

The 74th Okazaki Conference
Frontier of X-ray Absorption Spectroscopy and Molecular Science

Date: February 3, 2015 – February 5, 2015

Site: Okazaki Conference Center (OCC), Conference Room C (2nd floor)
<http://www.ims.ac.jp/english/location/access.html>

Outline

The Okazaki conference has been one of the most important activities in Institute for Molecular Science (IMS), with its origin dated back to just after the foundation of IMS. The Conference has been normally held once or twice per year, with focusing on some specific topic that is emerging as a fundamental issue in the field of molecular science and related research area. The 74th Okazaki Conference is designated as “Frontier of X-ray Absorption Spectroscopy and Molecular Science.” We would like to discuss new science that can be opened by advanced XAFS techniques like spatial and/or time-resolved measurements. Although XAFS has matured as a sophisticated promising technique, recent progress based on the advance of synchrotron radiation light sources is still outstanding. We will summarize here the advanced XAFS methods and discuss near-future XAFS techniques and more importantly new science. It will be also fruitful if the new XAFS science can contribute to construction plans of diffraction-limited synchrotron radiation facilities in Japan.

Program

February 3, 2015

17:00- Reception @OCC, Conference Room B (1st floor)

February 4, 2015

10:00-10:10 **Iwao OHMINE** (IMS) Opening Address

10:10-10:20 **Toshihiko YOKOYAMA** (IMS) Scope of the Conference

(Chair: K. Asakura)

10:20-11:05 **Tsun-Kong SHAM** (Univ. Western Ontario) “Soft and Tender X-ray Spectroscopy, Some Recent Development and Applications”

11:05-11:30 **Hiroyuki OYANAGI** (NAIST) “Synchrotron Radiolysis Synthesizes Novel Nanoclusters”

11:30-11:55 **Hitoshi ABE** (KEK-PF) “XAFS Microscopy and Dynamics for Materials Science”

11:55-12:15 Photo

12:15-13:30 Lunch @OCC, Conference Room B (1st floor)

(Chair: H. Oyanagi)

13:30-14:15 **Andrei ROGALEV** (European Synchrotron Radiation Facility) “Polarization Dependent X-ray Spectroscopy: Recent Advances”

14:15-14:40 **Satoru TAKAKUSAGI** (Hokkaido Univ.) “3D Structure Analysis of Atomically Dispersed Metal Species on an Oxide Single Crystal Surface by Polarization-Dependent Total-Reflection Fluorescence XAFS”

- 14:40-15:05 **Mizuki TADA** (Nagoya Univ.) “In situ XAFS Characterization of PEFC Electrocatalysts”
- 15:05-15:30 **Takuya MASUDA** (NIMS) “In situ XAFS and XPS for Electrochemical Processes at Solid Liquid Interfaces”
- 15:30-15:50 **Yasumasa TAKAGI** (IMS) “Ambient Pressure Hard X-ray Photoelectron Spectroscopy of Polymer Electrolyte Fuel Cell Catalysts”
- 15:50-16:10 Coffee
(Chair: H. Abe)
- 16:10-16:55 **Peter FISCHER** (Lawrence Berkeley Nat. Lab. & Univ. California Santa Cruz) “Future Opportunities with Magnetic Soft X-ray Spectromicroscopies”
- 16:55-17:20 **Motohiro UO** (Tokyo Medical & Dental Univ.) “Application of SR-XRF and XAFS for the Clinical Diagnosis”
- 17:20-17:40 **Takuya OHIGASHI** (IMS) “Present Status of Scanning Transmission Soft X-ray Microscopy at UVSOR-III”
- 17:40-18:00 **Masanari NAGASAKA** (IMS) “Soft X-ray Absorption Spectroscopy of Liquid and its Application to Electrochemical Reaction”
- 19:00-20:30 Banquet @Okazaki New Grand Hotel (Sky Restaurant PARIS, 9th floor)

February 5, 2015

(Chair: Y. Takahashi)

- 09:30-10:15 **Lin X. CHEN** (Argonne Nat. Lab. & Northwestern Univ.) “How Can Transient X-ray Structural Methods Aide Solar Fuel and Solar Electricity Conversion Research?”
- 10:15-10:40 **Shin-ichi ADACHI** (KEK-PF) “Capturing Structural Dynamics of Photochemistry by Picosecond X-ray Pulses”
- 10:40-11:05 **Tetsuo KATAYAMA** (JASRI, SPring-8) “Ultrafast XAFS Using Femto-Second X-ray Pulses”
- 11:05-11:30 **Tomoya URUGA** (JASRI SPring-8) “Temporally and Spatially Resolved XAFS at SPring-8”
- 11:30-11:50 **Yohei UEMURA** (IMS) “Picosecond and Femtosecond X-ray Absorption of WO₃ Photocatalyst”
- 11:50-13:10 Lunch @OCC, Conference Room B (1st floor)
(Chair: T. Yokoyama)
- 13:10-13:55 **Stephen P. CRAMER** (Univ. California Davis) “Nuclear Resonance Vibrational Spectroscopy as an X-Ray Absorption Technique”
- 13:55-14:20 **Naoki ISHIMATSU** (Hiroshima Univ.) “ α - ϵ Transition of Iron: an EXAFS Study under High Pressure”
- 14:20-14:45 **Yoshio TAKAHASHI** (Univ. Tokyo) “Molecular Environmental Geochemistry Using XAFS”
- 14:45-15:10 **Takafumi MIYANAGA** (Hirosaki Univ.) “XAFS study for Ag clusters”

15:10-15:40

Kiyotaka ASAKURA (Hokkaido Univ.) Summary & Discussion

15:40

Closing

Abstract

10:20-11:05, Feb. 4

Soft and Tender X-ray Spectroscopy, Some Recent Development and Applications

Tsun Kong SHAM

Department of Chemistry, University of Western Ontario

A number of recent development and applications of X-ray spectroscopy techniques will be presented. These include: X-ray Absorption Fine Structures (XAFS), X-ray emission, X-ray excited optical luminescence (XEOL) in both energy and time domain and Scanning Transmission X-ray Microscopy (STXM). Studies of group IV nanostructures, ZnO-ZnS nano-composites, transition metal doped metal oxide semiconductors as well as LiFePO₄ battery materials among others will be described to illustrate the unique solutions provided by synchrotron technology. The prospects of emerging techniques such as High Energy X-ray Photoelectron Spectroscopy, High Energy Resolution X-ray Fluorescence and Resonant Inelastic X-ray Scattering Spectroscopy and their applications will also be noted.

11:05-11:30, Feb. 4

Synchrotron Radiolysis Synthesizes Novel Nanoclusters

HiroYuki OYANAGI

National Institute of Advanced Industrial Science and Technology (AIST)

Ionizing radiation liberates bound electrons from atoms or molecules, thereby breaking bonds and creating ions and excited species. Synchrotron radiation as a tunable source of ionizing radiation and local donation of electrons around excited atoms has a potential of synthesizing and stabilizing novel nanoclusters under controlled wet chemistry. In this work, we demonstrate that nanoclusters of late transition metal with unusual electronic states are grown by synchrotron radiolysis [1]. The local structure of copper aggregates grown by reducing Cu(II) complex using focused synchrotron x-ray beam from an x-ray undulator of the 6.5 GeV storage ring (PF-AR) was studied *in situ* by x-ray absorption spectroscopy (XAS). The results of XAS data and detailed DFT calculations identified the nanocluster as Cu₁₃ with an icosahedral "charged cluster" core which were stabilized by electron-donating amido molecules formed by radiation-induced deprotonation of ligand amines. Monodispersive deposition of nanoclusters was enabled by controlling the type and density of "monomers", in remarkable contrast to the conventional wet chemical growth of metallic nanoparticles.

[1] Scientific Reports 4, 7199 (2014) doi:10.1038/srep07199.

11:30-11:55, Feb. 4

XAFS Microscopy and Dynamics for Materials Science

Hitoshi ABE, Yasuo TAKEICHI, Hiroaki NITANI, Yasuhiro NIWA, Masao KIMURA

Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK)

We are developing the frontiers of the XAFS techniques from a materials-science point of view: (a) microscopy and (b) dynamics of various reactions.

- (a) In microscopy, we emphasize multi-scale analysis from few tens of nm (in 3D, XAFS-CT at PF-AR NW2A in a few years) to few tens of μm (in 2D, XAFS and XRD at PF BL-15A1). *In situ* observation is also planning.
- (b) In dynamics, we focus on observation of one-way time evolutions using DXAFS for growing demands to understand the dynamics in “real” materials. Another focus is reactions at surfaces using Kramers-Kronig reflection XAFS (KK-XAFS). The relatively new method can be combined with the DXAFS technique, and surface phenomena will be observed in a time resolution of at least microseconds with great surface sensitivity.

13:30-14:15, Feb. 4

Polarization Dependent X-ray Spectroscopy: Recent Advances

Andrei ROGALEV

European Synchrotron Radiation Facility

Development of the third generation synchrotron radiation sources has boosted X-ray spectroscopy, as illustrated by the discovery of a variety of new experimental techniques associated with the exploitation of the polarisation properties of x-rays. The detection of X-ray magnetic linear and circular dichroism in magnetic systems, the discovery of X-ray natural circular dichroism in gyrotropic single crystals as well as the observation of non-reciprocal X-ray linear dichroism and X-ray magneto-chiral dichroism in magnetoelectric systems are particularly interesting. In combination with sum rules these spectroscopies appear as remarkable tools to study fundamental properties of matter via various order parameters, e.g., spin and orbital moments, electric dipole moment, toroidal moments etc. In this talk we report on advanced instrumentation developed at the ESRF beam line ID12 which is dedicated to polarization dependent x-ray spectroscopy at photon energies above 2keV. Several examples have been selected to show the recent advances in this field.

14:15-14:40, Feb. 4

3D Structure Analysis of Atomically Dispersed Metal Species on an Oxide Single Crystal Surface by Polarization-Dependent Total-Reflection Fluorescence XAFS

Satoru TAKAKUSAGI

Hokkaido University

Precise size control of metal species on oxide surfaces, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on oxide surfaces. Our group has developed the “premodified surface method” to obtain a highly dispersed metal species, where an oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before deposition of metal atoms. We have succeeded in preparing atomically dispersed Cu, Au and Ni species on a $\text{TiO}_2(110)$ surface precovered with mercaptobenzoic acid (MBA) molecules, whose 3D structures were determined by using polarization-dependent total reflection fluorescence (PTRF) EXAFS.

14:40-15:05, Feb. 4

In situ XAFS Characterization of PEFC Electrocatalysts

Mizuki TADA

Research Center for Materials Science, Nagoya University

Polymer electrolyte fuel cells (PEFC)s are promising alternative power sources and Pt-based electrocatalysts have been used as cathode electrocatalysts for oxygen reduction reaction (ORR). Under PEFC working conditions, it is well known that the serious degradation of cathode electrocatalysts occurs at cathode. We have investigated the structural kinetics of surface events on a Pt/C and Pt-M/C cathode electrocatalysts in membrane electrode assemblies (MEAs) in PEFC by in situ time-resolved XAFS. The rate constants of structural changes in the Pt-based cathode catalysts in MEAs were successfully estimated by the analysis of a series of in situ time-resolved XAFS spectra. The structural kinetics of the Pt-based catalysts suggested the roles of additional metals (Co and Ni) in the Pt-alloy catalysts to improve PEFC performances.

15:05-15:30, Feb. 4

In situ XAFS and XPS for Electrochemical Processes at Solid Liquid Interfaces

Takuya MASUDA

National Institute for Materials Science (NIMS), Japan Science and Technology Agency (JST), Hokkaido University

In order to improve the efficiency of the energy conversion devices such as fuel cells, batteries, and photocatalysts, it is very important to understand the mechanisms of key electrochemical processes taking place at the solid/liquid interfaces. We have utilized various x-ray techniques using synchrotron radiation light source to investigate those interfacial processes under electrochemical potential control in situ. In this talk, I will present our recent progresses regarding in situ XAFS clarification of role of ceria in the enhancement of oxygen reduction reaction activity in PEM fuel cell electrocatalysts and development of an in situ electrochemical XPS apparatus for the solid/liquid interfaces.

15:30:-15:50, Feb. 4

Ambient Pressure Hard X-ray Photoelectron Spectroscopy of Polymer Electrolyte Fuel Cell Catalysts

Yasumasa TAKAGI

Institute for Molecular Science

We have constructed a near ambient pressure X-ray photoelectron spectroscopy instrument that use with hard X-ray radiation at the BL36XU of SPring-8 and have successfully achieved *in-situ* hard X-ray photoelectron spectroscopic measurements of catalytic electrodes of a polymer electrolyte fuel cell under working conditions. The oxidized Pt peaks were observed in the Pt 3d_{5/2} level of Pt nanoparticles in the cathode, and the peaks clearly depended on the applied voltage between the anode and cathode. This instrument will enable us to observe various fuel cell electrodes during operation in the future, promoting the development of fuel cell electrodes and catalyst materials.

16:10-16:55, Feb. 4

Future Opportunities with Magnetic Soft X-ray Spectromicroscopies

Peter FISCHER

Center for X-ray Optics, Lawrence Berkeley National Laboratory and Physics Department, University of California, Santa Cruz

Over the last decade magnetism research focused on a fundamental understanding and controlling spins on a nanoscale. The next step beyond the nanoscale will be governed by mesoscale phenomena, since those are supposed to add complexity and functionality, which are essential parameters to meet future challenges in terms of speed, size and energy efficiency of spin driven devices. Magnetic soft X-ray spectro-microscopies provide unique characterization opportunities combining X-ray magnetic circular dichroism (X-MCD) as element specific magnetic contrast mechanism with spatial (2D and 3D) and temporal resolution down to fundamental magnetic length and time scales.

16:55-17:20, Feb. 4

Application of SR-XRF and XAFS for the Clinical Diagnosis

Motohiro UO

Tokyo Medical and Dental University

The oral and the respiratory mucosae are exposed to various dental restorative materials and inhaled airborne debris and induce various symptoms. Therefore, the analysis of eroded metallic ions and foreign objects in tissues is important for the definite diagnosis. However, the histopathological specimens are specific to each case and patient, thus, the elemental analysis should be carried out non-destructively. Synchrotron radiation X-ray fluorescence (SR-XRF) analysis is the suitable method for the trace element analysis in the histopathological specimens.

We applied SR-XRF for the detection of the eroded metallic elements from the dental restoratives and implants into oral mucosa. Also, the inhaled foreign objects, which induced characteristic lung disease, could be identified by SR-XRF. Those analyses could be carried with the thin sectioned paraffin embedded specimens which are popularly used for the histopathological analysis. Therefore, it would be versatile method for various tissue analysis.

17:20-17:40, Feb. 4

Present Status of Scanning Transmission Soft X-ray Microscopy at UVSOR-III

Takuya OHIGASHI

UVSOR Synchrotron, Institute for Molecular Science

After the second upgrade project of the UVSOR synchrotron in 2012, the beam emittance of 15 nmrads resulted in the diffraction limit VUV source and the top-up operation and the technology of the in-vacuum undulator made it reasonable to realize spectro-microscopy with 30 nm spatial resolution. In the spring of 2012, we started construction of a scanning transmission X-ray microscopy (STXM) beamline at the UVSOR-III, and operation for general users started a year later. Since then, we have carried out 44 user's research programs by 29 groups. In this

talk, some selected results by using newly developed sample cells and several improvements in the STXM beamline BL4U will be shown.

17:40-18:00, Feb. 4

Soft X-ray Absorption Spectroscopy of Liquid and its Application to Electrochemical Reaction

Masanari NAGASAKA

Institute for Molecular Science

A transmission-type liquid flow cell has been developed for X-ray absorption spectroscopy (XAS) in soft X-ray region below 1 keV including C, N, and O K-edges. By using the developed liquid flow cell, we have measured XAS spectra of several aqueous solutions, such as methanol-water binary solutions, and revealed the local structures of aqueous solutions. We have also applied XAS of aqueous solutions to electrochemical reaction by using a liquid flow cell with built-in electrodes. Electrochemical reaction of iron sulfate solutions has been measured by in operando XAS in Fe L-edge with potential modulation at a same scan rate as in cyclic voltammetry (100 mV/s).

09:30-10:15, Feb. 5

How Can Transient X-ray Structural Methods Aide Solar Fuel and Solar Electricity Conversion Research?

Lin X. CHEN

Argonne National Laboratory & Northwestern University

Fundamental processes in solar energy conversion involve excited state formation and subsequent conversion to electricity, heat and fuels. Research needs to be carried out in search of optimal structural, energetic and dynamic parameters for efficient synthetic systems for solar energy conversion. Intense X-ray pulses from synchrotrons and X-ray free electrons lasers coupled with ultrafast lasers open up new opportunities to reveal transient structural information as photochemical processes in photocatalysis, photosensitization, and photovoltaics. Such studies combined with materials design can provide feedback for generating efficient, cost-saving, and durable materials. The lecture will highlight current solar fuel and solar electricity research using intense X-ray pulses to take molecular snapshots/movies.

10:15-10:40, Feb. 5

Capturing Structural Dynamics of Photochemistry by Picosecond X-ray Pulses

Shin-ichi ADACHI

Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK)

Ultrafast X-ray spectroscopy is becoming a general and powerful tool to explore structural dynamics in various materials. This method enables to produce “atomic movies” at picosecond temporal resolution. It will be fascinating to apply such capability to capture ultrafast structural dynamics of photochemical reactions in liquid or on solid surface. Photon Factory Advanced Ring (PF-AR) at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan is a 6.5-GeV electron storage ring dedicated for single-bunch operation and is suitable for the picosecond time-resolved X-ray studies. An in-vacuum undulator beamline NW14A at the PF-AR was designed

and constructed to conduct a wide variety of time-resolved X-ray measurements, such as time-resolved X-ray diffraction, scattering and spectroscopy. Successful examples of time-resolved XAFS studies applied to photochemistry will be presented in the talk.

10:40-11:05, Feb. 5

Ultrafast XAFS Using Femto-Second X-ray Pulses

Tetsuo KATAYAMA

Japanese Synchrotron Radiation Research Institute

Time-resolved x-ray absorption spectroscopy (TR-XAS) has been utilized to trace the transient change of both the electronic states and local geometrical structure. The ultrashort pulse duration of x-ray free electron lasers (XFELs) can improve the time resolution of TR-XAS down to the femtosecond regime. At SPring-8 Angstrom Compact Free Electron LAser (SACLA), we have developed both dispersive and wavelength-scanning schemes [1,2] for TR-XAS. These methods are now routinely used to probe light-induced chemical reaction, phase transition, and many other processes.

[1] T. Katayama et al., *Appl. Phys. Lett.* **103**, 131105 (2013)

[2] Y. Obara et al., *Opt. Express* **22**, 1105 (2014)

11:05-11:30

Temporally and Spatially Resolved XAFS at SPring-8

Tomoya URUGA

Japanese Synchrotron Radiation Research Institute

Recently, temporally and spatially resolved XAFS techniques were applied to various research fields especially in development of new materials and devices, such as catalysts, batteries, fuel cells, electric and magnetic devices and so on. In this talk we will present on advanced instrumentation and some recent results concerning time and spatial resolved techniques developed at the newly constructed beamlines and experimental stations at SPring-8.

11:30-11:50, Feb. 5

Picosecond and Femtosecond X-ray Absorption of WO₃ Photocatalyst

Yohei UEMURA

Institute for Molecular Science

WO₃ is a photocatalyst which can absorb visible light and can promote oxygen evolution from H₂O. Although fast processes of photoexcitation were studied by observation of lives of photocarriers, changes of structures and electronic states of WO₃ haven't been studied. The changes of structures and electric states are important to understand mechanisms of photocatalysts. In this study, we have investigated electronic states of W in WO₃ under laser excitation with transient XAFS. Transient XAFS of WO₃ measured at PF-AR and SACLA. Decay processes in different time scales were found in the experiments.

13:10-13:55, Feb. 5

Nuclear Resonance Vibrational Spectroscopy as an X-Ray Absorption Technique

Stephen P. CRAMER

University of California, Davis

Nuclear resonance vibrational spectroscopy is a relatively new technique. Although the nuclear transitions technically involve gamma-rays, the energies are in the x-ray region familiar to most synchrotron scientists. In this talk I will summarize the technology developments that have allowed this technique to become applicable to Fe enzymes. I will present some recent results on hydrogenase and nitrogenase. I will conclude with prospects for the future.

13:55-14:20, Feb. 5

α - ϵ Transition of Iron: an EXAFS Study under High Pressure

Naoki ISHIMATSU

Graduate School of Science, Hiroshima University

To investigate trigger and pathway of the α - ϵ transition of iron, combined measurements of extended x-ray absorption fine structure (EXAFS) and x-ray magnetic circular dichroism at the Fe K edge have been performed under quasihydrostatic pressures. The combined measurements reveal that collapse of the ferromagnetism simultaneously occurs with the α - ϵ structural transition. Our model developed to fit the EXAFS profiles takes into account the crystal symmetry, which enables us to determine displacements via shear and shuffle movements during the martensitic transformation. Importance of shear stress to initiate the α - ϵ transition is demonstrated in this talk.

14:20-14:45, Feb. 5

Molecular Environmental Geochemistry Using XAFS

Yoshio TAKAHASHI

Department of Earth and Planetary Science, The University of Tokyo

X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool in earth and environmental sciences in terms of speciation of various elements in the terrestrial materials. It has been found that the information of the oxidation state and local chemical environment at the atomic scale of each atom in various natural samples is clearly linked to the macro-scale phenomena we observe in natural systems. In this presentation, I would like to give some examples of the linkage between the macros-scale phenomena and atomic-scale information given by XAFS such as (i) solid-water distribution of various elements in natural waters, (ii) isotopic fractionation of molybdenum in the marine environment, (iii) behaviour of radiocesium and radioiodine at earth surface, and (iv) chemical reactions of calcium and iron in aerosols related to their influences on environment.

14:45-15:10, Feb. 5

XAFS study for Ag clusters

Takafumi MIYANAGA

Hirosaki University

We studied the relation between structures of the Ag clusters produced in Ag-type zeolite and properties of photo luminescence (PL) by in-situ XAFS. Ag clusters were produced in the cavity of Ag-type zeolite-A which was cooled to room temperature after heated at 500°C for 24 hours under vacuum or atmosphere. We investigated the structural change of the Ag clusters when various gases (oxygen, nitrogen, water vapor, and their mixture) are introduced in the cavity. The Ag clusters collapsed when H₂O gas was introduced and the breakdown of the cluster is indispensable to appear the strong PL band. Finally we discuss the coordination number for Ag nanoparticles obtained by EXAFS from the view point of small electron mean free path.