériaux et Environnement (LGE) – Université Paris Est Marne La Vallée – 77420 champs sur marne – France. 2: Institut de Physique du Globe Paris (IPGP) – CNRS : UMR7154 -75005 Paris - France

ABSTRACT

L'utilisation du plomb (Pb) dans les verres est très ancienne. Depuis la fin du premier millénaire, en orient comme en occident, l'homme a façonné des matières vitreuses avec le plomb comme constituant principal. Mais ce n'est qu'en 1676 [1] qu'on a parlé du verre au plomb (cristal) suite aux travaux du marchand anglais George Ravenscroft. Sa toxicité est elle aussi bien connue depuis l'antiquité. Le plomb ainsi que le cadmium sont aussi les éléments qui constituent la principale toxicité présente dans les REFIOM (Résidus d'Epuration de Fumée d'Incinération des Ordures Ménagères).

Cette étude présente un double objectif : 1) mieux comprendre le rôle et la spéciation du plomb dans des verres modèles et des verres industriels ; 2) mettre en œuvre et caractériser des nouveaux matériaux pour l'immobilisation durable d'éléments toxiques tels que le plomb et le cadmium contenus dans les déchets. Deux matériaux sont ciblés : les verres et les vitrocéramiques synthétisées à partir des verres par un processus de nucléation-croissance.

Ainsi, la première étape a consisté à synthétiser différents verres ayant des compositions simples et modèles (PbO-SiO₂), (PbO-Al₂O₃-SiO₂) et (CaO-PbO-Al₂O₃-SiO₂). Des expériences de spectroscopie d'absorption des rayons X (EXAFS) au seuil du plomb en mode dispersif ont été réalisées sur ces verres, sur la ligne de lumière ODE du synchrotron Soleil : ces expériences ont été réalisées *in situ* dans un four à fil chauffant (conçu par Mysen et Frantz, 1992 [2]) et ont permis de caractériser l'environnement du plomb dans le verre et son évolution avec la température, notamment en dessous et au-dessus de la Tg, lors de processus de nucléation et dans le melt. La caractérisation de ces verres a été complétée en laboratoire par des observations et analyses en spectroscopie Raman, réalisées aussi dans le fil chauffant.

Les premiers résultats sur la composition PbO/ SiO₂ 50 :50 en mole, montrent notamment un déplacement vers les faibles énergies lorsque la température augmente, ce qui peut être attribué à une réduction du degré d'oxydation du plomb de (Pb⁴⁺) en (Pb²⁺). D'autre part, le spectre du verre (PbO/SiO₂ 50 :50) et celui du le minéral correspondant alamosite (PbSiO₃) présentent des similitudes pouvant révéler un environnement du plomb proche dans les deux matériaux. Les résultats préliminaires sur l'influence du calcium et de l'aluminium sur l'environnement du plomb dans ces verres modèles sont également présentés.

REFERENCES

2. Mysen, B. O., and J. D. Frantz (1992). Raman spectroscopy of silicate melts at magmatic temperatures : Na₂O-SiO₂, K₂O-SiO₂ and Li₂O-SiO₂ binary compositions in the temperature range 25-1475°C, Chem. Geol., 96, 321–332.

^{1.} Anne Bouquillon et al.(2007) . L'actualité chimique, 40-46.

XANES Study of Thermoelectric Skutterudites $Yb_yCo_4Sb_{12}$ (y = 0.10, 0.15, 0.20)

<u>M. Benyahia¹</u>, O. Rouleau¹, V. Paul-Boncour¹, J. Monnier¹, K. Provost¹, E. Alleno¹

¹ ICMPE, UMR 7182 CNRS – UPEC, 2 rue H. Dunant, 94320 THIAIS, France * email of corresponding author: <u>benyahia@icmpe.cnrs.fr</u>

ABSTRACT

 $Yb_{0.2}Co_4Sb_{12}$ is a thermoelectric skutterudite which has good thermoelectric performances, with a figure of merit $ZT = \alpha^2 T/\rho\lambda$ (α is the Seebeck coefficient, σ the electrical conductivity, λ the thermal conductivity and T the average temperature) larger than 1 at 800K. These good performances are related, among other things, to exceptional and not well understood electronic transport properties for a rare-earth based skutterudite. We surmised that it is related to the possible non integer valence of Yb (2.5 reported in literature).

Therefore, we carried out XANES experiments at the Yb-L_{III} edge on the SAMBA beam line in Soleil, on Yb_yCo₄Sb₁₂ compounds (y = 0.1, 0.15, 0.20). For all Yb contents, the XANES spectra show a strong divalent peak and a weaker trivalent peak leading to a valence close to 2.1 - 2.2 which remains temperature-independent (20, 70, 130, 200, 300K). Based on complementary X-ray data and resistivity measurements, we infer that the valence of Yb is equal to 2 in Yb_xCo₄Sb₁₂ (x = 0.1, 0.15, 0.20) and that the trivalent contribution arises from Yb₂O₃ as a secondary phase.

The thermoelectric properties of the skutterudites $A_yCo_4Sb_{12}$ (y < 1, A = Na, K, Ca, Sr, Ba, La, Ce, Nd, Sm, Eu, Yb, In, TI ...) depends on the valence of A, because the electron mobility in this skutterudites with divalent A atom is higher compared to trivalent A atom, this leads to the increase of their electrical conductivity. Further, the Yb is a heavy atom that reduces the thermal conductivity, and therefore increases their ZT compared to other lighter A atoms. This new valence estimation of Yb in these skutterudites explains their good performances.

In situ X-ray Study of the Formation of Oxidesupported Gold Nanoparticles using Micelle Nanolithography

<u>V. Dhanasekaran¹</u>, Y. Garreau², A. Resta¹, A. Coati¹, B. Mbenkum³, A. Vlad¹

¹Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, Gif-sur-Yvette, France ²Université Paris Diderot, Sorbonne-Paris-Cité, MPQ, UMR 7162 CNRS, Paris Cedex 13, France ³NanoArc LtD,Auckland, New Zealand

ABSTRACT

Gold nanoparticles have been extensively studied for their high catalytic activity in CO oxidation reaction [1]. The preparation techniques of the nanoparticles and the type of support have great impact on the catalytic behavior of the system, but the origins of these effects are not yet fully understood [2]. Here, we synthesized gold nanoparticles via micelle nanolithography, a self-assembly technique which utilizes the aggregation of diblock copolymers into micelles in order to produce an ordered array of metal nanoparticles on various substrates. The deposition of the micelles on surface in a well-arranged pattern is followed by a plasma etching process in order to decompose the polymeric matrix and reduce the metal contained in the salt. This method offers clear advantages, such as a narrow size distribution of nanoparticles, the control of inter-particle distance; the possibility to use different substrates and various precursors salts [3].

We have studied the in situ formation of 3 nm and 15 nm gold nanoparticles on MgO(100) by surface-sensitive x-ray scattering measurements in the UHV end-station of the SixS beamline at Synchrotron Soleil. The micelles spin-coated on the substrates formed a quasi-hexagonal arrangement, the SEM images are obtained using the microscope available at SOLEIL/IPANEMA. Atomic oxygen and hydrogen were used to remove the organic micelles and to form the metallic gold nanoparticles. The systematic approach taken to disentangle the effects of the specific gas, oxygen or hydrogen, used for the particles formation process allows us to shine some light on the structural differences of the particles final state. The main techniques used for this study are GISAXS (grazing incidence small angle x-ray scattering), GIXD (grazing incidence x-ray diffraction) and x-ray reflectivity. The natural following step for this study will be to test the structural difference found in this study towards the CO oxidation in the flow reactor available on SixS beamline, at Synchrotron SOLEIL.

- 1. M. Haruta et al, J. Cat., 1989, 39-45
- 2. B. Hvolbaek et al, Nanotoday, 2007, 14-19
- 3. N. G. Kang et al, React. Funct. Polym., 2009, 470-479

The Local Environment of Substitutional Al³⁺ In Goethite Probed by XANES and First-principles Calculations

M. Ducher¹, D. Cabaret¹, M. Blanchard¹, R. Nemausat¹, D. Vantelon²

¹ IMPMC, UPMC, UMR 7590, case 115, 4 place Jussieu, 75005 Paris ² Synchrotron SOLEIL, L'Orme des Merisiers, 91190 Saint-Aubin

ABSTRACT

X-ray absorption near edge structure (XANES) spectroscopy is a technique of choice to obtain qualitative information on the local structure/environment. However, experimental data, often, require simulations to be interpreted.

Previous study [1] on aluminous goethite, which is an Al-bearing iron oxyhydroxide known to substitute Fe with Al up to 33 mol % [2], showed differences in the edge region of the spectra as the concentration of Al changed. A lack of resolution did not allow studying the pre-edge region. The work suggested that numerical simulations could explain the spectral features.

We present new Al K-edge XANES spectra of aluminous goethites and diaspore, which is the aluminium end-member of the partial solid solution goethite/diaspore, at the LUCIA beamline at synchrotron SOLEIL (Figure 1). The experimental spectra display a change in absorption peaks intensity at both the pre-edge and the edge region. First principles calculations done with the XSpectra code [3], based on density functional theory (DFT) in a

pseudopotential plane wave framework [4], allow gaining insights on the local environment of Al when the Al concentration changes.

The comparison between theoretical and experimental spectra and the investigation of the structure give information about the AI distribution. Furthermore, the calculated spectra reproduce successfully the experimental trends. Therefore, the structural modifications can be linked to the spectral differences. In particular, the larger A-B peak spacing in diaspore, compared to AI-bearing goethites, is found to be related to the first cation neighbours around the absorbing AI atom. The decrease of the B/A intensity ratio with increasing AI concentration is due to smaller cation-cation distances and the distortion of the



Figure 1: Experimental AI *K*-edge XANES spectra of aluminous goethites and diaspore.

 $AIO_3(OH)_3$ octahedron. Finally, the decrease in intensity of the pre-edge features with increasing AI concentration are compared with partial density of states (PDOS) calculations and is unambiguously related to the decrease in the number of Fe atoms.

This study illustrates the advantages of combining numerical simulations and experimental measurements to extract information about the local structure from the spectra that goes beyond the usual speciation information extracted from XANES.

- 1. P. Ildefonse and D. Cabaret and P. Sainctavit, Physics and Chemistry of Minerals 25, 112-121 (1998).
- 2. R. W. Fitzpatrick and U. Schwertmann, Geoderma 27, 334-347 (1982)
- 3. C. Gougoussis and M. Calandra, A. P. Seitsonen and F. Mauri, Physics Review B 80, 075102 (2009)
- 4. P. Giannozzi et al., Journal of Physics: Condensed Matter 21, 395502 (2009)

Mechanical Study of Multilayered Thin Films under Continuous Controlled Biaxial Deformation

<u>R. Guillou¹</u>, E. Le Bourhis¹, P. Goudeau¹, P.-O. Renault¹, P. Godard¹, D. Faurie², G. Geandier³, C. Mocuta⁴, D. Thiaudière⁴

¹Institut PPRIME – CNRS/Université de Poitiers/ENSMA, Futuroscope, France ²LSPM – Université Paris 13, Villetaneuse, France ³IJL – CNRS/Université de Lorraine, Nancy, France ⁴Synchrotron SOLEIL, Gif sur Yvette, France

ABSTRACT

Thin film technology is pervasive in microelectronics, optics, magnetic, micro-mechanics. However, the mechanical stability of such nanoscale structure is crucial for applications since it is related to device lifetime. Synchrotron X-ray diffraction is a powerful tool to analyse the mechanical behavior of multiphase materials due to its selectivity. Using a biaxial tensile setup developed during an ANR project on the DiffAbs beamline at synchrotron SOLEIL (Figure 1), we performed controlled biaxial deformation tests on composite such as metallic



thin films deposited on polyimide substrate (Kapton). Simultaneously stress analysis of both phases of a W/Cu thin multilayer has been performed during a continuous equi-biaxial loading. During deformation, the sublayers' stresses are monitored thanks to a 2D detector and the macroscopic stresses are measured thanks to Digital Image Correlation. In order to achieve accurate stress analysis, the 2D detector is located at large distance from the sample.

Figure 1 : biaxiale tensile setup

Evolution of the total stress (residual and applied) of both W and Cu sublayers will be study during the tensile test thanks to $ln(1/sin\theta)-sin^2\psi$ plots. The stresses in the two phases increase linearly with the applied load and reach a plateau revealing the presence of cracks (Figure 2).



Figure 2: Evolution of $ln(1/sin\theta) - sin^2\psi$ plots and associated linear regression with increasing loading steps. The inserts show the evolution of the slope of $ln(1/sin\theta) - sin^2\psi$ plots as function of the applied force.

Ammonia Monohydrate at High Pressure

C. Liu^{1,2}, <u>J.-A. Queyroux</u>¹, K. Beneut¹, G. Le Marchand¹, S. Ninet¹ and F. Datchi¹

 ¹ Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Université Pierre et Marie Curie – Paris 6, CNRS UMR 7590, Paris, France
 ² Institute of Atomic and Molecular Physics, Jilin University, Changchun, 130012, China

ABSTRACT

Knowing the properties of H_2O , NH_3 and their mixtures under high pressure and temperature is important for planetary science because these H-bonded ices are present in Jovian planets and their satellites under a wide range of pressure (P) and temperature (T) conditions. The high P-T properties of the pure ice compounds have been the focus of many investigations, which have revealed a rich polymorphism. In particular, our group has recently shown the existence of superionic and ionic phases of ammonia^{1,2}, which had been previously predicted by first principles calculations^{3,4}. In these phases, proton transfers between molecules give rises to ionic species NH^{4+} and NH^{2-} , which may be relevant to explain the magnetic fields of Neptune or Uranus. By contrast with the pure components, the properties of (H_2O , NH_3) mixtures under extreme P-T conditions have been much less explored although these systems are possibly more relevant for planetary physics.

This presentation will focus on the properties of the ammonia monohydrate (AMH) solid compound, with stoechiometry 1 NH₃:1 H₂O. Experimental high-pressure studies on these systems have been mostly limited to P < 10 GPa and T < 300 K and reveal a rich polymorphism as at least 6 phases are reported. The known phases are all molecular and present heteronuclear O...H-N and N-H...O hydrogen bonds, as encountered in more complex macromolecules such as DNA. Nevertheless, a recent theoretical study⁵ has suggested that AMH transforms into an ionic solid composed of NH⁴⁺ and OH⁻ ions, in a similar fashion as the self-ionization observed in pure ammonia², but at much lower pressures (10 GPa instead of 150 GPa), thus much easier to reach in experiments. To check this surprising prediction, we have performed the first infrared absorption studies of AMH up to 40 GPa at 300 K and 100 K on SMIS beamline and X-ray diffraction experiments over a wide range of pressure and temperature on PSICHE beamline and on ID 27 at ESRF. The molecular/ionic phase transition is indeed observed, as evidenced by the appearance of vibrational modes from NH⁴⁺ and OH⁻ species, but the observed structure is not compatible with the predicted one. We will discuss our results in this presentation.

REFERENCES

4, Chris J Pickard and RJ Needs. "Highly compressed ammonia forms an ionic crystal". In: Nature materials 7.10 (2008), pp. 775–779.

^{1,} S. Ninet, F. Datchi, and A. Saitta. "Proton Disorder and Superionicity in Hot Dense Ammonia Ice". In: *Phys. Rev. Lett.* 108 (16 2012), p. 165702.

^{2,} S. Ninet et al. "Experimental and theoretical evidence for an ionic crystal of ammonia at high pressure". In : Phys. Rev. B 89 (17 2014), p, 174103

^{3,} C. Cavazzoni et al. "Superionic and Metallic States of Water and Ammonia at Giant Planet Conditions". In: Science 283.5398 (1999), pp. 44–46.

^{5,} Gareth I.G. Griffiths et al. "High pressure ionic and molecular crystals of ammonia monohydrate within density functional theory". In: *The Journal of Chemical Physics* 137.6, 064506 (2012).

Strain State in Ultrathin Metallic Nanowires Vertically Epitaxied In Oxide Matrix

V. Schuler¹, Y. Zheng¹, F. Vidal¹, D. Demaille¹, A. Coati², A. Vlad², Y. Garreau^{2,3}, M. Sauvage-Simkin², A. Novikova^{2,4}, E. Fonda²

¹ Université P. & M. Curie, INSP, CNRS UMR7588, 4 place Jussieu, 75005 Paris.
 ² Synchrotron Soleil, L'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette.
 ³ Université Paris Diderot, MPQ, CNRS UMR7162, Case courrier 7021, 75205 Paris Cedex 13.
 ⁴ Université de Versailles Saint-Quentin en Yvelines, GEMaC, CNRS UMR8635, 78035 Versailles.

ABSTRACT

Strain engineering is a powerful tool in order to tailor the physical properties of materials stacked coherently in an epitaxial heterostructure. Such an approach, applied to the mature field of planar heteroepitaxy, has yielded a variety of new phenomena and devices. Recently, the field of heteroepitaxial vertically aligned nanocomposites has emerged as an alternative to planar structures. Due to the peculiar geometry of such nano-architectures, it is expected that efficient strain control can be achieved, opening the way to novel functionalities.

Here, we show the growth of ultrathin Ni and CoNi alloy nanowires (NWs) vertically selfassembled in oxide matrix (CeO₂ or SrTiO₃) on SrTiO₃(001) substrate [1]. For both types of matrix, the NWs grow epitaxially and are highly strained: while their radial strain is negligible within the precision of the measurements, axial strain can reach very large values of the order of 1 % over length of several hundreds of nanometer. Moreover, this axial strain depends sensitively on the diameter of the NWs in the 3-6 nm range, reflecting its epitaxial nature and the balance of interface and elastic energies. Furthermore, it is shown experimentally that such strain is metastable in agreement with calculations performed in the framework of the Frenkel-Kontorova model [2]. The diameter dependence and metastability provide ways to control the strain, an appealing feature for the design of functional nanoarchitectures. The magnetic behavior of NWs depending on their strain will be shown and the underlying magneto-elastic coupling discussed.



Fig. 1: (a) Scheme of a Ni NW in $SrTiO_3$ matrix. On the top: a transmission electron microscopy (TEM) plane view of one NW; on the left, a TEM cross section view where the NW is visualized by the Moiré pattern. (b) Reciprocal lattice map of 202 obtained on the SIXS beamline. The axial tensile strain in the NWs is evidenced.

- F.J. Bonilla, A. Novikova, F. Vidal, Y. Zheng, E. Fonda, D. Demaille, V. Schuler, A. Coati, A. Vlad, Y. Garreau, M. Sauvage–Simkin, Y. Dumont, S. Hidki and V.H. Etgens, ACS Nano 7, 4022 (2013).
- 2. V. Schuler, F.J. Bonilla, D. Demaille, A. Coati, A. Vlad, Y. Garreau, M. Sauvage-Simkin, A. Novikova, E. Fonda, S. Hidki, V.H. Etgens, F. Vidal and Y. Zheng, submitted.

Bond Stretching Phonon Softening and Kinks in the Angle-resolved Photoemission Spectra of under Doped La_{2-x}Ba_xCuO_{4+δ} Superconductors

D.R. Garcia,^{1, 2} <u>Z. Zhang</u>,³ G. Dhalenne,⁴ S. Denis,⁴ P. Le Fèvre,⁵ A. Taleb-Ibrahimi,⁵ C. Decorse,⁴ P. Berthet,⁴ A. Lanzara,^{1, 2} and M. d'Astuto^{3, *}

¹Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

²Department of Physics, University of California Berkeley, CA 94720, USA

³Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), Université Pierre et Marie Curie - Paris 6, case 115, 4, place Jussieu, 75252 Paris cedex 05, France

⁴ICMMO, Universit Paris 11, 91405 Orsay, France

⁵Synchrotron SOLEIL, L Orme des merisiers, 91192 Gif sur Yvette Cedex, France

ABSTRACT

In the high-temperature (Tc) cuprate superconductors, a growing body of evidence suggests that charge ordering competes with superconductivity [1-3]. However, in cuprates such as La_{2-x}Ba_xCuO₄ (LBCO) and La_{2-x-y}Nd_ySr_xCuO₄ (LNSCO), whether the charge-modulations favor or compete with superconductivity, and their effect on the electron-phonon coupling are not yet understood, although an effect of the stripe order on the Cu-O bond-stretching mode is observed. We investigated the electronic structure of a La_{2-x}Ba_xCuO_{4+ δ}(LBCO) sample which displays simultaneously high temperature superconductivity and well defined Cu-O bond stretching softening, possibly due to the charge order instability. We find a kink in the band dispersion at a constant energy over the entire Fermi arc, at an energy matching the one of the softened Cu-O bond stretching phonon. Moreover, supposing that the scattering of this mode with the charge carriers quasi-particles is at the origin of the observed ARPES kink we also find a good match with the wave-vectors range of this mode softening.

^{1.} Chang, J. *et al.* Direct observation of competition between superconductivity and charge density wave order in YBa₂ Cu₃ O_{6.67}. *Nature Phys.* **8**, 871–876 (2012).

^{2.} Comin, R. et al. Charge order driven by Fermi-arc instability in Bi2 Sr2-x Lax CuO_{6+δ}. Science 343, 390–392 (2014).

^{3.} Da Silva Neto, E. H. *et al.* Ubiquitous interplay between charge ordering and high-temperature superconductivity in cuprates. *Science* **343**, 393–396 (2014)

List of Other Posters

PO-01	BM02 - D2AM French CRG Beamline at the ESRF Dedicated to Anomalous Characterization in Materials Science <i>N. Blanc</i>				
PO-02	High-resolution Infrared Spectroscopy of Cubane, C ₈ H ₈ V. Boudon				
PO-03	Let's ROCK <i>V. Briois</i>				
PO-04	Noncollinear Spin Structure in Ferrimagnetic DyCo4 Film <i>K. Chen</i>				
PO-05	In Situ X-ray Diffraction Studies on PZT Thin Films T.W. Cornelius				
PO-06	X-ray Crystallographic Parameters Investigations of Aluminium-based alloys <i>M. Draissia</i>				
PO-07	A Photoemission Study of Selenium and Sulfur Interaction with Cu(100) and Cu(111) Surfaces <i>V.A. Esaulov</i>				
PO-08	Crystal Structure of a Zinc-responsive MarR Family Member, Lactococcus lactis ZitR <i>P. Fernández Varela</i>				
PO-09	Structural Biology of Regulators of Membrane Traffic and Cell Motility Y. Ferrandez				
PO-10	Studies of Vanadate Heterostructures and Polar Interface by HAXPES A. Fouchet				
PO-11	Structural Study of Unconventional Proteins, the Membrane Hairpin Proteins, using DISCO Light <i>M. Froissard</i>				
PO-12	Synchrotron X-ray Hydroxyl Radical Footprinting Mass Spectrometry to Probe Structure of Proteins in Interactions Y. Gohon				
PO-13	Following Enzyme Localization and Cell Wall Modification During Biomass Hydrolysis by Autofluorescence and Infrared Imaging <i>F. Guillon</i>				
PO-14	Band Mass Anisotropy in the Metallic Boron Doped Diamond <i>H. Guyot</i>				
PO-15	New Electron States at the Bi/InAs(111) Interface K. Hricovini				
PO-16	K-shell Photoionisation of Molecular lons (CH^+ , CH_2^+) E.T. Kennedy				

PO-17	Photoelectron-photoion Coincidence Spectroscopy for Multiplexed Detection of Intermediate Species in a Flame <i>J. Krüger</i>				
PO-18	In situ Synthesis of Magnesium Carbides at HPHT Conditions 0.0. Kurakevych				
PO-19	Effect of Symmetry Breaking on Electronic Band Structure: Gap Opening at the High Symmetry Points <i>D.Malterre</i>				
PO-20	Investigating the Early Steps of Bio-mineralization in Calcite Mollusk Shell with 2D Bragg Ptychography <i>F. Mastropietro</i>				
PO-21	The Multi-technique Hard X-ray Scanning Imaging Station of Nanoscopium Possibilities for Biological Studies <i>K. Medjoubi</i>				
PO-22	Simultaneous DAFS and XAFS Analyses to Evidence the Y- and Ti- species in Nano-structured ODS Steels <i>D. Menut</i>				
PO-23	SAXS Studies of Nanoparticles Formed by Laser Ablation and in Electric Arcs <i>J.B.A. Mitchell</i>				
PO-24	Double Photoionization in Ring Molecules: Search of the Cooper Pair Formation <i>J. Palaudoux</i>				
PO-25	Multiple Photoionization Processes of Hg, K and Rb Atoms <i>J. Palaudoux</i>				
PO-26	Influence of Pressure on Structural and Magnetic Transitions in $Y_{1\text{-}x}Tb_xFe_2D_{4,2}$ Compounds V. Paul-Boncour				
PO-27	New Amplitude Criteria for Scattering Path Selection in EXAFS Fit. Application to bis(S thiocyanato)(cyclohexanediamino)Platinum(II) <i>K. Provost</i>				
PO-28	Double Core-hole States in SiX ₄ (X = F, Cl, Br, and CH ₃) Molecules Derived by Photoelectron and KLL Auger Spectroscopy <i>R. Püttner</i>				
PO-29	In situ X-ray Scattering Investigations on SiGe Nanowires: Growth, Strain and Dance <i>G. Renaud</i>				
PO-30	HERMES: A Dual-branch Soft X-ray Spectromicroscopy Beamline at SOLEIL S. Swaraj				
PO-31	$\rm CH_3^+$ Formation in the Dissociation of Energy-selected $\rm CH_3F^+$ lons Studied with Double Imaging Electron/Ion Coincidence X. Tang				
PO-32	High-resolution Imaging of Mechanical Properties using a Mid-infrared Synchrotron Radiation <i>O. Vitrac</i>				

PO-33	Photo-chemical Processes of Interstellar Polycyclic Aromatic Hydrocarbon (PAH) Cations with Synchrotron Irradiation <i>J. Zhen</i>				
PO-34	Synergy Between Gold and Mo ₂ N Leading to Platinum-like Activity for Hydrogen Evolution <i>A. Zitolo</i>				

BM02 - D2AM French CRG Beamline at the ESRF Dedicated to Anomalous Characterization in Materials Science

N. Blanc, N. Boudet, S. Arnaud

Univ. Grenoble Alpes, Inst NEEL, F-38000 Grenoble, France CNRS, Inst NEEL, F-38042 Grenoble, France

ABSTRACT

The BM2-D2AM Beamline is a French CRG dedicated to Materials Science, which was one of the first lines to operate at start-up of the ESRF in 1994. It is dedicated to studies of the microscopic structure of materials using two principle techniques: (i) wide angle X-ray scattering, which provides information on long-range ordering at the atomic scale and (ii) small angle X-ray scattering, which provides information on the shapes of objects at the mesoscopic scale (typically 0.1to 1 micron). Both of these methods can be coupled with "anomalous" X-Ray scattering, which yields additional chemical information by providing contrast between different kinds of atoms.

The beamline has been completely refurbished with the aim of providing state-of-the-art optics on a bending magnet beamline and versatile instruments where users in-situ apparatuses can be inserted. Recent developments in materials science require the ability to

perform X-ray characterization on heterogeneous, multi-scale samples under specific conditions, such as:

• In operando and time-resolved studies of advanced materials used for energy production and storage (batteries, membranes)

• In situ mechanical stress applied to biopolymers

• In situ and time-resolved annealing of thin films, nanostructures, ... under controlled atmosphere to obtain new structural properties.

In 2015 some new apparatus will be set up to continue our efforts on the upgrade of the beamline:

- a new pixel detector with a special "O-shaped" design for simultaneous saxs-waxs measurements;
- a cryostat for low temperature studies. Less than 10 K will be achievable for *in situ* studies on the kappa goniometer without loosing of the 6 circle possibilities;
- high temperature studies. A in-house designed furnace will allow in air or in vacuum high temperature studies up to 1500 C;
- micro beam. A kirkpatrick-Baez system will reduce the beam to a few tens of microns in order to perform grazing incidence studies and diffraction tomography.

High-resolution Infrared Spectroscopy of Cubane, C₈H₈

M. Lamy^a, F. Dugue-Boyer^a, <u>V. Boudon</u>^a, O. Pirali^b, S. Gruet^b, L. D'accolti^c, E. Alikhani^{d,e}

 ^a Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS Université de Bourgogne, 9 avenue Alain Savary, B.P. 47870, F-21078 Dijon Cedex, France.
 ² Ligne AILES – Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Gif-sur-Yvette, France.
 ³Dipartimento di Chimica, Università di Bari A. Moro, Bari, Italy.
 ⁴Sorbonne Universiés, UPMC Univ. Paris 06, UMR 8233, MONARIS, F-75005, Paris, France.

⁵CNRS, UMR 8233, MONARIS, F-75005, Paris, France.

ABSTRACT

Carbon-cage molecules have generated a considerable interest from both experimental and theoretical point of views. We recently performed a high-resolution study of adamantane $(C_{10}H_{16})$, the smallest hydrocarbon cage belonging to the diamandoid family¹. There exists another family of hydrocarbon cages with additional interesting chemical properties: the so-called Platonic hydrocarbons that comprise dodecahedrane $(C_{20}H_{20})$ and cubane (C_8H_8) . Both possess C–C bond angles that deviate from the tetrahedral angle (109.8°) of the *sp*³ hybridized form of carbon. This generates a considerable strain in the molecule. Cubane itself has the highest density of all hydrocarbons (1.29 g/cm³). This makes it able to store large amounts of energy, although the molecule is fully stable. Up to now, only one high-resolution study of cubane has been performed on a few bands².

We report here a new wide-range high-resolution study of the infrared spectrum of cubane. The sample was synthesized in Bari upon decarboxylation of 1,4-cubanedicarboxylic acid thanks to the improved synthesis of literature³; its ¹H and ¹³C NMR, FTIR, and mass spectrometry agreed with reported data⁴. Several spectra have been recorded at the AILES beamline of the SOLEIL French synchrotron facility. They cover the 800 to 3100 cm⁻¹ region. Besides the three infrared-active fundamentals (v₁₀, v₁₁ and v₁₂), we could record many combination bands, all of them displaying a well-resolved octahedral rotational structure. We present here a preliminary analysis of some of the recorded bands, performed thanks to the SPVIEW and XTDS software, based on the tensorial formalism developed in the Dijon group⁵.

A comparison with *ab initio* calculations, allowing to identify some combination bands, will be also presented.

- 1. O. Pirali, V. Boudon, J. Oomens, M. Vervloet, J. Chem. Phys., 136, 024310 (2012).
- 2. A. S. Pine, A. G. Maki, A. G. Robiette, B. J. Krohn, J. K. G. Watson, Th. Urbanek, J. Am. Chem. Soc., 106, 891-897 (1984).
- 3. P. E. Eaton, N. Nordari, J. Tsanaktsidis, P. S. Upadhyaya, Synthesis, 1, 501, (1995).
- 4. E. W. Della, P. T. Hine, H. K. Patney, J. Org. Chem., 42, 2940 (1978).
- 5. Ch. Wenger, V. Boudon, M. Rotger, M. Sanzharov and J.-P. Champion, J. Mol. Spectrosc., 251 102–113 (2008).

Let's ROCK

L. Barthe, S. Belin, <u>V. Briois</u>, C. La Fontaine, Th. Moreno, V. Pinty

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

ABSTRACT

The ROCK beamline (acronym for Rocking Optics for Chemical Kinetics) is the new Quick-EXAFS beamline at SOLEIL dedicated to the study of fast kinetic processes in materials used in catalysis and energy storage. This beamline was granted in 2011 by the Agence Nationale de la Recherche in the framework of the national "Grand Emprûnt". The commissioning of the complete installation will start in February 2015 before to open progressively the beamline to the users during the first semester of 2015.

The beamline is equipped with two equivalent Quick-EXAFS monochromators (Si(111) and Si(220)) originally designed at SOLEIL and successfully used at the SAMBA beamline from 2009 to 2013 [1]. ROCK will cover permanently the 4-40 keV energy range and will offer a time resolution of 50 ms per spectrum. The lateral size of the beam at the sample position can range from a few mm to ~450 μ m by changing the sample position inside the experimental hutch as illustrated Figure 1. This will allow varying the density of photons on the sample keeping nearly constant the flux and then the time resolution performance of the beamline. Automatization of fast exchange of monochromators will be implemented in order to fully use the potentiality of the beamline to study multi-edges quasi-simultaneously.



Fig. 1: First beams observed at different positions along the travel of photons inside the ROCK's experimental hutch (at the top) compared to the calculated ones (at the bottom).

REFERENCES

 E. Fonda, A. Rochet, M. Ribbens, L. Barthe, S. Belin, V. Briois "The SAMBA quick-EXAFS monochromator: XAS with edge jumping" J. Synchrotron Rad. 2012, 19, 417 - 424

Noncollinear Spin Structure in Ferrimagnetic DyCo4 Film

K. Chen

Synchrotron SOLEIL, L'orme des Merisiers, Saint Aubin – BP48, 91192 Gif-sur-Yvette Cedex

ABSTRACT

Synchrotron soft x-ray magnetic circular (XMCD) spectroscopies at the Dy $M_{4,5}$ and Co $L_{2,3}$ edges are reported to investigate the temperature dependent magnetic properties of rare earth-transition metal(RE-TM) DyCo4 alloy film. The element specific measurements of XMCD and the application of the sum rules allow one to monitor the detailed changes in the magnetic contribution from both sites separately. In a temperature region between 4.4K and 300K, the two sites of Co and Dy are ferrimagnetic alloy coupled, with the Dy (Co) magnetization aligned to the applied field as the dominant site below (above) the compensation temperature ($T_{comp} = 250$ K)[see Fig.1]. Twisted and noncollinear spin structures in DyCo4 alloy are observed with bulk or surface twist inhomogeneous magnetic states around T_{comp} [see Fig.2].



FIG. 1. (color Online) XAS and XMCD with the magnetic field applied out of plane for Co L_{2,3} at 4.4K(a) and 300K(b) and Dy M_{4,5} at 4.4K(c) and 300K(d). Magentic moment of Dy and Co are $6.5\mu_{\rm B}/{\rm atom}$ and $-1.3\mu_{\rm B}/{\rm atom}$ at 4K, and $-3.47\mu_{\rm B}/{\rm atom}$ and $1.56\mu_{\rm B}/{\rm atom}$ at 300K, respectively.



FIG. 2. (color Online) Hysteresis measured from ($\sigma^+ - \sigma^-$) with the magnetic field applied out of plane for Dy M₅ and Co L₃ from 4.4K to 300K (top to buttom). The compensation temperature T_{comp} is between 230 and 270K.

In Situ X-ray Diffraction Studies on PZT Thin Films

<u>T.W. Cornelius¹</u>, A. Davydok¹, C. Mocuta², E.B. Araújo³, E.C. Lima⁴, O. Thomas¹

¹Aix-Marseille Université, CNRS, IM2NP (UMR7334), Marseille, France ²DiffAbs beamline, Synchrotron SOLEIL, France ³Departamento de Física e Química, Universidade Estadual Paulista, Ilha Solteira, SP, Brazil ⁴Universidade Federal do Tocantins, Porto Nacional, TO, Brazil

ABSTRACT

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

For studying the piezoelectric properties of Pb(Zr_{0.5}Ti_{0.5})O₃ (PZT) thin films consisting of few tens of nanometer sized grains, *in situ* time resolved X-ray diffraction has been performed at the DiffAbs beamline at Synchrotron SOLEIL. For this purpose, gold electrodes of 0.3 mm in diameter were deposited on top of the thin film. One electrode was contacted electrically (see Fig. 1(a)) and the diffraction signal from an area under the electrode (beam size: $4.5 \times 7 \ \mu m^2$) was monitored as a function of the applied electric field. Two-theta curves of the 110-PZT Bragg reflection extracted from the recorded XPAD images is presented in Fig. 1(b) showing a shift of the Bragg peak to lower 2theta values for an applied voltage of 9 V, i.e. a piezoelectric extension. The piezoelectric strain as a function of the applied voltage displayed in Fig. 1(c) reveals a "butterfly loop" [3]. The asymmetry and the fact that the loop is not closed most probably originate from a self-polarization of the thin film. These findings are supported by piezoelectric force measurements revealing an asymmetry of the hysteresis loops towards positive electric fields (not shown here) which are a clear signature of a macroscopic self-polarization effect in the studied PZT films.



Fig. 1: a) Optical microscopy image of PZT thin film with gold electrodes deposited on top of which one is contacted electrically. b) Two-theta curve of the 110-PZT Bragg peak at a voltage of 0 and 9 V. c) Piezolectric strain as a function of applied voltage at two different positions on the PZT thin film.

^[1] J.F. Scott and C.A. Araujo, Science 246, 1400 (1989).

^[2] J.F. Scott, Ferroelectric Memories (Springer, Heidelberg, Germany, 2000).

^[3] M.C. Ehmke. J. Glaum, M. Hoffman, J.E. Blendell, K.J. Bowman, J. Am. Ceram. Soc. 96, 2913 (2013).

X-ray Crystallographic Parameters Investigations of Aluminium-based alloys

<u>M. Draissia</u>¹, S. Boulkhessaim^{1,2}, A. Boutouta¹, Y. Souilah¹, H. Bedboudi^{1,3}, A . Bourbia^{1,4}

 ¹Lm2S, Département de Physique, Faculté des Sciences, Université Badji-Mokhtar de Annaba, PB 12, Annaba 23000, Algeria.
 ² Université 20 Août 1955 Skikda, BP26 route d'El-Hadaiek, 21000 Algérie.
 ³ Ecole Normale Supérieure d'Enseignement Technologique de Skikda, Algeria.
 ⁴ Ecole Préparatoire aux Sciences & Techniques de Annaba, Algeria.

ABSTRACT

In this research work contribution, we present used modes to determine the crystallographic parameters of some aluminium-based alloys structures from X-Ray patterns. XRD (I, 20°) (ORIGIN 6.0 software), Rietveld refinement (Maud-v2.3) and deduced crystallographic parameters from relevant parameters (JCPDS-ICDD 1997) cards of the binary Al-Ti system of a heat-treated (1h, 500°C) Al-20 m.%Ti alloy made under vacuum by the hf (300 kHz) induction melting process [1-2].



Peak	IR	Measured	Identified	hkl	Calculated
line		20°	Phase		20°
1	15	35,48	α-Ti	100	35,093
2	19	36,2	Ti₃Al	200	35,951
3	3	39,16	AI	111	38,472
4	9	41,72	Ti₃Al	201	41,201
5	4	44,12	AI	200	44,738
6	10	62,04	Al₃Ti	213	62,903
7	3	66,04	AI	220	65,133
8	α	71,72	Ti₃Al	203	72,093
9	63	75,16	Al ₃ Ti	116	74,914
10	20	79,4	Ti₃Al	401	79,626

Figure, Table : XRD (I, 20°) Rietveld refinement and deduced crystallographic parameters of AI-20 m.%Ti alloy.

^{1.} M. Draissia, 21st International conference on X-Ray and Inner-Shell Processes, Paris June 22-27 2008 .

Salim Boulkhessaim, Yamina Souilah, Hayette Bedboudi, Amel Bourbia and Mohamed, Draissia, Characterization of the Al3Ti phase in Al-Ti alloys, The European Physical Journal Applied Physics 62 (1) 10701 (2013) DOI: 10.1051/epjap/2013120509.

^{3.} A Bourbia, S Boulkhessaim, H Bedboudi and M Draissia, Phase transformation in rapidly solidified Al–Al2O3alloys by high-frequency melting Physica Scripta 85 (5) 055601 (2012) DOI: 10.1088/0031-8949/85/05/055601.

A Photoemission Study of Selenium and Sulfur Interaction with Cu(100) and Cu(111) Surfaces.

T. Jiang*, Y. Tong*[§], A. Bendounan[§], F. Sirotti[§] and <u>V.A. Esaulov*</u>

*Institut des Sciences Moléculaires d'Orsay, ISMO, UMR 8214, Université Paris Sud, Bâtiment 351, 91405 Orsay, France [§]L'Orme des Merisiers, Synchrotron SOLEIL, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex, France

ABSTRACT

In recent years interaction of sulfur and selenium with various metal surfaces has been the object of renewed attention in relation with questions of selfassembly of organic molecules and formation of self-assembled monolayers (SAMs) such as alkane and aromatic thiols and dithiols and thiophenes. It is also noteworthy that there has been recently much interest in various sulfides, selenides and sulfo selenides. Some of these are semiconducting materials. Copper sulfides, including thin films, have been investigated in view of potential applications in solar cells, optical filters, nanoswitches, photoacoustic imaging, thermoelectric and photoelectric transformers, and gas sensors. In this context various Cu_2S , Cu_2Se , CuS_xSe_{2-x} nanostructures have been synthesized. However accurate high resolution photoemission data on core level binding energies (CLBEs) of sulfur and copper even for well-ordered submonolayer chemisorption structures on monocrystalline Cu surfaces, which would be helpful in the aforementioned investigations, are missing. We recently reported on S and Se adsorption on Ag¹, Cu², and Pd³. In this work our objective was to obtain spectroscopic information on CLBE's for Se chemisorption on Cu(111) and Cu(100) and we also investigate S and Se coadsorption. As for thiols⁴, this would be useful in differentiating between molecular Se and chemisorbed atomic Se in molecular adsorption⁵ and also in studies of ultrathin chalcogenide layers like in the case of MoSe₂ whose characteristics could differ from the more bulklike selenides.

Se adsorption was performed by immersion of pristine samples into aqueous Na2S, which provokes strong selenisation of copper. A high resolution study of the CLBE's for Cu, S and Se was performed on the TEMPO beamline at Soleil synchrotron. Samples were annealed progressively. Annealing leads to partial elimination of Se and progressive formation of well-ordered surface Se phases followed here by LEED. This translates into sizable Cu 2p core level binding energy (CLBE) shifts as well as changes in the Se 3d binding energies. Sulfoselenide adsorption was performed by immersion of pristine samples into aqueous Na₂S/Na₂Se solutions. In case of S-Se coadsorption both S and Se is adsorbed, but annealing to above 500°C seems to lead to partial elimination of sulfur.

Jia, J.; Bendounan, A.; Harish, M. N. K.; Chaouchi, K.; Sirotti, F.; Sampath, S.; Esaulov, V. A. Selenium Adsorption on Au(111) and Ag(111) Surfaces: Adsorbed Selenium and Selenide Films. J. Phys. Chem. C 2013, 117, 9835–9842.
 M. P. Brown and K. Austin, Appl. Phys. Letters 85, 2503-2504 (2004).

Jia, J.; Bendounan, A.; .; Chaouchi, K.;; Esaulov, V. A, Sulfur Interaction with Cu(100) and Cu(111) Surfaces: A Photoemission Study. J. Phys. Chem. C, 2014, 118 (42), pp 24583–24590, dx.doi.org/10.1021/jp5078517

^{3.} Jia, J.; Bendounan, A.; Chaouchi, K.; Kubsky, S.; Sirotti, F.; Pasquali, L.; Esaulov, V. A. Chalcogen Atom Interaction with Palladium and the Complex Molecule-Metal Interface in Thiol Self Assembly. J. Phys. Chem. C 2014, DOI: 10.1021/jp507051q.

^{4. 1,4-}Benzenedimethanethiol Interaction with Au(110), Ag(111), Cu(100), and Cu(111) Surfaces: Self-Assembly and Dissociation Processes J.Jia, A.Giglia, M.Flores, O. Grizzi, L.Pasquali, and V. A. Esaulov J. Phys. Chem. C, 2014, 118,, 26866–26876

^{5.} Spectroscopic ellipsometry of self assembled monolayers: interface effects. The case of phenyl selenide SAMs on gold.

M.Canepa,G.Maidecchi, C.Toccafondi, O.Cavalleri, M. Prato, V.Chaudharicd and V.A. Esaulov, *Phys.Chem. Chem. Phys.*, 2013, **15**, 11559

Crystal Structure of a Zinc-responsive MarR Family Member, *Lactococcus lactis* ZitR

<u>P. Fernández Varela^{1,2}</u>§, P. Legrand¹, C. Velours³, B. Pineau¹, I. Poquet^{4,5}

 ¹Synchrotron SOLEIL, L'Orme des Merisiers – Saint Aubin BP 48 91190 Gif-sur-Yvette, France
 ^{2*}Laboratoire d'Enzymologie et Biochimie Structurales, Centre de Recherche de Gif, CNRS, Gif-sur-Yvette, France.
 ³IMAGIF, Centre National de la Recherche Scientifique, Centre de recherche de Gif, Avenue de la Terrase - 91190 Gif-sur-Yvette, France
 ⁴Institut Micalis (UMR1319), INRA, Domaine de Vilvert, 78352 Jouy-en-Josas, France
 ^{5*}LPBA, Institut Pasteur, Bât. Calmette, 75015 Paris, France

ABSTRACT

Zinc is a transition metal vital in trace amounts. In *Streptococcaceae* (lactococci and streptococci), unlike the wide majority of bacteria, ABC systems for zinc uptake at high affinity are not controlled by Zur proteins (Fur family), but instead by ZitR or AdcR proteins of the MarR (multiple antibiotic resistance) family. In this extensively studied family characterized by a conserved winged helix fold, ZitR and AdcR are the only proteins implicated in the regulation of metal (zinc) transport. *Lactococcus lactis* ZitR protein was examined, in the presence of DNA fragments containing its binding sites or not, by circular dichroism and calorimetry. These studies revealed that ZitR protein is very stable and confirmed that it is able to bind the previously identified palindromic sites. The structure of *L. lactis* ZitR protein complexed to Zn(II) was solved. ZitR folding pattern is similar to other MarR family members especially in the winged HTH domain, and highly similar to that of *Streptococcus pneumoniae* AdcR protein. Nevertheless, the molecular bases of Zn(II) binding present some difference between ZitR and AdcR.

Structural Biology of Regulators of Membrane Traffic and Cell Motility

S. Fetics, V. Campanacci, M. Folly-Klan, Y. Ferrandez,

S. Veyron, J. Cherfils

ENS Cachan, CNRS

J. Perez, A. Thureau

SOLEIL Synchrotron

ABSTRACT

We are studying molecular reactions that govern the functions of small GTPases in cellular traffic and cytoskeleton dynamics. We will present a survey of our recent X-ray crystallography and/or SAXS studies of guanine nucleotide exchange factors that regulate Arf GTPases in endocytosis [1,2] and Rho GTPases in osteolysis [3], of effectors from bacterial pathogens that hijack Arf [4,5] and Rab GTPases [6], and of a new protein involved in inhibitory signaling in the nucleation of branched actin networks [7].

REFERENCES

[1] Aizel et al., PLoS Biol 2013
 [2] Padovani et al., PNAS 2014
 [3] Vives et al., Nature Comm. 2014 (accepted)
 [4] Folly-Klan et al., PloS Path 2013

[5] Folly-Klan et al., J. Struct. Biol. 2014 (in press)

- [6] Campanacci et al., EMBO J. 2013
- [7] Dang et al., Science 2014

Studies of Vanadate Heterostructures and Polar Interface by HAXPES

<u>A. Fouchet1^{*}</u>, J. E. Rault², J.-P. Rueff², M. Allain¹, B. Berini¹, Y. Dumont¹, N. Keller¹

¹Université Versailles St Quentin, CNRS, Groupe d'Étude de la Matière Condensée (GEMaC), 78035 Versailles, France. *Email: <u>fouchet@physique.uvsq.fr</u> ² Synchrotron-SOLEIL, BP 48, Saint-Aubin, F91192 Gif sur Yvette CEDEX, France.

ABSTRACT

With the improvement of thin films growth, novel properties at oxide interfaces appear and lead to the development of new functionalities through **material confinement and engineering**. Understanding these properties brings up new challenges including control of the growth, characterization and interpretation. All-new chemistry and physics appear with oxide ultrathin films: electronic correlations, structure, strain, intermixing, oxygen deficiency, surface reconstructions, are the means to control the properties of oxide heterostructures. In condensed matter physics, Mott-Insulator - Metal Transition (MIT) is one of the most fascinating phenomena. For example, $SrVO_3$ (SVO) perovskite shows a *3d1* electronic configuration and is a paramagnetic metal in bulk. It is a typical system where control of the dimensionality can induce Metal-Insulator Transition (MIT) and even novel properties such as Mott insulator ferromagnetism [1].

In our group, the films were deposited by pulsed laser deposition (PLD) and the MIT has been characterized by transport measurements when the thickness of the films is reduced from 7 nm to 1 nm. In this transition region, transport evolves from a metallic to a strongly localized behavior, where the evolution of the upturn in the resistivity can be explained by the Quantum correction of the conductivity and variable range hopping model [2].

Furthermore, the upturn of the resistivity can also be controlled by interface engineering in embedding SVO ultrathin films in between insulators $SrTiO_3$ (STO) and $LaAIO_3$ (LAO) (a few nm) in order to control the electronic correlations at the interface. SVO sandwiches have shown interesting features compare to only SVO on STO substrate with a decrease of the resistivity of the embedded film and a control of the upturn of the resistivity with thickness. Electronic correlations are indeed strongly affected by the presence the LAO layer and polar discontinuities can be an explanation in order to control the electronic properties as in LAO/STO heterostructures [3].

At the GALAXIES beamline, we have conducted hard x-ray photoemission spectroscopy (HAXPES) of core levels on SrVO₃ heterostructures with and without LAO thin films in order to better understand the interfacial effects. For this, we have taken advantage of near-total reflection to access depth-resolved properties of the vanadate thin films to better understand the difference between surface, interface and bulk like chemical composition of the different heterostructures.

- 1. V. Prado & W. E. Pickett, PRB 81, 245117 (2010).
- 2. M. Allain et al. (submitted to PRB)
- 3. A. Ohtomo & H. Y. Hwang, Nature 427 (2004) 423

Structural Study of Unconventional Proteins, the Membrane Hairpin Proteins, using DISCO Light

J.-D.Vindigni¹, C. Cebo², R. Tâche¹, F. Jagic¹, A. Giuliani^{3,4}, F. Wien⁴, T. Chardot¹, Y. Gohon¹, <u>M. Froissard¹</u>

¹Institut Jean-Pierre Bourgin⁻ INRA AgroParisTech, UMR1318, Versailles, France 2Génétique Animale et Biologie Intégrative, INRA AgroParisTech, UMR1313, Jouy-en-Josas, France ³Département Caractérisation et Elaboration des Produits Issus de l'Agriculture, U1008 INRA, 44 316 Nantes ⁴Synchrotron SOLEIL, Gif-sur-Yvette, France

ABSTRACT

Membrane proteins are proteins that interact with biological membranes. They are targets of over 50% of all modern medicinal drugs. Membrane proteins perform a variety of functions vital to the survival of organisms: signal reception and transduction, transport of molecules and ions across the membrane, enzymatic activities, etc. Various topologies are described such as, transmembrane proteins spanning the phospholipid bilayer or proteins attached to only one side of the membrane via hydrophobic loop, amphipathic helices or lipid anchor. However, one class of membrane protein is poorly described in the literature: membrane hairpin proteins. These proteins are present in all organisms and some of them are found associated with lipid droplets (LD). These observations suggest that membrane hairpin proteins share biological and biophysical properties.

LD are lipid storage intracellular nanoparticles consisting mainly of a core of neutral lipids (triacylglycerols and/or steryl esters) enclosed in a monolayer of phospholipids. LD contain a number of proteins which vary considerably with the species. Some structural hydrophobic proteins stabilize the interface between lipid core and cellular aqueous environment. Seed LD are completely covered by oleosins, which belong to the membrane hairpin protein family.

We developed a genetic approach using *Saccharomyces cerevisiae* to obtain heterologous expression of plant oleosins [1], but also mammalian stomatin and caveolin, and hepatitis C virus core protein. These transformed yeasts and purified LD were used for functional and structural studies. Yeast expressing oleosins overaccumulated LDs leading to a specific increase of storage lipids and these LDs harbor a high level of oleosins. Purified LDs were exposed to synchrotron light on DISCO beamline. We obtained structural data on whole cellular organelle and on oleosins inserted in LD using Sychrotron Radiation Circular Dichroism (SRCD) [2].

¹ M; Froissard, S. D'andrea, C. Boulard and T. Chardot. FEMS Yeast Research, 9, 428-438 (2009)

² J. D. Vindigni, F. Wien, A. Giuliani, Z. Erpapazoglou, R.Tâche, F. Jagic, T. Chardot, Y. Gohon and M. Froissard. BBA Biomembranes, 1828, 1881-1888. (2013)

Y. Gohon¹, P. Jolivet¹, M. Froissard¹, R. Tâche¹, T. Chardot¹, A. Giuliani², P. Mercere², M. Vermachova³, A. H. Młynarczyk⁴, R. Daniel⁴ and F. Gonnet⁴

¹ INRA, AgroParisTech, UMR1318 Institute Jean-Pierre Bourgin, Saclay Plant Sciences 78000 Versailles, France

² Synchrotron Soleil, DISCO and Metrology beamlines, BP48, 91192 Gif-sur-Yvette, France ³ Institute of chemical Technology, Department of Biochemistry and Microbiology, Prague, Czech Republic

⁴ CNRS, UMR 8587, Université d'Evry-Val-d'Essonne Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement (LAMBE), Bd Francois Mitterrand, 91025 Evry Cedex, France

ABSTRACT

Getting structural information about bio-molecular assemblies remains a challenging work. OH° radical footprinting is an approach allowing solvent accessible surfaces to be determined. Combined with mass spectroscopy analysis, it enables fine variations detections of surface exposition resulting from complex formation or conformational changes. Since two years three labs with common structural question about their biomolecules of interest collaborate to settle a novel approach on Soleil Beamlines. We present here results of two kind of protein interactions 1) protein-protein interactions implicated in human immune response; 2) proteins partially embedded in lipid droplets.

RX radiations from Metrology beamline were used to generate OH° radicals through water molecules radiolysis. OH° radicals oxidize reactive functional groups of the target bio-molecules in contact with surrounding water¹. In the present case solvated amino-acids (a. a.) will be oxidized in a time resolved manner.

1) In the innate immune system, Factor H is a key protein for the regulation of the alternative pathway of the complement system. This large protein (155 kDa) is composed of 20 repetitive domains and interacts with the C3b complement protein. To date, only partial structural data² are available on the C3b-Factor H complex. Results presented here, give new insight of this complex and propose and complete model of the interaction.

2) In Lipid Droplets (LDs), intracellular lipid storage organelles, some proteins are tightly bound at the surface of the hemi-membranes. These proteins (oleosins³ in plant LDs) have a large hydrophobic domain (~70 a. a.) flanked by two hydrophilic N and C terminal domains. The overall structure of these proteins in their native lipidic environment is poorly known⁴. Results presented here show that the hydrophobic part of these proteins is certainly buried in the oil core of LDs.

- 1. Takamoto and Chance (2006) Annu. Rev. Biophys. Biomol. Struct. 35pp. 251-276

J. Wu, et al. (2009) Nat. Immun. 10 (7), pp. 728-734.
 Kim et al. (2002) J. Biol. Chem. 277, pp. 22677-22684.
 J.-D. Vindigni et al. (2013) Biochim. Biophys. Acta 1828, pp. 1881–1888.

Following Enzyme Localization and Cell Wall Modification During Biomass Hydrolysis by Autofluorescence and Infrared Imaging

<u>F. Guillon¹</u>, W. André², E. Bonnin¹, B. Bouchet¹, S. Durand¹, C. Alvarado¹, P. Robert¹, B. Chabbert³, G. Paës³, V. Aguie³,

F. Jamme² and M.-F. Devaux¹. ¹UR1268 BIA, INRA, F-44300 Nantes .²Synchrotron SOLEIL, BP 48 F- 91192 Gif-sur-Yvette. ³UMR614 FARE, INRA, F-51100 Reims.

ABSTRACT

The enzymatic conversion of lignocellulosic materials for the production of fine and bulk chemicals in place of the pretoleum feedstock is a very promising approach due to enzyme high selectivity and mild use conditions. However, the complex architecture of plant cell walls make them very resistant to degradation. In addition, a huge heterogeneity in cell wall composition is observed according to cell types leading to difficulties to elucidate this recalcitrance. Techniques able to simultaneously observe enzymes and cell walls during the reaction are required to get a deeper insight into the barriers that limit the degradation.

The objective of the present work was to investigate the potential of using the synchrotron source and the experimental devices available at synchrotron SOLEIL to follow both the enzyme and cell wall composition changes. The differences in enzymatic degradation according to cell types was studied in maize stems tissues using cellulase and hemicellulase. The enzyme localisation was followed at the DISCO beamline thanks to autofluorescence of tryptophan in the DUV range. Cell wall structure was visible in a separate channel thanks to autofluorescence of phenolic compounds. For both enzymes, contrasts between cell types were evidenced: enzymes were excluded from sclerenchyma and from some parenchyma cells that were concentrated on the cell walls. Using cellulase, the result was a separation between adjacent cells followed by a complete degradation of cell walls. Using hemicellulase, after a partial degradation of cell walls, the enzymes were released in the medium.

The evolution of cell wall composition was tracked by FT-IR spectroscopy on the SMIS beamline using a microfluidic cell. The microfluidic device available at the SMIS beamline was adapted for maize section enzymatic degradation. ZnS windows were retained to be able to analyse the sugar fingerprint region and therefore built specifically for the microfluidic cell. Spacer masks of 20 μ m thickness were cut to ensure fluid circulation and the positioning of the sample. The whole cell volume was about 1 μ L. Enzyme was delivered with a flow of 2 μ L/min. Spectra of cell walls of different cell types could be obtained by taking the aqueous medium as background. In non-degraded cells, spectra did not changed during the reaction time while in degraded cell walls at least a variation in intensity was observed until the full disappearance of the spectra. Further analysis of the spectra is required to investigate more specific changes in composition.

The first results obtained were very promising. Next step is to extract the quantitative data from the whole set of data according to cell types and time lapse.

Band Mass Anisotropy in the Metallic Boron Doped Diamond

H. Guyot ^{A,B}, A. Nicolaou^C, A. Taleb^C and E. Bustarret^{A,B}

A. Université Grenoble Alpes, F-38000 Grenoble, France
 B. Institut Néel, CNRS-UJF, BP 166, 38042 Grenoble Cédex 9, France
 C. 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 band structure measured in two directions of high symmetry is found to be in good agreement with the theoretical DFT band structure after correction. The parametric k.p model also describes the experimental bands with accuracy and the analysis of the band tops leads to determining the anisotropy of the hole masses.

New Electron States at the Bi/InAs(111) Interface

<u>K. Hricovini^{1,2}</u>, J.-M. Mariot³, L. Nicolaï^{1,2,7}, U. Djukic¹, M. C. Richter^{1,2}, O. Heckmann^{1,2}, T. Balasubramanian⁴, M. Leandersson⁴, J. Sadowski⁴, J. Denlinger⁵, I. Vobornik⁶, J. Braun⁷, H. Ebert⁷, J. Minar^{7,8}

¹LPMS, Université de Cergy-Pontoise, 5 mail Gay-Lussac, F-95031 Cergy-Pontoise, France ²DSM, IRAMIS, SPEC, CEA-Saclay, F-91191 Gif-sur-Yvette, France

³ UPMC Univ~Paris~06, UMR~7614, LCP–MR, 11 rue P. et M. Curie, F-75005 Paris, France ⁴ MAX-lab, Lund University, P.O. Box 118, S-221 00 Lund, Sweden

⁵ALS, 1 Cyclotron Road, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

⁶Elettra-Sincrotrone Trieste, SS 14 – km 163,5 in Area Science Park, I-34149 Basovizza, Trieste, Italy

⁷LMU Münich, Butenandtstr. 11, D-81377 Münich, Germany

⁸University of West Bohemia, Plzen, Czech Republic

ABSTRACT

The Bi(111) surface is a prototype system to study Rashba splitted surface states [1]. Theoretical studies [2] predicted non-trivial topological surface states appearing on single bilayer of Bi(111) and a more complex behaviour was suggested for a variable film thickness as a function of layer thickness [3]. This clearly indicates that the electronic properties of thin films of this material are far from being understood. The Bi(111) film actually represents a special interesting class of films having an intermediate inter- bi-layer coupling strength that may have a significant influence on the topological property.

As reported in the literature, Bi thin films are grown almost exclusively on Si(111), see e.g. [4], [5]. Here we present combined theoretical and ARPES studies of the electronic structure of Bi(111) films grown on an alternative substrate, InAs(111). Bi growth is epitaxial and a Bi monocrystal of very high quality is obtained after depositing several monolayers. For film thicknesses > 10 bi-layers a 6x1 reconstruction appears in the LEED patterns. The reconstruction results in a new set of unexpected surface states close to the \overline{M} point coexisting with the pristine Bi(111) electronic structure.

We show that a proper description of the photoemission process is necessary to understand a majority of these new states. They correspond to novel bulk-like features observed close to the \overline{M} point. These effects are included in the one-step model of photoemission implemented in the SPR-KKR package [6].

- 1. Yu. M. Koroteev, et al., Phys. Rev. Lett. 93, 046403 (2004)
- 2. M. Wada et al., Phys. Rev. B 83, 121310 (2011)
- 3. Z. Liu, et al., Phys. Rev. Lett. 107 136805 (2011)
- 4. Hirahara T. et al., Phys. Rev. Lett. 97 146803 (2006)
- 5. A. Takayama, et al., Nano Lett. 12, 1776 (2012)
- 6. H. Ebert, D. Ködderitzsch, J. Minar, Rep. Prog. Phys. 74, 096501 (2011)

K-shell Photoionisation of Molecular lons (CH^+ , CH_2^+)

J.M. Bizau^{2,3}, D. Cubaynes^{2,3}, S. Guilbaud², C. Carniato⁴, N. Sisourat⁴,

A. Puglisi⁴, E.T. Kennedy¹ and J.P. Mosnier¹

¹School of Physical Sciences and NCPST, Dublin City University, Dublin 9, Ireland ²Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS UMR 8214, Univ. Paris-Sud, Bât. 350, F-91405 Orsay cedex, France

³Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP 48, F-91192 Gif-sur-Yvette, France ⁴CNRS, UMR 7614, Lab. de Chimie Physique-Matiére et Rayonnement, F-75005, Paris, France

ABSTRACT

Considerable progress has been made in experimental and computational investigations of inner shell resonance structures and photoionisation cross sections for atomic ions. This is not the case however for *molecular* ions, the study of which is still in its infancy.

During a successful run at SOLEIL in 2013, we initiated studies of inner-shell photoionisation for the *molecular ions* SiH⁺, SiH₂⁺ and SiH₃⁺. We now report 2014 experiments on the homologous carbon based hydride molecular ions. Carbon is of particular interest as it is ubiquitous in nature and is the fundamental building block of life. As carbon and hydrogen are respectively the fourth and first most populous species in the universe, C/H based molecular ions are of longstanding direct astrophysical interest.

The MAIA setup on the PLEIADES beamline was used for the experiments reported here. Carbon atomic (C⁺) and molecular hydride ions (CH⁺, CH₂⁺) were produced from methane (CH_4) in an ECR source via plasma heating by a 12.6-GHz microwave power supply.

Mapping of the resonances and photoionisation limits for (C⁺) in the inner shell spectral region allowed us 1) to extend a previous ALS [1] study up to the K edge while providing improved values for the atomic ion absolute cross section 2) to provide a benchmark for the various R matrix calculations [1-3] and 3) to provide a direct comparison with the corresponding molecular ion species CH⁺ and CH₂⁺. Our results constitute the first exploration of the K-shell excitation spectra for both CH⁺ and CH₂⁺. The data were recorded by detecting the C²⁺ dissociation channel for each molecular ion species. The isolation of the individual ions in the initial ion beams was excellent. The photoionisation spectra show systematic changes as the number of attached ligand H atoms is increased from zero (for C⁺) to 2 (for CH₂⁺). Particularly significant is the dramatic change in the main resonance feature on going from CH⁺ to CH₂⁺. No signal was observed in the H⁺ dissociation channel. We note that our set up does not allow detection of neutral fragments.

The experiments demonstrate the continuing versatility and performance of the MAIA-PLEIADES combination.

^{1.} Schlachter A S et al J. Phys. B 37 L103 (2004)

Hasoglu M F et al Astro. J. 724 1296 (2010)
 Wang G L and Zhou X X Chin. Lett. 16 2361 (2007)

Photoelectron-photoion Coincidence Spectroscopy for Multiplexed Detection of Intermediate Species in a Flame

<u>J. Krüger^b</u>, G. A. Garcia^b, D. Felsmann^a, K. Moshammer^a, A. Lackner^a, A. Brockhinke^a, L. Nahon^b, and K. Kohse-Höinghaus^a

^aDepartment of Chemistry, Bielefeld University, Universita itsstraße 25,D-33615 Bielefeld, Germany. E-mail: kkh@uni-bielefeld.de; Tel: +49 521 106-2052 ^bSynchrotron SOLEIL, L'Orme des Merisiers, St Aubin, B.P. 48, 91192 Gif sur Yvette, France

ABSTRACT

Complex reactive processes in the gas phase often proceed via numerous reaction steps and intermediate species that must be identified and quantified to develop an understanding of the reaction pathways and establish suitable reaction mechanisms. Here, photoelectronphotoion coincidence (PEPICO) spectroscopy has been applied to analyse combustion intermediates present in a premixed fuel-rich (phi=1.7) ethene-oxygen flame diluted with 25% argon, burning at a reduced pressure of 40 mbar. For the first time, multiplexing fixedphoton-energy PEPICO measurements were demonstrated in comparison with the scanning "threshold" TPEPICO approach used in recent pioneering combustion investigations. The technique presented here is capable of detecting and identifying multiple species by their cations' vibronic fingerprints, including radicals and pairs or triplets of isomers, from a single time-efficient measurement at a selected fixed photon energy.

Vibrational structures for these species have been obtained in very good agreement with scanning-mode threshold photoelectron spectra taken under the same conditions. From such spectra, the temperature in the ionisation volume was determined. Exemplary analysis of species profiles and mole fraction ratios for isomers shows favourable agreement with results obtained by more common electron ionisation and photoionisation mass spectrometry experiments. It is expected that the multiplexing fixed-photon-energy PEPICO technique can contribute effectively to the analysis of chemical reactivity and kinetics in and beyond combustion.⁽¹⁾

J. Krüger, G. A. Garcia, D. Felsmann, K. Moshammer, A. Lackner, A. Brockhinke, L. Nahon, and K. Kohse-Höinghaus, "Photoelectron-photoion coincidence spectroscopy for multiplexed detection of intermediate species in a flame", Phys. Chem. Chem. Phys. 16, 22791-22804 (2014).

In situ Synthesis of Magnesium Carbides at HPHT Conditions

O.O. Kurakevych,¹ T.A. Strobel,² Y. Le Godec,¹ N. Guignot,³ W.A. Crichton,⁴ J. Guignard,⁴ D.Y. Kim²

1. IMPMC, UPMC Sorbonne Universités, UMR CNRS 7590, Muséum National d'Histoire Naturelle, IRD UMR 206, Paris, 75005, France 2. Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA 3. Synchrotron SOLEIL, Gif-sur-Yvette, 91192, France 4. European Synchrotron Radiation Facility, Grenoble, 38043, France

ABSTRACT

After exploring pressure as additional dimension for chemistry of the Mg-C system, four magnesium carbides are now known: (1) tetragonal MgC₂, (2) orthorhombic α -Mg₂C₃, (3) monoclinic β -Mg₂C₃ [1] and (4) cubic Mg₂C [2]. Taking into account that at ambient pressure and below 5 GPa the elements do not interact at any temperature, it is quite astonishing to observe such rich chemistry. Our results indicate that the previously suggested phase diagram of Mg-C system should be completely revised under high pressure [3].



Figure. In situ synthesis of β -Mg₂C₃. (a) Caesar 2-D energy-angle-intensity data. (b) In situ XRD probing of chemical interaction between Mg and glassy C. (c) Structural refinement using angle-dispersive data.

- 1. T.A. Strobel, O.O. Kurakevych, D.Y. Kim, Y. Le Godec, W. Crichton, J. Guignard, N. Guignot, G.D. Cody, A.R. Oganov, Inorg. Chem. 4, 53, 7020-7027 (2014).
- O.O. Kurakevych, T.A. Strobel, D.Y. Kim and G.D. Cody, *Angew. Chem. Int. Ed.* 52, 8930-8933 (2013).
 O.O. Kurakevych, Y. Le Godec, T.A. Strobel, D.Y. Kim, W.A. Crichton and J. Guignard, *J. Phys. Chem.* C 118, 8128–8133 (2014).

Effect of Symmetry Breaking on Electronic Band Structure: Gap Opening at the High Symmetry Points

G.Vasseur¹, Y. Fagot-Revurat¹, M. Sicot¹, B. Kierren¹, A. Taleb-Ibrahimi. P. Le Fevre², F. Bertran², <u>D.Malterre</u>¹,

¹Institut Jean Lamour, UMR 7198, Université de Lorraine - CNRS, Vandoeuvre-les-Nancy, France ²Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, Gif sur Yvette, France

ABSTRACT

Some characteristic features of band structures like the band degeneracy at high symmetry points or the existence of energy gaps usually reflect the symmetry of the crystal, or more precisely the symmetry of the wave vector group at the relevant points of the Brillouin zone. We'll illustrate this property by considering two-dimensional (2D)-hexagonal lattices characterized by a possible twofold degenerate band at the K points with a linear dispersion (Dirac points). By combining scanning tunneling spectroscopy and angle-resolved photoemission, we study the electronic properties of the Ag/Cu(111) interface reconstruction characterized by an hexagonal superlattice and we show that the gap opening at the K points of the Brillouin zone of the reconstructed cell is due to the symmetry breaking of the wave vector group. We'll also present a methodology to determine the periodic potential of a surface from angle resolved photoemission spectroscopy (ARPES). By mapping the band structure and measuring the energy gap widths at high symmetry points of the surface Brillouin zone with ARPES, we are able to estimated the first Fourier components of the electronic potential corresponding to the triangular reconstruction of Ag/Cu(111). We use the potassium atom doping to precisely tune the band gap energies. This potential determination allows to calculate the local density of states which is found to be in very good agreement with scanning tunneling spectroscopy data.



<u>Fig1</u>: Band dispersion in the Γ M and Γ K directions determined from the K-doped surface. Symbols are experimental values and the solid lines represent the calculated band structure obtained with a potential built from the Fourier components extracted from experimental gaps.

REFERENCES

[1] D. Malterre et al. New J. Phys. 13, 013026 (2011).

[2] G. Vasseur, Y. Fagot-Revurat, B. Kierren, M. Sicot and D. Malterre, Symmetry 5, 344 (2013).

[3] G. Vasseur, Y. Fagot-Revurat, B. Kierren, M. Sicot and D. Malterre, Phys. Rev. B 89, 121409 (2014).

Investigating the Early Steps of Bio-mineralization in Calcite Mollusk Shell with 2D Bragg Ptychography

<u>F. Mastropietro¹</u>, M. Allain¹, J.-P. Cuif³, Y. Dauphin³, C. Chevallard⁴, P. Guenoun⁴, J. Daillant⁵, V. Jacques⁶, S. Ravy⁵, V. Chamard¹

¹ Aix Marseille Université, CNRS, Institut Fresnel UMR 7249, Marseille, France
 ³ IDES, Université Paris-Sud 11, Orsay, France
 ⁴ CEA Saclay LIONS - SIS2M Gif-Sur-Yvette, France
 ⁵ Synchrotron SOLEIL, Gif-sur-Yvette, France
 ⁶ Laboratoire de Physique des Solides UMR8502 CNRS/Université Paris-Sud XI, Orsay, France

ABSTRACT

Shells of bivalve marine species exhibit complex organization of crystalline calcareous/organic structures, composed at the sub-micrometric scale by an assembly of rounded granular units [1], which is common to all calcifying biological specimen. This architecture is particularly intriguing regarding the apparently high crystalline quality of the calcite prism units [2,3] observed in *Pinna nobilis* or *Pinctada margaritifera*, for instance. Hence, understanding the growth mechanisms of biominerals calls for a detailed and quantitative description of the crystalline structure at the very initial stage of the growth.

Bragg ptychography, a lens-less x-ray microscopy approach, has been proposed for imaging the crystalline properties of extended nanostructured specimen [4] and is therefore quite promising to tackle the bio-mineral problem. It is based on the acquisition of several coherent diffraction patterns obtained with a focused illumination at different beam-to-sample positions. The large overlapping between two successive illumination areas onto the sample ensures the redundancy needed to solve the phase problem, this latter being achieved using dedicated phase retrieval algorithms [5].

Here we present the successful use of 2D Bragg ptychography in transmission geometry onto juvenile *Pinctada margaritifera* shells, performed at the CRISTAL beamline. The sample was placed in Bragg diffraction conditions onto a dedicated nano-positioning set-up and illuminated with a coherent beam focused down to $3 \times 1 \mu m^2$. The collected intensity data-set was obtained over a surface of 50 x 50 μm^2 covering entirely a prism unit. The phase retrieval analysis gave access to the spatially dependant strain and lattice orientation functions, exhibiting details smaller than the beam size. Surprisingly, structural crystalline inhomogeneities (mostly lattice mis-orientation) were observed over the prism area. This additional structural information will have to be integrated into the biomineralisation growth scheme.

This work is founded by the french ANR under the contract number ANR-11-BS10-005.

- 1. A. Baronnet et al., Mineralogical Magazine 72, 617 (2008).
- 2. L. Addadi et al., Advanced Materials 15, 959 (2003).
- 3. X. Li et al., NanoLetters 4, 613 (2004).
- 4. P. Godard et al., Nature Communications 2, 568 (2011).
- 5. P. Godard et al., Optics Express 20, 23 (2012).

The Multi-technique Hard X-ray Scanning Imaging Station of Nanoscopium Possibilities for Biological Studies

K. Medjoubi, G. Baranton and A. Somogyi

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

ABSTRACT

The Nanoscopium [1,2] 155 m-long nanoprobe beamline of Synchrotron Soleil (St Aubin, France) is dedicated to scanning multi-modal imaging in the 5-20 keV energy range. The optical design of the beamline [1] aims to create a high stability nano-beam by the horizontally reflecting main beamline optics, the overfilled secondary source, and the high stability beamline environment.

Both continuous fast scanning with millisecond dwell times and high precision step-scan mode operation are foreseen at the beamline for scanning imaging and tomography [3, 4]. Multi-scale and multi-technique imaging provide unprecedented information on metal concentration and distribution together with sample morphology by coupling modalities such X-ray fluorescence, absorption, phase contrast and dark field.

We present here the first proof of principle experiments performed at the multi-technique station of Nanoscopium, which is under commissioning. The first biological samples measured at the beamline demonstrate the future possibilities offered by Nanoscopium in biology.

Acknowledgements

We would like to acknowledge the colleagues of the support groups of Soleil (Electronic, Computing and Detectors groups) for their significant contribution, continuous help, and outstanding technical support to the Nanoscopium project.

^[1] A. Somogyi, F. Polack, and T. Moreno, "Nanoscopium: a Scanning Hard X-ray Nanoprobe Beamline at Synchrotron Soleil", AIP Conf. Proc. **1234**: 395-398. (2010).

^[2] A. Somogyi, K. Medjoubi, C.M. Kewish, V. Le Roux, M Ribbens, F. Polack, J.P. Samama, "Status of the Nanoscopium scanning nanoprobe beamline of Synchrotron Soleil", Proc. SPIE, 8851:art.n° 885104 (2013).

^[3] K. Medjoubi, N. Leclercq, F. Langlois, A. Buteau, S. Lé, S. Poirier, P. Mercère, M. C. Sforna, C. M. Kewish, A. Somogyi, "Development of fast, simultaneous and multi-technique scanning hard X-ray microscopy at Synchrotron Soleil", J. Synch. Rad. 20: 293– 299 (2013).

^[4] K. Medjoubi, A. Bonissent, N. Leclercq, F. Langlois, P. Mercère, A. Somogyi, "Simultaneous fast scanning XRF, dark field, phase-, and absorption contrast tomography", Proc. SPIE, 8851:art.n° 88510P (2013).

Simultaneous DAFS and XAFS Analyses to Evidence the Y- and Ti- species in Nano-structured ODS Steels

D. Menut¹, J.-L. Béchade¹, D. Thiaudière²

¹CEA, DEN, Service de Recherches Métallurgiques Appliquées, 91191 Gif-sur-Yvette, France ²Synchrotron SOLEIL, Ligne de lumière DIFFABS, L'Orme des Merisiers, Saint Aubin BP48, 91192 Gif-sur-Yvette, France

ABSTRACT

ODS materials are promising candidates for structural components of GEN IV and fusion reactors. Enhanced mechanical properties, especially high creep rupture strength, are due to reinforcement by homogeneous dispersion of nano-sized Y-Ti-O hard particles, ranging from 0.2 to 0.6 Wt%. The detailed characters of the nano-oxides, that precipitate from the Fe-Y-Ti-O solid solution during the consolidation at high temperature of the mechanically alloyed powders, are still not well understood. They are formed with different densities, sizes, compositions, and structures depending both the alloy composition and on thermomechanical treatment imposed during the fabrication process. However, the oxides in the Y-Ti-O system that are the most relevant are Y_2O_3 , TiO, TiO₂, and complex oxides Y_2TiO_5 and $Y_2Ti_2O_7$. Further, Ti has also to be considered in solid solution in the Fe-Cr matrix, which is not the case for Y. Thus, the interpretation of XAFS results for nano-oxides is more challenging than for a homogeneous material, or when the target species are clearly partitioned to a specific phase.

Diffraction Anomalous Fine Structure (DAFS) [1], which measures the elastic Bragg reflection intensities versus photon energy, combines the long-range order and crystallographic sensitivities of x-ray diffraction with the spectroscopic and short-range order sensitivities of x-ray absorption techniques. The kappa diffractometer end-station of the DIFFABS beamline was set-up in reflection-XRD geometry using an energy-resolved Silicon Drift Detector to perform Near Edge (DANES) and Extended (EDAFS) DAFS measurements. These analyses were done both at the Ti K- (4.966 keV) and Y K-edge (17.069 keV). XAFS spectra were recorded simultaneously in X-Ray Fluorescence mode, which is very important for energy calibration during data collection and, in addition, in the case of highly absorbing material, for absorption correction.

In the DY ODS steel analysed (Fe-13Cr-1.46Mo-0.1Al+ 1.0 TiO₂ + 0.5 Y_2O_3 , Wt%) [2], the difference observed between DAFS and XAFS proves that a significant part of Ti atoms are located in the Fe-Cr BCC matrix [3, 4]. Likewise, both Ti and Y atoms were observed in the intermetallic χ -phase (1 µm width and 10 µm length with a volume fraction estimated around 17% [5]) that precipitates mainly on grain boundaries. Unfortunately, DAFS measurements on Y-Ti-O nano-oxides were not possible due to the weak and broadened diffraction peaks.

- 1. J. O. Cross, Analysis of Diffraction Anomalous Fine Structure, PhD Dissertation, Univ. of Washington (1996).
- 2. I. Monnet et Al., J. Nucl. Mater. 335, 311-321 (2004).
- 3. S. Liu et Al., J. Nucl. Mater. 445, 50-56 (2014).
- 4. P. He et Al., J. Mat. Chem. Phys. 136, 990-998 (2012).
- 5. C. Zakine et Al., J. Nucl. Mater. 230, 78-83 (1996).

SAXS Studies of Nanoparticles Formed by Laser Ablation and in Electric Arcs

E. Carvou¹, S. Carles¹, E. Lee Choi¹, M. Girault², J.-M. Jouvard², M. Kerkar³, L. Lavisse², J.-L. Le Garrec¹, M.C. Marco de Lucas², J. Menneveux⁴, J.B.A. Mitchell¹, F.-X. Ouf⁵, V. Potin², J. Yu⁴

¹ Institut de Physique de Rennes, UMR 6251 CNRS-Université de Rennes 1, 35042 Rennes Cedex, France

² Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 6303 CNRS-Université de Bourgogne, 9 Avenue A. Savary, BP 47870-21078 Dijon Cedex, France

 ³ Faculté des Sciences Exactes, Université Abderrahmane Mira – Béjaïa, Algérie.
 ⁴Institut Lumière Matière (ILM), UMR5306 CNRS - Université Claude Bernard Lyon 1, Domaine Scientifique de La Doua, Bât. Kastler, 10 rue Ada Byron, 69622 Villeurbanne CEDEX, France
 ⁵ Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SCA, LPMA, Gif-Sur-Yvette, 91192

ABSTRACT

Nanoparticles can be formed in extreme environments such as flames, plasmas, electric arcs and by laser ablation and in recent experiments on the Swing Beamline at Soleil, we have examined the latter two systems. In both these cases, the nanoparticles are formed via the condensation for an extremely hot (several 1000°K) plasmas and by direct ejection from surfaces. Arcs occurring in electrical switching devices produce damage to the contacts limiting the service life of the components. In electrical cables, they can lead to fires and nanoparticles seem to play a role in sustaining arcing under AC power. Nanoparticle formation is the desired goal in Laser Ablation, whether for the formation of thin films or for the removal of material as in paint stripping.

We have used Small Angle X-Ray Scattering [1-3] to study the particles formed in both arcs and by laser ablation. In the former case it was found that AgSnO₂ electrodes yielded smooth particles while those formed with pure silver contacts were aggregated. Particles formed from graphite electrodes were rough and too large to be characterized with our experimental parameters (target to detector distance). The same applied to the silver aggregates. In a run at the end of November2014 we shall use a target to detector distance to sample the larger particles and to complete these studies.

In the case of laser ablation, the particles formed are much smaller (4-8 nanometers depending upon the target material) and the effects of different atmospheres on particle formation have been examined. This has allowed us to gain insight into the formation mechanism of the particles and the influence of oxygen on this process. The experimental results can be compared with recent simulations performed at the Université de Lyon.

These data shall be presented at the meeting.

^{1.} L. Lavisse et al., Applied Physics Letters 100, 164103 (2012).

^{2.} E. Carvou et al., AIP Advances 3, 032139 (2013);

^{3.} E. Carvou et al. IEEE Transactions on Plasma Science, Vol. 41, 3151 (2011)
Double Photoionization in Ring Molecules: Search of the Cooper Pair Formation

K. Jänkälä,¹,* P. Lablanquie,^{2,3} F. Penent,^{2,3} <u>J. Palaudoux</u>,^{2,3} L. Andric,^{2,3,4} , J-M. Bizau^{5,6}, D. Cubaynes^{5,6} and M. Huttula¹

¹ Department of Physics, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland
 ² UPMC, Université Paris 06, LCPMR, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
 ³ CNRS, LCPMR (UMR 7614), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
 ⁴ Université Paris-Est, 77454 Marne La Vallée Cedex 2, France

⁵ ISMO, CNRS UMR 8214, Université Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France ⁶ Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, F-91192 Gif-sur-Yvette cedex, France

ABSTRACT

In a recent paper Wehlitz et al [1] discovered a new phenomenon: so-called Cooper pair formation, to explain the observation of a hitherto unseen "hump" in the ratio of doubly charged to singly charged ions in photoionization of aromatic polycyclic molecules. Moreover when the symmetry is broken by replacing a carbon atom in the ring by an oxygen or nitrogen atom this "hump" disappears.

This was the starting point of our study on double photoionization (DPI) of benzene and pyrrole. In order to confirm the presence of such "hump" in the double photoionization process, we have detected the two photoelectrons in coincidence at different photon energies above the DPI threshold and looked at the energy sharing for a selected final state of the dication. This experiment was carried out using a magnetic-bottle electron time-of-flight coincidence setup at the incident photon energy region of 25–120 eV on PLEIADES beamline. We confirm the finding of a new two-electron continuum resonance structure observed at about 30–70 eV above the double ionization threshold in benzene when the ion is formed in is ground (meta)stable state and the absence of any equivalent structure in pyrrole [2]. However we do not observe any preferential equipartition of the energy between the two electrons as it could be expected for Cooper pair. A theoretical simple explanation of this process was given recently [3]: the resonance is related to Coulomb pairing in the periodic potential of cyclic molecules but when the electrons are released they are no longer correlated and the "strict" Cooper pair interpretation of the process is probably dubious.

- 1. R. Wehlitz et al., Phys. Rev. Lett. 109, 193001 (2012)
- 2. K. Jänkälä et al, Phys. Rev. Lett. 112, 143005 (2014)
- 3. D.L. Huber, Phys. Rev. A 89, 051403® (2014)

Multiple Photoionization Processes of Hg, K and Rb Atoms

J. Palaudoux^{1,2}, P. Lablanquie^{1,2}, L. Andric^{1,2}, F. Penent^{1,2}, K. Ito^{1,2,3}, J-M. Bizau^{3,4}, D. Cubaynes^{3,4}, S.M. Huttula⁵, K. Jänkälä⁵ and 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 Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, F-91192 Gif-sur-Yvette cedex, France.
 ⁴ ISMO, CNRS UMR 8214, Université Paris-Sud, Bâtiment 350, F-91405 Orsay cedex, France.
 ⁵ Department of Physics, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland.

ABSTRACT

Studies of multiple photoionization of metal atoms by synchrotron radiation are still scarce. We have studied inner-shell (5p, 4f...) ionization of atomic Hg ([Kr] $5s^25p^64f^{14}5d^{10}6s^2$) followed by (multiple) Auger decay. First, that has provided direct spectroscopy of triple and quadruple ionized states of Hg [1]; here, we give the detail of all the various Auger processes. We have also extended our investigations to K and Rb alkali atoms to understand the role of the additional electron (compared to, respectively, Ar and Kr atoms): K=[Ar]4s : Rb=[Kr]5s, in multiple photoionization process.

The experiments were carried out at the PLEIADES beam line with the HERMES (High Energy Resolution Multi Electron Spectrometer) setup [2] which is a 2m long magnetic bottle time of flight electron spectrometer allowing the detection in coincidence of all the electrons (up to 5) emitted in multiple photoionization process (valence double ionization, core-valence DI, inner-shell ionization followed by Auger decay...).

For Hg, our data reveal all the various multiple photoionization processes. The Auger decay channels of the $4f_{5/2,7/2}$ and $5p_{1/2,3/2}$ core holes are resolved individually. An unexpectedly strong core(4*f*)-valence double ionization is observed that can be related to the very fast (<100as) Coster Kronig decay of the 5*s* level. For K and Rb atoms, the first difference with Ar and Kr is that inner-valence K(3*s*) and Rb(4*s*) ionization leads to Auger decay with emission of a low energy Auger electron while this process is not accessible in Ar and Kr. In K, direct or sequential following $2s^{-1}$ Coster Kronig decay, core-valence $2p^{-1}3I^{-1}$ double ionization presents strong similarities with the similar process in Ar [3]. The coupling of the outer 4*s* electron multiplies however the number of possible states and makes the subsequent Auger decay more rich. In both K and Rb atoms, the Auger spectra following inner-shell ionization does not result only from the decay of the inner-shell holes ($2p_{3/2,1/2}$ in K or $3d_{3/2,5/2}$ in Rb) because the outer electron (4*s* in K and 5*s* in Rb) can be noticeably excited in the ionization process giving rise to multiple satellite states. The Auger decay of the main states and of all satellites can be filtered out very efficiently compared to other experiments [4]. Double Auger decay has also been observed as in Ar and Kr atom [5].

- 1. M. Huttula et al, PRA 83, 032510 (2011).
- 2. F. Penent et al, Phys. Rev. Lett. 95, 083002, (2005).

- 4. K. Jänkälä et al, PRA 74, 062704, (2006).
- 5. P. Lablanquie et al, JESRP 156-158 (2007) 51. J. Palaudoux et al, PRA 82, 043419 (2010).

^{3.} S.M. Huttula et al, PRL 110, 113002 (2013); P. Lablanquie et al, PCCP 13, 18355 (2011).

Influence of Pressure on Structural and Magnetic Transitions in Y_{1-x}Tb_xFe₂D_{4.2} Compounds

V. Paul-Boncour^{1*}, O. Isnard², K. Provost¹, L. Nataf³, A. Polian⁴, J.-P. Itié³, F. Baudelet³, A. Patissier¹, F. Couturas¹, J.C. Crivello¹, J. Monnier¹,

¹ICMPE, CNRS and Univ. Paris-Est Créteil, UMR7182, 2-8, rue Henri Dunant, Thiais, France
 ²Institut Néel, CNRS and Univ. Joseph Fourier, UPR2940, BP 166, 38042 Grenoble Cedex 9, France
 ³SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 48, 91192 Gif-sur-Yvette, France
 ⁴IMPMC, Université P. et M. Curie, UMR 7590, 4 Place Jussieu, 75252 Paris CEDEX 05, France

ABSTRACT

Hydrogen absorption in RFe_2 Laves phases (R= rare earth) can induce several changes in their structural and magnetic properties [1-3]. They form $RFe_2H(D)_y$ hydrides (deuterides) with different structures derived from the parent C15 cubic structure depending on the H(D) content [2-3]. A particularly interesting behaviour is observed around y = 4.2 H(D)/f.u..

 $YFe_2D_{4.2}$ is monoclinic at room temperature (RT) but undergoes an order-disorder transition towards a cubic structure upon heating above 340 K. A previous structural study on $YFe_2D_{4.2}$ by X-ray diffraction under pressure has shown that a structural transition occurs also around 4 GPa at RT [6]. But due to the low instrumental resolution of the laboratory diffractometer, it was difficult to solve the new structure occurring above 4 GPa. We have therefore performed diffraction experiments on the PSICHE beam line at SOLEIL under pressure at RT. It is observed that the transmission medium is a key parameter to maintain a hydrostatic pressure and solve the structural transformation. The structural evolution of $YFe_2D_{4.2}$ under pressure will be presented and discussed.

In addition, YFe₂D_{4,2} displays upon cooling a transition from an antiferromagnetic (AF) towards a ferromagnetic (F) structure at T_{F-AF} = 84 K [4]. This transition is very sensitive to any volume change. For example, T_{F-AF} increases up to 131 K upon H-D isotopic substitution due to a cell volume increase $\Delta V/V=$ 0.78 % [5]. On the contrary, it decreases and even disappears for an applied pressure of 0.5 GPa [6]. T_{F-AF} can be also tuned by substituting Y by another R element [7]. The substitution of Tb for Y induces a cell volume increase and a shift of T_{F-AF} to higher values. For $Y_{0.5}Tb_{0.5}Fe_2D_{4.2}$, T_{F-AF} = 130(1) K for $\Delta V/V$ = 0.35 %, i.e. for a smaller volume than for YFe₂H_{4.2}. This indicates that the role of Tb substitution is not purely magnetovolumic. The purpose of this work was therefore to understand more clearly the relative role played by the volume change and the Tb magnetic moment on the F-AF transition by studying the magnetic properties of these compounds under pressure. XMCD measurements versus pressure and temperature were performed on ODE beam line (SOLEIL) at the Fe-K edge for $YFe_2D_{4.2}$ and $Y_{0.5}Tb_{0.5}Fe_2D_{4.2}$ and at the Tb L_{III} edge for Y_{0.5}Tb_{0.5}Fe₂D_{4.2}.The results will be presented and discussed in with the light of magnetic measurements under pressure and taking into account the cell volume decrease induced by the applied pressure.

- [2] V. Paul-Boncour, L. Guénée, 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.

G. Wiesinger G. Hilscher, in Handbook of Magnetic Materials; Vol. 6, edited by K. H. J. Buschow Elsevier North-Holland, Amsterdam, 1991, p. 511.

New Amplitude Criteria for Scattering Path Selection in EXAFS Fit. Application to bis(S thiocyanato)(cyclohexanediamino)Platinum(II)

K. Provost^a, B. Ravel^b and A. Michalowicz^a

^aICMPE, UMR 7182 CNRS UPEC, 2-8 rue Henri Dunant, 94320 Thiais, France ^bNational Institute of Standards and Technology, Gaithersburg MD, USA

ABSTRACT

Scattering path selection is an important step when fitting the whole signal of an EXAFS spectrum. This step is facilitated when an efficient amplitude criterion can be defined to sort the scattering paths, before a more precise analysis of each path signal. When using FEFF [1,2] for calculating the theoretical signal on the basis of a structural model, the usual amplitude criterion is FEFF's curve wave amplitude ratios. However, we observed in different studies that this amplitude criterion sometimes attributed high amplitude ratios to scattering paths presenting a non-significant signal in the fitting *k*-range.

We consider different ways of integrating FEFF scattering path signals to define new amplitude criteria, and compare them to FEFF's curve wave amplitude ratios. Each criterion is used to sort the different scattering paths. The efficiency of each amplitude criterion is analyzed in terms of: i) ability of the criterion-based path order to reproduce the whole EXAFS theoretical signal in a particular *k*-range (typically the fit *k*-range), with the lowest number of scattering paths; ii) ability of this path selection to lead to a statistically good EXAFS fit.

This approach is illustrated on the case of the degradation product of oxaliplatin by thiocyanate, bis(S-thiocyanato)(cyclohexanediamino)platinum(II). On this example, we show that the *k*-range, k^n -weighting and mean square displacement σ^2 used in the integration process have a non-negligible impact on the path order, and, thus, on the path selection process. On this example, criteria based on the fit *k*-range and a k^3 -weighting are the most efficient criteria to define the optimized scattering path set for the EXAFS fit.

These criteria are implemented as new tools in MAX-RoundMidnight [3] and Artemis [4] codes.

- 1. A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, Phys. Rev. B 58, 7565-7576 (1998).
- 2. A. L. Ankudinov, C. E. Bouldin, J. J. Rehr, J. Sims and H. Hung, Phys. Rev. B 65, 104107 (2002).
- 3. A. Michalowicz, J. Moscovici, D. Bouvet-Muller and K. Provosť, J. Phys. Conf. Ser. 190, 012034 (2009).
- 4. B. Ravel and M. Newville, J. Synchrotron Radiat. 12, 537-541 (2005).

Double Core-hole States in SiX₄ (X = F, Cl, Br, and CH₃) Molecules Derived by Photoelectron and KLL Auger Spectroscopy

<u>R. Püttner¹</u>, T. Marchenko^{2,3}, R. Guillemin^{2,3}, L. Journel^{2,3}, G. Goldsztejn^{2,3}, J.-P. Rueff⁴, D. Céolin⁴, J.M. Ablett⁴, D. W. Lindle⁵, A. Lago⁶, K. Ueda⁷, O. Takahashi⁸, M. N. Piancastelli^{2,3,9}, and M. Simon^{2,3,4}

¹Institut für Experimentalphysik, Freie Universität Berlin, Germany, ²CNRS, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, France,³Sorbonne Universités, UPMC Univ Paris 06, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, France,⁴Synchrotron SOLEIL, Gifsur-Yvette, France,⁵Department of Chemistry, University of Nevada, Las Vegas, USA,⁶Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC), Santo André-SP, Brazil, ⁷Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan,⁸Department of Chemistry, Hiroshima University, Japan,⁹Department of Physics and Astronomy, Uppsala University, Sweden

ABSTRACT

In recent years double core-hole states are intensively studied since their chemical shifts provide detailed information about initial-state and relaxation effects in a molecule. Most of these measurements are done either by coincidence spectroscopy and single-photon absorption using synchrotron radiation (e.g. [1]) or by two-photon sequential absorption using free electron lasers as light (e.g. [2]) sources. However, some of these double core-hole states can also be obtained by other means. This holds in particular for 2s⁻², 2s⁻¹2p⁻¹, and 2p⁻² core-hole states as a result of KLL Auger decay, which can readily be measured using conventional photoelectron spectroscopy.

Using the new experimental setup for high-resolution HAXPES (HArd X-ray PhotoElectron Spectroscopy) in gas phase, which is mounted at the GALAXIES beamline of the synchrotron SOLEIL, we measured the Si KLL Auger spectra of the molecules SiX₄ with X = F, Cl, Br, and CH₃. Complementary photoelectron spectra of these molecules were recorded in order to derive the Si 1s⁻¹, 2s⁻¹, and 2p⁻¹ single core-hole binding energies. Using these binding energies, the chemical shifts of the Si 2s⁻², 2s⁻¹2p⁻¹, and 2p⁻² double core-hole binding energies were derived from the Auger spectra. The obtained binding energies are compared with theoretical results [3] revealing good agreement. Moreover, the results were used to create Wagner plots (i.e. plotting single core-hole energies versus double core-hole energies) which give a detailed insight in the initial state and relaxation effects [4].

Moreover, for all SiX₄ molecules Si $1s^{-1}2s$,p⁻¹ double core-hole shake up satellites measured with conventional photoelectron spectroscopy are presented. In summary, we show that KLL Auger and photoelectron spectroscopy are well suited to derive information about double core-hole states.

- 3. O. Takahasi et al., Chem. Phys. 384, 28 (2011).
- 4. T. D. Thomas, J. Phys. Chem. A 116, 3856 (2012).

^{1.} P. Linusson et al., Phys. Rev. A 83, 022506 (2011), and references therein; P. Lablanquie et al., Phys. Rev. Lett. 110, 163001 (2013), and references therein.

^{2.} N. Berrah et al., PNAS 108, 16912(2011) 16912; P. Salen et al., Phys. Rev. Lett. 108, 153003 (2012), and references therein.

In situ X-ray Scattering Investigations on SiGe Nanowires: Growth, Strain and Dance

T. Zhou¹, V. Cantelli¹, O. Ulrich¹, O. Geaymond², N. Blanc² and <u>G. Renaud¹</u>

¹ Univ. Grenoble Alpes, CEA/INAC/SP2M, F-38000 Grenoble. France ² Institut Néel, CNRS Univ. Grenoble Alpes, F38000 Grenoble France

ABSTRACT

The INS (In situ - Nanostructure - Surface/interface) end station of the BM32 beamline at the European Synchrotron Radiation Facility (ESRF) has been used for years to analyse the structural properties of nanoparticles in situ, in ultra-high vacuum (UHV), during their growth by molecular beam epitaxy, combining Grazing Incidence X-ray Diffraction (GIXD) and Grazing Incidence Small Angle X-ray Scattering (GISAXS) [1]. An UHV-Chemical Vapour Deposition (CVD) injection system has been recently added to allow investigation of the growth of Si/Ge nanowires (NWs) using disilane and digermane gas sources [2].

Results on the growth of Si NWs on Si(111) will first be presented, as a demonstration of the in situ capability of the instrument. The real time NWs length and their size distribution can be measured with X-ray techniques without removing the sample from the UHV chamber. The deposition of the metal catalysts and the injection of the precursor gases are carried out side by side, which makes it possible to probe the very early stage of growth. The well-known sidewall dodecagon sawtooth faceting is clearly recognizable from reciprocal space mapping of both GIXD and GISAXS.

The strain relaxation in Si-Ge core-shell NWs will then be presented. The samples are kept under UHV during the entire process to avoid oxidation and contamination. The level of strain is measured in situ as a function of the overgrowth amount. The composition distribution in the heterostructure is also determined using anomalous X-ray scattering [3].

Finally, results on the deformation of as-grown NWs by oriented deposition of various materials on one side of the NWs will be presented. The NWs danc back and forth with increasing amount of deposition as revealed by live stationary measurements with a 2D detector. The magnitude of the stress can then be deduced by analysing dedicated reciprocal space maps [4].

- G. Renaud, R. Lazzari, F. Leroy Surf. Sci. Rep. (2009) 64, 255.
 V. Cantelli, O. Geaymond, O. Ulrich, T. Zhou, N. Blanc and G. Renaud, submitted.
- [3] T. Zhou, O. Geaymond, G. Renaud, in preparation.
- [4] T. Zhou, O. Robach, G. Renaud, in preparation.

HERMES: A Dual-branch Soft X-ray Spectromicroscopy Beamline at SOLEIL

R.Belkhou¹, <u>S. Swaraj¹</u>, S. Stanescu¹, A. Besson¹, D. Dallé¹, B. Lagarde¹, F. Polack¹

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

ABSTRACT

HERMES (High Efficiency and Resolution beamline dedicated to X-ray Microscopy and Electron Spectroscopy) is an undulator based soft x-ray beamline at SOLEIL synchrotron facility. High flux, high resolution, high spectral purity and polarization control over a wide energy range (70eV to 2500 eV) are some of the beamline characteristics.

The beamline is equipped with two complimentary microscopy techniques, STXM (Scanning Transmission X-ray Microscopy) and X-PEEM (X-ray PhotoEmitted Electron Microscopy). X-PEEM is a photon-in-electron-out technique and hence this branch will provide mainly a surface-interface sensitive microscopy and spectroscopy with an ultrahigh vacuum sample environment. STXM, being a photon-in-photon-out based microscopy technique, will allow the investigation of "bulk" properties of natural and synthetic materials with possibilities for versatile sample environments. Both the branches will offer a spatial resolution better than 25nm along with a wide variety of detection techniques. Many different fields, including those related to earth and environmental science, magnetism, nanomaterials and soft condensed matter will benefit from HERMES beamline. X-PEEM branch is already open to users while the STXM branch will be open to users in 2015. A detailed description of the beamline will be presented.

CH₃⁺ Formation in the Dissociation of Energy-selected CH₃F⁺ Ions Studied with Double Imaging Electron/Ion Coincidence

X. Tang, G. Garcia, and L. Nahon

Synchrotron SOLEIL, L'Orme des Merisiers, St. Aubin BP 48, 91192 Gif sur Yvette, France

ABSTRACT

The dissociation of energy-selected methyl fluoride ion CH_3F^+ along the CH_3^+ and F formation channel has been investigated in detail in the 12.2 - 19.8 eV energy range. Three low-lying electronic states of CH_3F^+ ion, X^2E , A^2A_1 and B^2E are prepared and analyzed by the method of double imaging photoelectron photoion coincidence (i²PEPICO). Three types of CH_3^+ fragment ions corresponding to the dissociation of X^2E , A^2A_1 and B^2E electronic states respectively have been observed and identified through their kinetic energy release distribution (KERD) curves, showing that the dissociation of CH_3F^+ ion in the different electronic states along the CH_3^+ formation channel is state-specific, even outside the Franck-Condon region. Highly excited vibrational levels of the X²E ground state can be populated through resonant or near-resonant autoionization process and undergo vibrational predissociation into CH_3^+ fragment ions. The A^2A_1 first excited state is repulsive along the F-loss coordinate and its dissociation is direct and fast. The CH_3F^+ ions in the B²E excited state first undergo an internal conversion towards the hot cation ground state X²E and then statistically dissociate into CH_3^+ and F

REFERENCES

1. G. A. Garcia, B. K. Cunha de Miranda, M. Tia, S. Daly, and L. Nahon, Rev. Sci. Instrum. 84, 053112 (2013).

 L. Nahon, N. De Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde, and F. Polack, J. Synchrotron Radiat. 19, 508 (2012),

High-resolution Imaging of Mechanical Properties using a Mid-infrared Synchrotron Radiation

J.-M. Vauvre¹, A. Patsioura¹, R. Kesteloot², M. Da Silva³, M. Nguyen¹, X. Fang¹, F. Jamme⁴, P.Dumas⁴ and <u>O. Vitrac¹</u>

1. INRA, UMR 1145 Ingénierie Procédés Alimentaires, F-91300 Massy, France

2. Régis Kesteloot conseil, 20 60 Avenue du Colonel Driant, 59130 Lambersart, France

3. McCain Foods Ltd., 28 Havers Hill, Scarborough, YO113BS, United Kingdom

4. Synchrotron SOLEIL, SMIS beamline, 24 L'Orme des Merisiers Saint-Aubin, BP 48, 91192 Gif-sur-Yvette cedex, France

ABSTRACT

Our general goal is to develop a generic methodology to image the mechanical behavior (rubber or glassy) of structured material based on vibrational spectra of constitutive macromolecules. The concept is illustrated in Figure 1a. It consists in measuring in attenuated total reflection (ATR) mode the local vibrational spectra of the material at different positions. The whole image can be reconstructed either from pencil-beam scanning of the sample (Figure 1a) or from the repetitions of contacts with ATR probe (Figure 1b). The first configuration is preferable for routine measurements, but the second one was used to devise the physical principles. Without any loss of generality, our final intent is to develop a methodology to identify how mechanical constraints propagate during deep frying in potato products. Our test material was accordingly emptied potato parenchyma cell walls (thickness ranging from 1 to 3 µm) equilibrated in super-heated steam prior observations. Measurements were carried out at various temperatures (from 24°C up to 140°C) and various relative humidity (RH from 0.099 to 0.71). These conditions cover a broad range of possible mechanical properties of cell wall constituents with apparent glass transition temperature (T_a) varying from 20°C to 115°C. Vibrational spectra of amorphous (pectins) and semi-crystalline components (cellulose) and mechanical properties are intimately entangled in a composite material. It was thought that the feasibility of the approach could be demonstrated if the displacements of specific bands of the FTIR absorption spectra were similar but opposite when temperature (T) and T_g were shifted. The concept of invariance with $T-T_{q}$ is indeed a key property of free-volume theory and central in plasticizing theory in polymer systems at thermodynamical equilibrium (without loading). The interpretation of isotherm measurements at different RH and of our temperature scans at constant RH confirmed our initial assumptions. Finally, it is proposed to use a scan temperature to detect regions below and above T_g as shown in Figure 1c. The displacement of COO⁻ stretching band of pectin (1590-1650 cm⁻¹) offers the best candidate to tailor the observations in parenchyma structures.



Fig. 1: Principles of mechanical imaging principles: a) using beam scan, b) by displacing the ATR probe, c) dependence of the vibrational spectra of cell-wall constituents with temperature at rubber and glassy states. i) Heating stage with controlled RH, ii) parenchyma cell walls, iii) ATR ZnSe prism, iv) synchrotron beam.

Photo-chemical Processes of Interstellar Polycyclic Aromatic Hydrocarbon (PAH) Cations with Synchrotron Irradiation

J. Zhen¹, P. Castellanos², D.M. Paardekooper², H. Linnartz², C. Joblin¹, L. Nahon³, A. G. G. M. Tielens²

1. Institut de Recherche en Astrophysique et Planétologie Université de Toulouse [UPS] - CNRS, 9 Av. Colonel Roche, BP 44346, 31028 Toulouse Cedex 4, France 2. Leiden Observatory, University of Leiden, PO Box 9513, NL 2300 RA Leiden, The Netherlands 3. Synchrotron SOLEIL, L'Orme des Merisiers, 91192 Gif sur Yvette Cedex, France

ABSTRACT

Quadrupole ion trap/time-of-flight spectrometry of Coronene, Ovalene, hexa-perihexabenzocoronene (HBC) and Dicoronylene radical cations exposed to synchrotron irradiation are presented. The radical cations - are produced by electron impact, then trapped and mass – analyzed using a quadrupole ion trap, time-of-flight mass spectrometry (1). The PAH cations were measured upon irradiation by the DESIRS laser for different experimental conditions. DESIRS beamline is well suited for the present studies because of its high photon flux (typically in the 10¹⁴ photon s-1 range in a 7% bandwidth in 0 order), and its broad and easy tenability in the 5-40 eV energy range (2).

When the photon energy is higher than the ionization potential, each of large PAH radical cation, like HBC cation, is found to ionize completely to dication or further to trication without fragmentation, the ionization yield parameter is close to 1; small PAH radical cation, like Coronene cation, is found have a less degree of fragmentation process compare to the ionize yield process, the ionization yield parameter is around 0.5. The extent of ionization not depends directly on irradiation power. We infer that PAH radical cation are inherently stable to UV and XUV irradiation but with highly ionization yield dication and trication process. The relevance of ionization to fragmentation of PAH radical cation on understand the unidentified interstellar infrared emission bands and the photochemistry of PAH in ISM are discussed in briefly (3-5).

- J. Zhen, D. M. Paardekooper, A. Candian, H. Linnartz, A. G. G. M. Tielens, Chem. Phys. Lett., 592, 211-216 (2014).
 L. Nahon, N. de Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouille, B. Lagarde & F. Polack, J. Synchrotron. Rad., 19, 508-520 (2012).
- 3. J. Montillaud, C. Joblin, and D. Toublanc, Astron & Astrophys, 552, A15 (2013).
- 4. S. P. Ekern, A. G. Marshall, J. Szczepanski, and M. Vala, The Astrophysical Journal, 488, L39–L41 (1997).
- 5. A. G. G. M. Tielens, Rev. Mod. Phys., 85, 1021-1081 (2013).

PO-34

Synergy Between Gold and Mo₂N Leading to Platinum-like Activity for Hydrogen Evolution

A. Morozan,^a V. Goellner,^a <u>A. Zitolo</u>,^b E. Fonda,^b B. Donnadieu,^a D. Jones^a and F. Jaouen^a

 ^a Institut Charles Gerhardt de Montpellier - UMR 5253, Place Eugène Bataillon, 34095 Montpellier cedex 5, France
 ^b Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin - BP 48, 91192 Gif-sur-Yvette, France andrea.zitolo@synchrotron-soleil.fr

ABSTRACT

Reduced size and direct electrochemical H₂ compression are two distinct advantages of electrolyzers based on the acid–polymer electrolyte membrane technology over those relying on alkaline electrolytes. However, recourse to catalysts based on the scarce platinum-groupmetals has hitherto been the price to pay. While the transition metal sulfides and nitrides of group VI have recently shown interesting activities for H₂ evolution, the remaining activity gap with Pt needs to be reduced. Platinum owes its high activity to its optimum metal–hydrogen bond strength for H₂ evolution, which is a proven descriptor of the activity on single-component catalysts. Here, we unravel a major synergetic effect between gold and molybdenum nitride which multiplies the hydrogen evolution activity ca. 100 times over that of either gold or molybdenum nitride. This two-phase catalytic material, featuring both strong and weak metal–hydrogen bonds, overcomes the limitations described by Sabatier's principle for single-component catalysts.

LIST OF COMMERCIAL EXHIBITORS

List of Commercial Exhibitors

Company		Contacts	Phone numbers	Email	Web site
AGILENT Technologies	Agilent Technologies	Stéphane GRANDAMAS Vincent HACHET	06 07 67 66 51 06 78 73 51 77	stephane.grandamas@agilent.com vincent.hachet@agilent.com	http://www.home.agilent.com
ALTEC Equipment	ALTEC equipment	Arnaud AUBERT	01 39 15 69 85	a.aubert@altec-equipment.com	http://www.altec-equipment.com
FERROVAC GmbH	RROVAC GMBH	Denys SUTTER	41 44 273 16 38	sutter@ferrovac.com	http://http://www.ferrovac.com
LESKER	Kurt J. Lesker	Pascal GAUTRAUD	06 98 50 00 11	louisep@lesker.com	http://www.lesker.com
MDC VACUUM PRODUCTS SARL		Anne-Sophie JAUBERT	09 75 77 62 81	asjaubert@mdcvacuum.fr	http://www.mdcvacuum.fr
NEWPORT	Newport. Experience Solutions	Dalila AIT AMIR Jean VILAIN	01 60 91 68 68 02 38 40 50 00	dalila.aitamir@newport.com jean.vilain@newport.com	http://www.newport.com
OERLIKON LEYBOLD VACUUN	cerlikon leybold vacuum	Jean-François TRETIN Christophe ZAFFANELLA	06 07 32 30 39 06 07 32 41 59	jean-francois.trentin@oerlikon.com christope.zaffanella@oerlikon.com	http://www.oerlikon-welding.fr
OPTOPRIM/AEROTECH	OPTOPRIM	Erwann MAURIER François SALAUN	07 77 60 82 60 06 16 17 90 04	<u>emaurier@optoprim.com</u> fsalaun@optoprim.com	www.optoprim.com
PI France SAS	PI	Nicolas COLLET Aliou SAMBOU	01 55 22 60 00 01 55 22 60 00	n.collet@pi.ws a.sambou@pi.ws	http://www.pi-france.fr
SPECS	S P C C S *	Michael MEYER	493 04 67 82 40	michael.meyer@specs.com	http://www.specs.de
SUMITOMO CRYOGENICS	SHI Cryogenics Group	Carlos DE AZEVEDO	06 22 87 23 01	cdeazevedo@shicryogenics.fr	http://www.shicryogenics.com
VG SCIENTA	VG SCIENTA	Robert MOBERG	46 703 252 345	robert.moberg@vgscienta.com	http://www.vgscienta.com
ZURICH INSTRUMENTS	X	Romain STOMP	33 786 258 507	romain.stomp@zhinst.dom	http://www.zhinst.com

COMPANIES ADVERTISEMENTS

DISCOVER VALUE IN VACUUM TECHNOLOGY

As the leader in high- and ultra-high vacuum solutions for research and instrumentation, Agilent Vacuum, formerly Varian, is your vacuum resource, with 65 years of experience leading to innovative new turbo and dry scroll pump technologies.

Agilent IDP-15 Dry Scroll Pump

- Designed specifically for low noise (<50 dBA) and vibration
- 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

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



Download the 2015 Catalog available on our new websit www.vacuum-choice.com





Agilent Technologies

Surrounding You With Expertise & Support!



On-Site Manufacturing

Talk To Us About Your Manufacturing Needs

- Largest Inventory of Quality Vacuum Products in Europe
- Highly Professional Customer Service
- Renowned Technical Expertise

.

Enabling Technology for a Better World | www.lesker.com





Beamline Instrumentation

SOPHISTICATED COMPONENTS AND SYSTEM SOLUTIONS



Optics alignment

- Nanometer resolution with mm stroke
- Radiation resistant
- Self-locking
- Minimum dimensions, high forces

Tomography stages

- 6DOF sample alignment
- Unmatched excentricity
- Air bearings & torque motor
- Direct metrology



End stations

- From customized multi-axis solutions to complete turn-key solutions
- UHV-compatible equipment

Ne manquez plus la moindre impulsion



600 MHz Boxcar Averager

2 unités boxcar en 1

LabOne. All in One.

www.zhinst.com

- Temps mort d'intégration <2 ns
- Taux de répétition de 450 MHz
- Boxcar à voies multiples
- Analyseur d'onde périodique (PWA)

Zurich Instruments révolutionne la façon de faire des mesures avec des lasers à impulsions brèves, fournissant une solution capable de mesurer 1000 fois plus vite qu'auparavant avec d'autres équipements. Le Boxcar Averager UHF-BOX est une option de la Détection Synchrone UHFLI 600 MHz, et permet un déclanchement rapide directement sur le taux de répétition du laser et offre de nombreux avantages: mesures plus rapides, amélioration du rapport signal-sur-bruit et simplification du montage expérimental. Par ailleurs, grâce à son implémentation tout numérique, des fonctionnalités innovantes ont pu être introduites qui rendent l'utilisation de la technique boxcar d'autant plus conviviale.

Zurich Instruments