

Introduction to the Workshop and Presentation of IUCr SR and XAFS Commissions Strategies toward Standardization

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The Q2XAFS workshop "**Improving the data quality and quantity for XAFS experiments**" is jointly organized by two Commissions on XAFS and Synchrotron Radiation of IUCr and International X-ray Absorption Society (IXAS). We believe it is high time to have a workshop to establish protocols for XAS experiments and implement them as international standards in order to facilitate and expand the use of synchrotron radiation for research on materials and life sciences.

IUCr has been always supportive in establishing standards in data acquisition, analysis and archiving for the benefit of international scientists sharing crystallographic results. It has done so by establishing crystallographic nomenclatures and protocols for data archiving as well as standards for scientific publications. The IUCr Commission on Synchrotron Radiation facilitates worldwide access to the SR facilities and Commission on XAFS promotes basic and applied sciences using XAFS, a technique naturally requiring synchrotron radiation. The synergy between the two commissions catalyzed discussions between the two commissions on quality control and standardization of XAFS data. IXAS has kindly joined us to co-organize a workshop to propose standard protocols for data acquisition, analysis and quality control, much like other disciplines like small molecule and protein crystallography.

As a good example to compare, PDB (protein data bank) was initiated 40 years ago by a group of protein crystallographers headed by Prof. Max Perutz when there had been only 6 or 7 protein structures known. Since then, it has grown rapidly and has become a *de facto* standard of protein structure database. In many journals it is now prerequisite to deposit structural data in PDB before manuscript submission. It is also crucial to validate structures for which a set of validation tools have been developed. More recently, a number of other structural methods have been or are being considered for inclusion in PDB: small angle scattering and electron microscopy. In the future, data deposition of hybrid methods will be considered.

We hope that the workshop helps establishing international standards in XAFS experiments and establish protocols to implement them as standard practice for publications in international journals. The results will be published in a special issue in Journal of Synchrotron Radiation, and follow-up discussions will be continued in subsequent workshops/meetings.

***In situ* observation of reduction reactions of iron oxides by XAFS [1].**

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[Background] Pig iron is produced by the reduction of sinter composed of iron oxides and calcium ferrites using a blast furnace. The reduction mechanism has been investigated mainly by use of quenched specimens because of experimental difficulties of direct observation *in situ* measurement technique of XAFS[1] to observe the reduction reaction of iron oxides and related oxides.

[Experiment] We have developed an *in situ* observation technique by the combination of QXAFS [2] and the *in situ* reaction cell [3] with a time resolution of a few seconds. The specimen can be heated up $T= 1173$ K by a rod heater, while switching the two types of gas: O_2/He and H_2/He .

[Results] The main oxide phase of sinter: Fe_2O_3 and a typical calcium ferrite: $CaFe_2O_4$ were used as specimens. The specimens were heated at $T= 1023$ K and 1173 K. XAFS spectra around Fe K-edge were measured with an interval of 20 s after switching the gas from O_2/He to H_2/He (= 20/80 ccm).

The change of XANES spectra showed a clear isosbestic point, suggesting two types of iron states : Fe(0) and Fe(III) are involved in the reaction. The fraction x $\left(x = \frac{Fe(0)}{Fe(0) + Fe(III)} \right)$ was

determined by curve fitting of XAFS spectra (Fig. 1). The change of $\ln(1-x)$ showed an

exponential dependence on time, and it is observed that the reaction rate of Fe_2O_3 is faster than that of $CaFe_2O_4$. It should be noted that an incubation time was observed in the reduction process of $CaFe_2O_4$.

[Summary] An *in situ* observation technique has successfully shown the fundamental information on the reduction of sinter. The difference was observed for the reduction processes among iron oxides.

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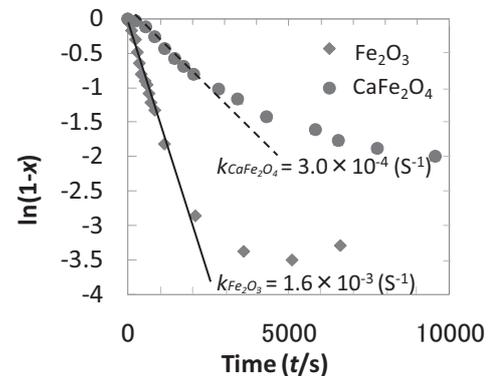


Fig.1: Relationship between the fraction x and the reduction time.

Understanding the Nature of the Kinetic Process in a VO₂ Metal-Insulator Transition

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Due to its intriguing thermochromic phenomena, originated from the occurrence of a fully reversible metal–insulator transition (MIT) that induce large changes in the electrical conductivity and in the near-IR optical properties, the vanadium oxide (VO₂) may become a reliable and effective energy-saving material in the future of our daily lives. As one of the prototype materials of correlation effects in condensed matter, the VO₂ MIT mechanism has been for long time a hot topic in condensed matter physics since the discovery of VO₂ MIT in 1950s. To contribute to the debate about the origin of the VO₂ structural phase transition, it is fundamental to monitor *in situ* both atomic and electronic structural changes during its MIT process triggered by temperature.

In this work, based on the temperature-dependent *in situ* x-ray absorption fine structure measurement and density-functional theory calculations, we have revealed that the monoclinic-to-tetragonal phase transition of VO₂ near the critical temperature is characterized by a sharp decrease of the twisting angle δ of the nearest V–V coordination. The VO₂ metallization occurs in the intermediate monocliniclike structure with a large twist of V–V pairs when the δ angle is smaller than 1.4 degree. The correlation between structural kinetics and electronic structure points out that the structural rearrangement is a key factor to narrow the insulating band gap. These results establish a clear correlation between the dynamics of the lattice structure and electronic properties and clarify a possible structural pathway and the mechanism of similar phase transitions in correlated materials.

New Development of 1W1B-XAFS Station in Beijing Synchrotron Radiation Facility

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1W1B-XAFS station in Beijing synchrotron radiation facility is a general purpose instrument. The light source of 1W1B-XAFS beamline is wiggler magnet with 1.1 mrad horizontal acceptance and 0.12 mrad perpendicular acceptance, The energy range from 5 to 25KeV, The resolution at 10KeV is 2-3eV, The photon flux at 10KeV is about 2×10^{11} photons.s⁻¹ under the electron energy of 2.5 GeV and stored current of 100 mA. The beam size at sample position is 0.7mm(H)*0.4mm(V). Currently, the detection methods and sample environments are developed. 19 elements germanium array detectors system has been set-up and used for fluorescent XAFS of trace elements, It greatly extends the applications of XAFS in life and environment science. On the other hand, multifunctional in situ sample instruments has been improved, including liquid helium temperature in situ XAFS cell, liquid nitrogen temperature XAFS cell, liquid sample cell, high pressure XAFS Instrument, which has supported XAFS measurements on the various conditions such as the low temperature, water solvent, organic solvent and also high pressure up to 40Gpa. Thanks to its versatility, it is useful to a broad scientific community.

Time-resolved XAS beamline at SLRI

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Abstract

This report presents the optical layout and the commissioning results of the energy dispersive X-ray absorption spectroscopy beamline at the Synchrotron Light Research Institute in Thailand. The beamline employs a bent Si(111) crystal as an energy dispersive monochromator (EDM). The beamline utilizes radiation from a bending magnet of 1.2 GeV storage ring. The EDM covers X-rays with photon energy from 3 to 8 keV. A linear image NMOS sensor consisting of 1024-element photodiode allows detection in transmission mode with a detector readout time of less than 100 ms, and thus time-resolved may be carried out at this beamline.

Keywords: synchrotron light, XAS beamline, energy dispersive

XANES Database in the CK, NK, and OK Regions of Standard Organic Compounds and Metal Compounds for Chemical Analysis

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XANES database in the CK, NK, and OK regions of standard compounds is necessary for the chemical analysis by using XANES of light-element materials including carbon (C), nitrogen (N), and oxygen (O). From the chemical analyses of graphitic carbons [1-3], diamond-related materials [4,5], C/N compounds [6], rubber [7], and other carbon materials [8], we have measured many XANES spectra of various organic compounds such as aromatic hydrocarbons [9, 10], aromatic compounds with oxygenated functional groups [1], aliphatic compounds with oxygenated functional groups [8], and aromatic compounds with nitrogenated functional groups [11] as standard compounds. We have also measured XANES of various metal carbides, nitrides, and oxides as standard compounds for chemical analysis of C, N, O in metal materials. These spectra were measured in the beamline BL-6.3.2 at the Advanced Light Source (ALS) with the energy resolution (E/dE) of 3000 – 5000.

In this study, we accumulate the XANES spectra in the CK, NK, and OK regions of the standard compounds to utilize the XANES database for chemical analysis.

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Total-Electron-Yield (TEY) Soft X-Ray Absorption Spectroscopy of the sp^2/sp^3 -Carbon Mixtures; Relationship between the TEY Efficiency and Electrical Conductivity

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Soft X-ray absorption spectroscopy (XAS) using a total-electron-yield (TEY) method has been a powerful tool for chemical/electronic-state analysis of functional materials. However, some difficulties often arise in TEY-XAS for quantitative analysis, because the TEY signal intensity may depend on the electrical property of the samples and the TEY ratios between sample compositions have not been clearly elucidated [1]. To apply the TEY-XAS for the quantitative analysis of sp^2 - and sp^3 -hybridized carbons, we have investigated the TEY efficiency between sp^2 -C (carbon black, carbon nanotube) and sp^3 -C (diamond) [2]. Thus, it can be found that TEY efficiency of sp^2 -C is higher than that of sp^3 -C.

To further confirm the TEY efficiency of sp^2/sp^3 -C and to reveal the relationship between the TEY efficiency and electrical properties of the compositions, we have measured the TEY-XAS of the sp^2/sp^3 -C powder mixtures (sp^2 -C: graphite, carbon black, carbon nanotube; sp^3 -C: diamond, polyethylene). TEY-XAS measurements were performed in a beamline BL-6.3.2 at the Advanced Light Source (ALS). Additionally, electrical resistivity and conductivity of the mixture samples were measured to compare the TEY efficiency. Thus, it is experimentally found that the logarithm of electrical conductivity of the sp^2/sp^3 -C mixture samples is qualitatively proportional to the TEY intensity. This suggests that TEY clearly depends on the electrical conductivity of sample compositions, and that we should consider the electrical properties of them for quantitative analysis by the TEY-XAS measurements.

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CONTINUOUS OBSERVATION BY DISPERSIVE XAFS TECHNIQUE FOR CATALYTIC REACTION

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Dispersive XAFS technique adopting the curved crystal enables us to observe XAFS spectra without mechanical movement at all. We have utilized the advantage of dispersive XAFS technique which is fast and stable observation, and applied to the structure and shape changes of Pd metal fine particles as automotive catalyst [1, 2]. Continuous observation with high relative precision and high frame rate creates many absorption spectra having a slight shift each other. Consistent and fast analysis of XAFS data is very important to obtain full information from many data sets.

Fig. 1 shows the variations of the XAFS parameters during a CO/NO successive flow for the Pd metal particles on the aluminum oxide with a frame rate of 0.2 Hz. From this figure, we determined the changes of structure, shape, and oxidation state for the Pd metal particles during the catalytic reaction. A precise determination of the states of metal particles is realized because the relative precisions of the interatomic distance and the edge shift are only 0.002 Å and 0.05 eV, respectively. We will present some examples of high relative precision and high frame rate with continuous observation.

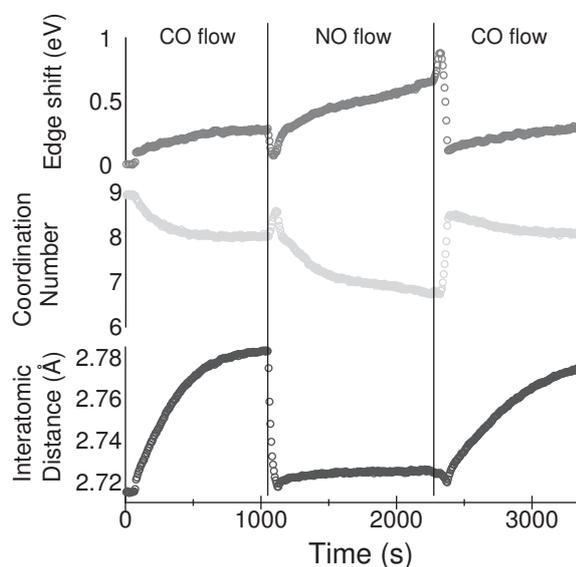


Fig. 1 Variations of XAFS parameters of Pd/Al₂O₃ at 400 °C during CO/NO catalytic reaction.

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XAFS measurements from Mg to Zn *K*-edges at Beamline 8 of Siam Photon Laboratory

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The beamline 8 (BL8) of Siam Photon Laboratory is routinely utilized for x-ray absorption fine structure (XAFS) experiments in various research areas, for examples, material science, biochemistry, environmental science, and archeology. The number of users has been steeply increased since 2006. A noted distinction of BL8 from other x-ray absorption beamlines is its ability to perform *K*-edge absorption for an element as light as magnesium (photon energy =1303 eV) up to zinc (9659 eV). Depending on the range of photon energy needed, there are four types of crystals available for the double crystal monochromator: KTP(011), InSb(111), Si(111), and Ge(220). Due to its small size and practical design of the monochromator, changing crystal and fine tuning can be quickly done within 1 to 2 hours. Near-edge and extended absorption fine structure spectra can be collected in either transmission or fluorescence modes. Elemental sensitivity is about 50 ppm. Instrumental specifications, functional control, and data acquisition of BL8 and its XAFS station will be described. An example of recent measurements on the mixed phases of tetrahedral and octahedral structures in MgZnO alloys will be present. It is found that XAFS results on the MgZnO alloys provide elemental specific information that was not seen by traditional x-ray powder diffraction.

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Time-resolved *in situ* XAFS studies on formation and oxidation of Pd-Zn nanoparticles on ZnO

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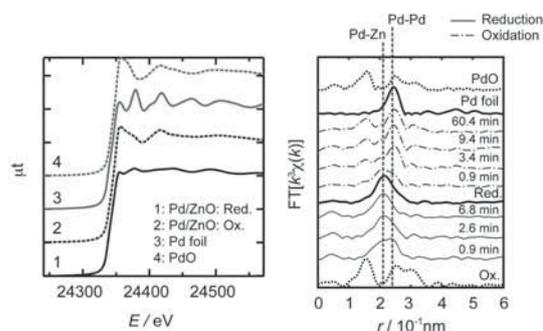
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Bimetallic nanoparticles are widely used as catalysts. Despite their potentials, the relationship between their catalytic activities and their chemical properties remains ambiguous, because there is not enough knowledge about their structures and electronic states under reaction conditions. Moreover, the recent study on Rh-Pd bimetallic nanoparticles revealed that the structures of bimetallic nanoparticles changed dynamically under reaction conditions.* We have studied formation and oxidation mechanism of PdZn nanoparticles supported on ZnO and γ -Al₂O₃ with time-resolved *in situ* XAFS (Quick XAFS and Dispersive XAFS) measurements. PdZn nanoparticles are active for the oxidative dehydrogenation of methanol. Our results pointed out that both formation and oxidation of PdZn nanoparticles proceed through a two-step reaction scheme.

Most of experiments were conducted in Photon Factory Advanced Ring (PF-AR), KEK, Tsukuba Japan. QXAFS experiments were conducted at NW10A and DXAFS experiments were conducted at NW2A. QXAFS experiments of Zn K edge were conducted at BL-9C, PF.

Fig. 1 a) shows *in situ* Pd K edge XANES of PdZn/ZnO at 400 °C. In Fig. 1a), Pd atoms in the reduced PdZn/ZnO is quite different from metallic Pd, which should be PdZn nanoparticles. On the other hand, the XANES of the oxidized PdZn/ZnO resembles that of PdO. Fig. 1 b) shows the Fourier transforms of *in situ* EXAFS of PdZn/ZnO. The Pd-Zn peak appeared at the end of the reduction, which means the formation of PdZn nanoparticles from PdO nanoparticles on ZnO



under the reductive condition. According to the detailed analyses, PdO nanoparticles are reduced to Pd nanoparticles, then PdZn nanoparticles are formed from these Pd nanoparticles on ZnO. On the other hand, the PdZn interaction quickly disappeared and the PdPd interaction appeared to form Pd nanoparticles in turn when oxidized. The Pd-O interaction was observed in 60 min, but its intensity was much smaller than that of the initial state of the reduction process. Pd nanoparticles emerged under oxidation conditions and they were very stable to not be oxidized even under 400 °C oxidative conditions. More details based on chemical kinetic analyses are going to be discussed.

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Determination of electronic and geometric structure of Molybdenum in molybdenum-based catalysts using L-edge X-ray Absorption Spectroscopy

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ABSTRACT

Mesostructured or mesoporous oxides have been the focus of intensive research for their successful applications in chemical, fuel and environmental processes as a catalyst support. Controlling the porosity of these materials is very desirable; it is interesting to note that the chemical/physical properties and structural texture are strongly related to the preparation procedure. The use of high surface area mesoporous oxide supports may give rise to well-dispersed and stable nanoparticles of catalyst in the pore surface and thus can improve the catalyst performance

In this research, molybdenum-based catalyst, which is well known to be active and selective in several types of reactions such as partial oxidation of hydrocarbons, partial oxidation alcohol as well as hydrodesulfurization [1], was prepared by impregnation method on mesoporous TiO₂-SBA15 composite support [2]. A well dispersed polymolybdate species in all solid and a homogenously deposit of anatase nanocrystals in the silica (SBA15) mesopores were confirmed by TEM and Raman spectroscopy. The catalyst supports, with molybdenum oxide loading between 5 and 40 wt%, was tested in thiophene hydrodesulfurization. The relationship between the catalytic performance and the structure of catalyst were studied by X-ray absorption spectroscopy (Mo L-edge). The experiment was carried out on the Beamline 8 at the Synchrotron Light Research Institute in Thailand. It was found that the loading concentration of catalyst may influence on the state of the oxo-molybdate phase and their catalytic activity as well.

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Weak Interaction Effect Study of Blue Copper Protein with XAS
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Non-covalent weak interactions play important roles for stabilization of protein structure and expression of function. In particular, non-covalent weak interactions near active site (second coordination sphere) of metalloprotein have great effect to tune the active site properties [1,2]. Pseudoazurin from *Achromobacter cycloclastes* is well characterized Type 1 copper protein, which has two His(His40, His81), Cys(Cys78) and Met(Met81) ligands with copper ion and exhibits significantly intense absorption band due to CysS⁻ → Cu(II) charge transfer (CT) transition around at 600 nm [3]. CT band is very sensitive and good probe to detect the precise electronic structure of active site. Spectroscopic and electrochemical studies of Met16X and Thr36X variants of pseudoazurin from *Achromobacter cycloclastes* have been performed to elucidate the effect of non-covalent weak interaction [4].

Here, we would like report tuning of blue copper site and protein stabilization induced by weak interaction accompanied by the unique pH dependency of Met16His/Thr36Lys PAz. X-ray absorption spectroscopic measurement (XAS) was performed to obtain the geometric features and electronic structure. The pre-edge intensity of various variants have good correlation with active site geometry, for the mixture of two conformers.

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XAS Studies on Electronic Structure of Metal Sites in a Blue Copper Protein, Plastocyanin from Fern *Dryopteris crassirhizoma*

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Non-covalent weak interactions play important roles in biological systems. In particular, such interactions in the second coordination shell of metal ions in proteins may modulate the structure and reactivity of the active site in functionally significant ways. Recently, π - π interactions between metal ion coordinated histidine imidazoles and aromatic amino acids have been recognized as potentially important contributors to the properties of metal ion site of a blue copper protein, pseudoazurin¹.

Plastocyanin is also well known to be a member of blue copper protein, which functions as electron carrier in photosynthesis. The reduced form of higher plant plastocyanin is deactivated at acidic pH by the dissociation of the solvent-exposed histidine ligand from the copper center². Plastocyanin isolated from a fern, *Dryopteris crassirhizoma* (DPc) maintains the electron transfer activity even under acidic pH conditions in contrast to the higher plant plastocyanin. Fern plastocyanin commonly has a Phe12 instead of Leu in the structurally identical position of higher plant plastocyanin, and Phe12 takes π - π interaction between coordinated His90. The π - π interaction in the second sphere has been considered as a factor for preventing the protonation of His90, which coordinated to Cu center.

X-ray absorption spectroscopy (XAS) is used to probe a electronic structure of metal site of protein molecules. XAS was measured to obtain the effect of non-covalent weak interaction in the second sphere on the electronic structure of the copper center in plastocyanin. XAS was performed at Stanford Synchrotron Light Source. Plastocyanin from *Ulva pertusa* (UPc) was measured for the comparison to DPc. Cu(I) K-edge of plastocyanins were measured at low pH condition and showed a band at 8982 eV. The Cu(I) K-edge of UPc indicated the coordination number of copper was decreased to be three-coordination. Cu(I) K-edge of DPc demonstrated the four-coordinated copper site. Cu(II) K-edge EXAFS data of plastocyanins were analysed based on the crystal structures. In the EXAFS of UPc, the distances between copper and coordinated atoms were evaluated to almost identical values of the crystal structural data.

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Status of the Toyota Beamline at the SPring-8

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We have designed and constructed an industrial research beamline BL33XU (the Toyota Beamline) at the SPring-8 in collaboration with JASRI and RIKEN. The beamline is aimed at studies in a wide variety of materials for our sustainable vehicle technologies (*e.g.*, automotive exhaust catalysts, secondary batteries, and fuel cells). Our recent interest is focused on developing apparatuses and programs for *in situ* measurement and analysis.

Some features of the Toyota Beamline are a tapered undulator and a compact monochromator, enabling XAFS measurement with time resolutions of several tens of milliseconds (super quick XAFS). Figure 1 demonstrates the performance of our super quick XAFS system. XANES spectra for Cu foil were measured with various time resolutions in an angular range of 0.2°. Well-defined spectra are obtained with the highest time resolution of 10 ms/spectrum. This super quick XAFS measurement system can be a very useful tool to observe dynamic phenomena in the process of chemical reactions.

Other feature is a high-speed gas reaction analysis system in our experimental hutch. The system consists of (i) three independent gas-supply lines, (ii) a high-speed gas switching and mixing apparatus, and (iii) a mass spectrometer at a sampling rate of 50 ms. They are embedded in the wall of the experimental facility building. This gas reaction analysis system enables us to conduct *operando* XAFS measurements under various atmospheric conditions. For instance, in the case of exhaust catalysts, the chemical state and the molecular structure of catalytically active sites can be clarified from XAFS analysis, and the catalytic activity can be evaluated from the gas analyzer. This *operando* system can make a real-time visualization of catalytic working state.

As mentioned above, *in situ* or *operando* XAFS measurement is crucial for investigating dynamic phenomena (*e.g.*, clarifying mechanism of bond formation in a material process and variation of the oxidation number of active species in exhaust catalysts and in electrochemical energy devices). Recently, we have been developing a program of EXAFS fitting analysis based on IFEFFIT for an enormous amount of XAFS spectra. The program makes it possible for us to find the change in coordination states as well as that in oxidation numbers of the interested atoms. Some examples will also be shown in our poster.

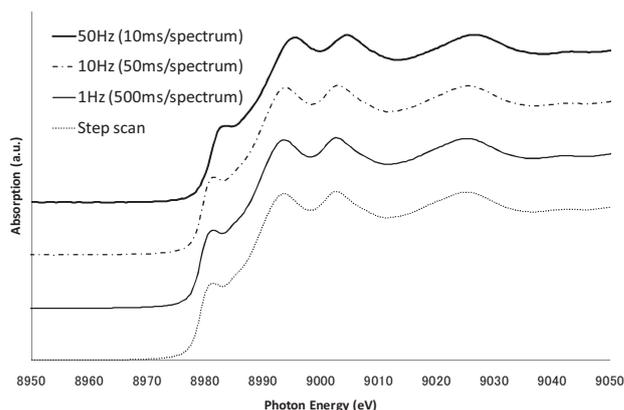


Figure.
Super quick XAFS spectra for Cu foil obtained with various temporal resolutions.

Dynamic Investigation of Photoinduced Phase Transition by picosecond time-resolved XAFS

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Prussian blue analogs have recently attracted great interest due to their various characteristics in the photoinduced phase transition (PIPT) as a photo-induced magnetization as well as photo-induced structural change.[1,2] The investigation of the dynamics of PIPT allows us to obtain information how the photo-excitation in the single site expands into a macroscopic phase transition. Picosecond time-resolved XAFS experiments were performed on the NW14A at the Photon Factory Advanced Ring (PF-AR).[3,4] The time-resolved XAFS spectra were collected by the pump-probe technique with a femtosecond laser system. In EXAFS and XANES regions, transient features attributed to the PIPT were obtained at 100 ps resolution. The detailed results will be presented.

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Observation of the $^3\text{MLCT}$ state of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ by picosecond Time-resolved Ru K -edge XAFS

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Ruthenium(II)-*tris*-2,2'-bipyridine ($[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$) has been extensively studied as an efficient photocatalyst for the conversion of solar energy.^[1-3] However, it is difficult to measure the structure of the $^3\text{MLCT}$ state with atomic resolution using conventional optical techniques. Thus, we conducted a study of the transient $^3\text{MLCT}$ state of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ using time-resolved X-ray absorption fine structure (TR-XAFS) to investigate the structure of the $^3\text{MLCT}$ state at KEK PF-AR undulator beamline NW14A.^[4,5]

The TR-XAFS study revealed that the Ru-N distances decrease in the $^3\text{MLCT}$ state compared with the ground state. The Debye-Waller factor increases in the $^3\text{MLCT}$ state, suggesting that the electron localized on a single bpy ligand causes structural distortion of the $^3\text{MLCT}$ state *versus* the ground state.

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Upgrade of the ESRF x-ray absorption spectroscopy beamlines:
The general purpose EXAFS beamline BM23

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In this poster, we describe the main features of the upgraded general purpose EXAFS beamline of the ESRF, BM23. This new beamline substitutes the former BM29, which has been closed in 2010. BM23 is optimized for standard EXAFS in transmission geometry in a large energy range (4-75 KeV). It also offers fluorescence detection, angle resolved XRD, as well as Quick-EXAFS on the second timescale.

Upgrade of the ESRF x-ray absorption spectroscopy beamlines:
The energy dispersive EXAFS beamline ID24

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In this poster, we describe the main features of the upgraded energy dispersive EXAFS beamline of the ESRF, ID24. The new ID24 has been rebuilt to host two independent EDXAS branches, which use beam on a time-shared basis. The new facility provides optimised x-rays for small and large spot activities, improved stability, and 1000-fold increase in time resolution for single shot studies.

Upgrade of the ESRF x-ray absorption spectroscopy beamlines: The scientific case

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The ESRF has started an ambitious project spread over 10 years aimed at an upgrade of the accelerator, beamlines and infrastructure. Through this upgrade, we have proposed a refurbishment of the scanning EXAFS beamline BM29 (rebuilt on BM23) and of the Energy Dispersive XAS (EDXAS) beamline ID24. This project (UPBL11), dedicated to time resolved and extreme conditions X-ray Absorption Spectroscopy, is the first of the upgrade projects to become operational: BM23 has been opened to user operation in March 2011 and the upgraded ID24 is planned to be operational for users starting in May 2012.

UPBL11 will provide the user community new opportunities for investigating industrially relevant materials, and matter at extreme conditions of pressure, temperature and magnetic field. Target experiments for the future include kinetic studies of chemical reactions at high pressure and temperature, and investigation of extreme states of matter that can be maintained only over very short periods of time.

High-accuracy measurements of the x-ray mass-attenuation coefficient of copperJ. L. Glover¹, C. T. Chantler¹, Z. Barnea¹, N. A. Rae¹, C. Q. Tran², D. C. Creagh³

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The x-ray mass-attenuation coefficient of copper was measured at 108 energies between 5 and 20 keV using synchrotron radiation. The measurements are accurate to between 0.09% and 4.5%, with most measurements being accurate to better than 0.12%. The imaginary component of the form factor of copper was also determined after subtracting the attenuation contribution due to scattering. Measurements were made over an extended range of experimental parameter space, allowing us to correct for several systematic errors present in the data. These results represent the most extensive and accurate dataset of their type for copper in the literature and include the important and widely studied region of the *K*-edge and x-ray absorption fine structure. The results are compared with current theoretical tabulations as well as previous experimental measurements and expose inadequacies in both.

XAFS and XANES analysis: A study in errors

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XAFS and XANES analysis are extremely effective and widely used techniques and can be used to obtain a multitude of parameters related to molecular and atomic structure and bonding. We will look at the limitations in the generic data collection approaches used worldwide with a view to how they limit XAFS and XANES analyses. A number of analysis techniques were investigated in both the near-edge and extended energy regions. Using experimental data of high accuracy and accurate theoretical tabulations of mass-attenuation coefficients, various experimental and analysis errors were simulated including harmonics, bandwidth, detector response and energy determination errors. Particular attention was paid to how these errors can affect the conclusions and derived parameters. We found the effectiveness of many XAFS and XANES analyses are limited by experimental and data reduction techniques, particularly relating to determinations of photon energy.

IXAS Strategy toward Standardization

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The rapid growth of synchrotron radiation (SR) facilities, particularly since the advent of the 3rd generation (3G) followed by accumulating number of experimenters has led to a significant increase of output of XAFS research. Unfortunately, the quality divide of users has in effect lead to the degradation of publications and loss of reliability. Expertise is achieved only through a slow process (learning and experience), although communication and information sharing technology dramatically progressed. Since the first meeting on “standards and criteria in x-ray absorption spectroscopy” in 1988 followed by a publication [1], round table discussions have been frequently held at previous XAFS conferences, under the same philosophy but with limited success.

The use of standardization is to implement guidelines, a design, or measurements in order to obtain solutions to an otherwise disorganized system. According to ISO, “when standards are absent, we soon notice,” implying our keen awareness of products (data) with poor quality, which do not fit, or are incompatible with the quality level (standard) that we already have. In our community, for example, a phase shift calculation code “FEFF” might be considered as one such “standards”, while some of the data analysis packages are close to this level. If data format is standardized as well, users can exchange resources with each other, making collaborations more possible between distant institutions and giving opportunities to researchers who have no access to the SR facilities. Other fields that need standardization or recommendations to improve quality are: criteria in energy scale accuracy, SR beam purity and stability, detector linearity, sample preparation and procedures etc.

How can we implement standards and recommendations? We need to reach a consensus on solutions that meet both the requirements of common science as well as the community. With a standard in place, users will be ensured with desirable characteristics of data and services such as quality, user friendliness, safety, reliability, efficiency and interchangeability - and at an economical cost. The necessary first step would be for the community to share a common understanding on the merits of standardization. The IXAS and IUCr can work together to discuss their roles to form and implement standardization.

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Toward the Standardization of XAFS, Transmission mode XAFS Setup

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Some workshops have been held to discuss the need for developing standards and criteria for the field of XAS and to recommend methods to implement any suggestions [1-3]. The setup and procedure of XAFS experiments in transmission mode seems to be well established.

1. energy calibration

Energy calibration is one of the most important points to standardize XAFS data and to make database. Many users use the tabulated energy of absorption edges to calibrate energy [4,5] and rely on the movement of monochromator at other data points. This method is sufficiently precise to measure EXAFS. $E-E_0$ is more important than the absolute energy scale in this case. However, there occurs high demand to XANES database in order to compare with the measured XANES, especially in case of trace elements etc. In this case, energy calibration becomes very important thus needs internationally standard energy scale. Evaluation of the energy or wavelength of certain structure in XAFS spectra using standard silicon crystal will be useful. Some such reports have been published and the energies of the absorption edges are tabulated [6, 7]. Since they are the energy of the maximum inflection point, the value depends on the energy resolution of the beamline. And some error sources are anticipated. Thus it will be required to reevaluate the absolute energy and make international standards.

Angular reproducibility of crystal monochromator is very high when the moving direction is defined. If it is suspected, third ionization chamber is used after putting reference sample. When measuring fluorescent XAFS, the fluorescence detector should be put not to detect the fluorescence X-rays from the reference sample. Glitches in I_0 can be used as internal energy standard to check the reproducibility of energy scale.

2. purity of incoming X-rays

EXAFS data analyses handle faint signal on high background. For example, EXAFS signal of $k^3\chi=1 \text{ \AA}^{-3}$ at $k=15 \text{ \AA}^{-1}$ means that χ is only 0.0003. Since higher energy X-rays transmit the sample more than the fundamental one, it is important to minimize the higher order X-rays from the monochromator. In general, Si(111) or Si(311) are used in order to minimize the second order reflection.

Higher orders can be reduced by using

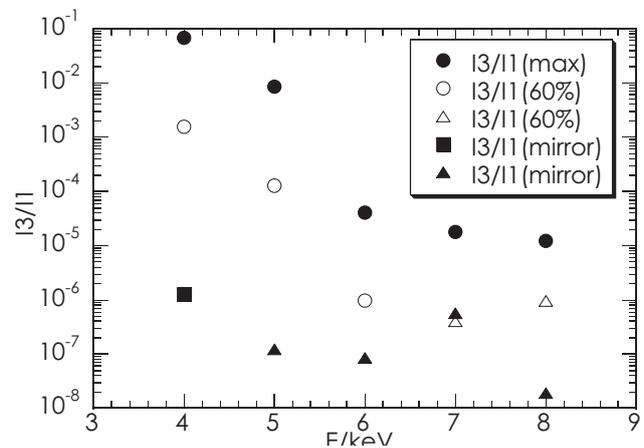


Fig. 1. Higher order ratios with detuning and with a double mirror system.

mirror(s) or detuning the DCM. A pair of mirrors is useful at lower energies such as less than 6 keV and detuning is equally useful at higher energy region. Since the spectrum of synchrotron radiation differs at beamline, at facility, operating condition, it should be carefully controlled. Comparison of spectra of difference thicknesses will be a simple and useful method to test it. Also the shape of pre-edge background is an index. If it is convex, the higher orders cannot be neglected.

3. linearity of detection systems

Linearity of detection system is also very important to get reliable results. Sufficiently high electric field between two electrodes is required to minimize recombination in ionization chamber. Saturation curve of ionization chamber with difference fill gas and under different fluxes are shown in fig. 2. At the Photon Factory, we recommend to apply twice high electric field than apparent saturation field. Air is not recommended to use for XAFS since recombination probability between ions is generally higher than that between electron and ion. When the ionization chambers are used correctly, EXAFS signal μt becomes continuous before and after beam injection thus was a good index to check the linearity of the detection systems. However, it is not easy to experience such beam injection because of top-up injection system. The same discussion can be applied to fluorescence X-ray detectors.

High voltage power supply is the major noise source of ionization chambers. Dry batteries were desirable voltage source but it is hard to purchase them.

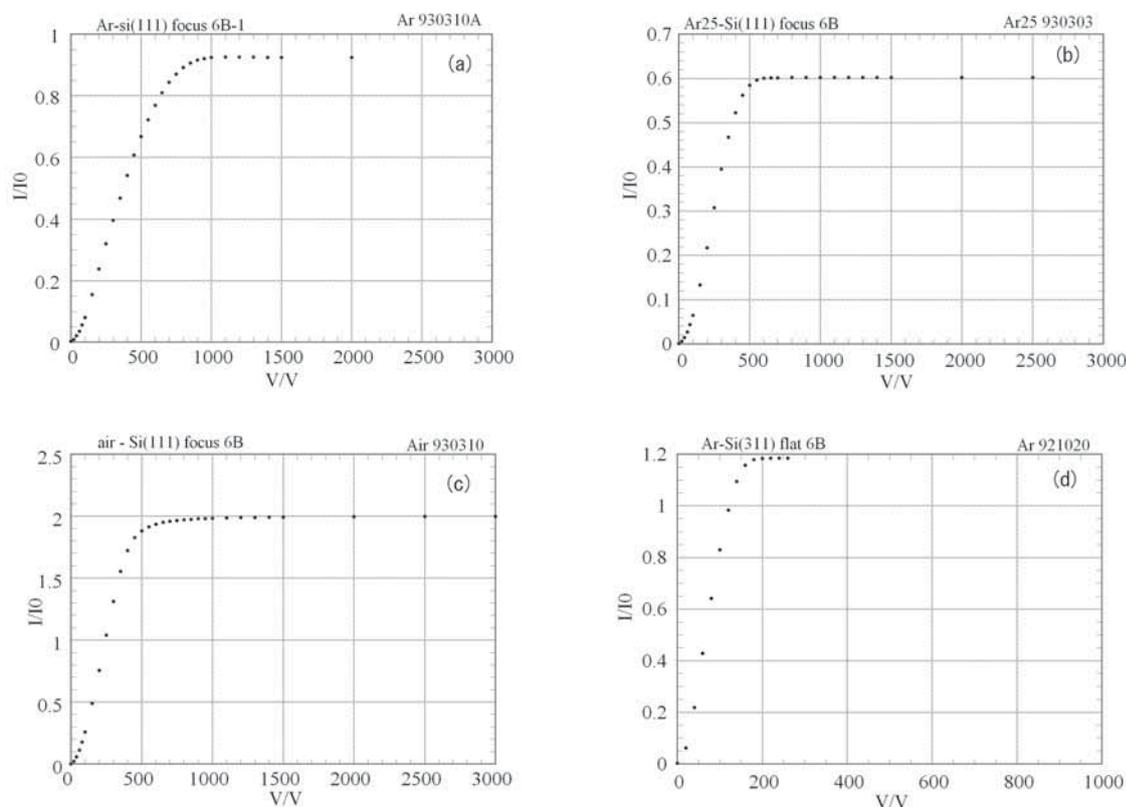


Fig. 2. Saturation curves of an ionization chamber. Incoming flux is similar among (a) to (c) but lower (d). When heavier gas is used, apparent saturation voltage increases except the case of air.

4. sample preparation

Uniform sample preparation of appropriate thickness will be the most important point to get reliable results from XAFS in transmission mode. Preparing enough fine powder is the first step and preparing uniform pellet is the second step. But so far as I know, these procedures are not well quantified yet. Measuring transmission image of X-rays may become an index. Glitches are good qualitative index to check if the sample is enough uniform. When the sample uniformity is suspected as the cause of not good spectrum, it is recommended to replace sample with metal foils, such as aluminum foils, of similar absorbance and measure XAFS. If glitches are canceled, the non-uniform sample is the most suspected.

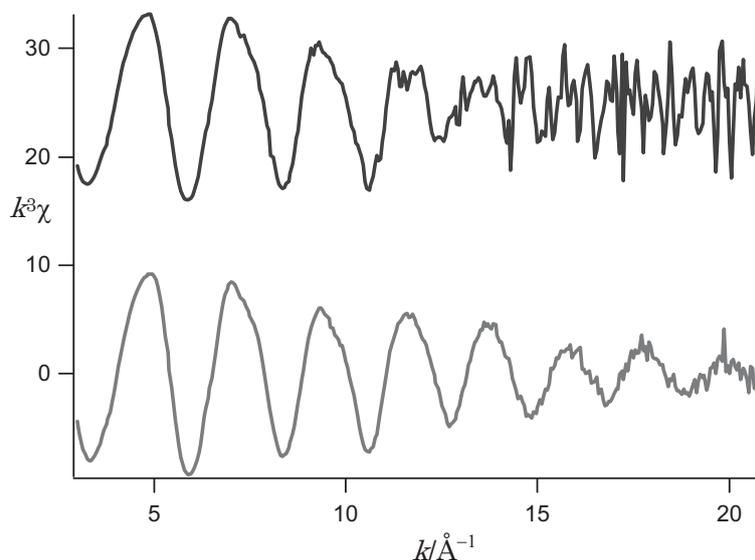


Fig. 3. Comparison of GeO₂ XAFS spectra with different pellet preparation.

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Toward the standardization of BioXAS

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Progresses in science are based on the reproducibility of results which requires validation of experimental procedures and data analysis. Although the bases for interpretation of EXAFS signal have been established since the 1970's [1] validation procedures and standardization should be further improved.

XAS is used in many areas of science and the experimental conditions may considerably change as function of the studied material. Specific set-ups include: sources (e.g. bending-magnet or high-flux undulator beamlines), detection mode (e.g. transmission, total electron yield or fluorescence modes), specific sample-holders (depending on the state of the sample: solid, liquid, crystal...), etc. The reactivity of the studied material could also require time-resolved measurements in XAS dispersive set-ups or quick-XAS beamlines. A global approach for XAS set-ups standardization is not easy due to this variability.

In this presentation, the standardization is discussed focusing on biological samples (BioXAS), in particular metal containing proteins. Critical aspects for validation of BioXAS experiments are indicated showing similarities and differences with protein crystallography (PX) experiments. BioXAS is highly complementary to PX as it adds atomic resolution on metal centres in metalloproteins to low and medium resolution diffraction data [2]. Moreover XANES measurements performed during a PX experiment allow to probe the redox state of metalloproteins, in order to detect photoreduction processes [3].

Some beamlines have been optimized in order to combine the two experimental approaches on the same set-up [3, 4, 5]. Considering that the crystallographic community has performed huge progresses toward standardization, it is proposed that XAS takes advantage from this experience, adopting similar procedures and adapting them to specific constrains. This approach, focussed on BioXAS standardization, could be later on extended to other applications of XAS.

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A Step toward Standardization: Development of Accurate Measurements of X-ray Absorption

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Increasingly, the standard of accuracy and insight of X-ray Absorption requires data with high intrinsic precision and therefore with allowance for a range of small but significant systematic effects. This is always crucial for absolute measurements of absorption, and is of equal importance but traditionally difficult for (usually relative) measurements of fluorescence XAFS or even absorption XAFS. The most crucial requirement is robust error analysis so the significance of conclusions can be tested within the uncertainties of the measurement. Furthermore, the errors should not just include precision uncertainty but should attempt to include estimation of the most significant systematic error contributions to the results. Preferably, and in a standard data format, these should be able to be incorporated by other readers in investigations of key conclusions and significances. In particular this will allow development of theoretical formulations to better serve the world-wide XAFS community, and a higher and more easily comparable standard of manuscripts.

Our presentation will illustrate a few of these principles; and will present a key step towards standardization – the development of accurate measurements of X-ray Absorption (and fluorescence), and of the measurement of accuracy therein. Experimental results presented will be based primarily on XERT data obtained at Tsukuba and Argonne.

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XAFS data collection; an integrated approach to delivering good data

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In this presentation I will briefly summarize the issues related with the measurement of good spectroscopy data, with the particular focus on the calibration of the energy scale and the reliable measurement of the intensity of the spectroscopic signal. The accurate determination of the energy scale is often established by using foils of optimum thickness to calibrate the monochromator. However, mechanical issues with the monochromator, movement of the source, or even the resolution of the spectrometer can have an effect on the measured energy scale. I will briefly review these factors, and summarize the most commonly techniques used to ensure the energy stability of the spectrometer that are based on an internal calibration.

In the second part of the presentation I will show how we have taken into consideration the above issues in the design of the versatile X-ray Absorption Spectroscopy Beamline, I20, at Diamond Light Source¹. This beamline is based around a four bounce monochromator². Two of the main characteristics of this device are: i) the resolution of the radiation delivered to the sample is solely given by the intrinsic spectral resolution of the crystals used to monochromate the beam, and ii) the crystal configuration separates the performance of the beamline from any instabilities of the source or of the optical elements upstream the monochromator.

Finally, I will mention how the energy calibration of data collected in Energy Dispersive mode is performed.

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A Data Interchange Standard for XAS and Related Spectroscopies

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The modern synchrotron experiment is an elaborate undertaking. A microprobe experiment involves coordinated operation of high precision actuators with complex optics while measuring multispectral data. An inelastic scattering experiment combines complex spectrometry with cutting-edge detector technology. A diffraction anomalous fine structure experiment involves coordinated motion of monochromator and goniometer. Even the venerable XAS experiment has become increasingly complex with in situ sample environments, quick-scanning monochromators, and high throughput methodology. At the end of the day, however, each of these measurements yields a scan of XAS data. At some point, the apparently simple problem of transferring that scan of XAS from the data acquisition software to the data analysis software must be solved. Having addressed that simpler problem, one must address the larger issue of organizing ensembles of data, which might represent the output of a single experiment, the results of a research topic, or a library of reference data. In this talk, I present a suggested solution to the problem of encoding a single scan of XAS data into a file that is easily read either by a computer or a human and that encodes metadata (i.e. conditions of the beamline and sample) in the file in an easily retrievable manner. Widely adopted, a formatting standard of this sort would promote interoperability between data acquisition and analysis software, would provide a mechanism for extracting XAS-like data from a multispectral data set or a complex data archive, and would increase the relevance and longevity of experimental data by reducing the amount of data archeology required in future times.

HDF5, NeXus and beyond: Approach to a Standard Data Format

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This presentation will offer an overview of different existing data formats and their advantages and disadvantages for their use as basis of a standard X-ray Absorption Spectroscopy data format. The suitability of ASCII based formats and binary ones like HDF5 will be thoroughly discussed. The NeXus initiative, followed by several European synchrotrons, will also be presented.

The talk will emphasize that different problems can require different solutions and compromises have to be adopted in order to fulfill the community needs.

References

- About HDF5: <http://www.hdfgroup.org>
- About NeXus: <http://www.nexusformat.org>

XAFS Data Library for Standard Data on Model Compounds

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As the volume of x-ray absorption spectra and the size of the community using XAS grow, there is an increasing need for seamless exchange of spectra between different facilities and analysis tools. This is particularly true for spectra measured on model compounds which are often used as reference spectra for XANES analysis or for calibrating analysis procedures.

Unfortunately, there is currently neither a standardized file format to exchanging data nor standard repositories of spectra. While efforts to standardize a single spectra to a plain text format are underway, I will present the a related effort to have a standard format for spectra libraries which can be shared or kept private, and can output individual spectra in a standard format. Preliminary efforts to build a library of spectra using a portable relational database will be discussed, and a prototype application to build and manage spectral libraries will be outlined.

Imagining a CIF-based XAFS data exchange framework

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The IUCr-sponsored Crystallographic Information Framework (CIF) has many desirable features for transferring XAFS data, including flexibility, syntactical simplicity, and semantic transparency. Comprehensive documentation and generic software tools are available. This talk focuses on how such an “XAFSCIF” data transfer protocol could be developed and managed. The primary development effort in producing XAFSCIF (as for any other protocol) would be directed towards creating the dictionaries that define the precise meanings of the data tags that appear in the data files. This involves agreeing on, and writing, the precise definitions of those tags, and filling in the machine-readable aspects of CIF dictionary definitions. Possible complications of the CIF approach include deciding on the data definition language (DDL) used to write these dictionaries; the potential difficulties involved in integrating an XAFS-centric data ontology with already existing IUCr ontologies; and the constraints imposed by the category-based approach of current CIF DDLs.

Data dictionaries require ongoing management due to expansion and development of scientific information and perspectives. For instance, new approaches and types of measurements require codification and integration into the existing ontology. Failure to adapt to these changing scientific needs will fragment the protocol as various groups seek incompatible ad-hoc solutions to problems. Therefore, in conjunction with development of the technical standard, the XAFS community need to nominate a custodian of the XAFSCIF dictionaries, and decide how to address these management challenges. Options include forming ad-hoc dictionary update groups as the need arises, or creating a permanent dictionary management group.

Structural Molecular Biology/XAS Beamline: Experiences at SSRL

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Metal ions have key roles in biological structure and function - from being active sites of many enzymes to shuttling electrons in key metabolic pathways, having roles in signaling pathways and being key elements of cancer chemotherapies and disease-related biological malfunctions. X-ray absorption spectroscopy (XAS) provides a unique tool to study biological structure in that it provides, at the molecular level, element-specific local structural information. It can furthermore be applied to most physical forms of biological systems. The XAS near-edge structure is sensitive to the electronic structure and geometric arrangement around an absorbing atom site, while the extended x-ray absorption fine structure energy region provides information on in particular the first-shell coordination sphere, and in some cases also outer coordination, in particular if multiple-scattering paths are present and can be determined. The talk will present and discuss SSRL facilities and a few biological applications.

The BioXAS beamlines at the Canadian Light Source

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The Canadian Light Source BioXAS facilities consist of three beamlines that currently are under construction. BioXAS-1 and BioXAS-2 consist of a side-station and end-station beamlines illuminated by a 2.1 Tesla flat-top field profile permanent magnet wiggler. These beamlines will be optimized for biological samples and will operate at X-ray energies between 5 and 28 keV. The side station will provide a high degree of automation in sample and configuration changes, and selection of fluorescence filters and calibration foil. Preliminary level automated data analysis, including EXAFS curve-fitting, will also be provided. The third beamline will provide a multi-functional X-ray fluorescence imaging and micro-XAS capability and is illuminated by a small-gap in-vacuum hybrid undulator (5.5 mm minimum gap). The scientific foundations, design features and challenges of the BioXAS beamlines will be discussed. Emphasis will be placed on ultra-low concentration XAS, high k -range EXAFS, and variable resolution capabilities for the X-ray fluorescence imaging and micro-XAS beamline.

Metal Speciation in Biological Systems with XANES and XAFS

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X-ray absorption spectroscopy (XAS) is unique among spectroscopic methods because of its ability to speciate a specific metal, or some specific metalloids or non-metals, in complex biological systems.¹ This can be achieved by performing linear regression analysis of XANES and/or XAFS from digestive juices (actual or artificial), blood components (serum), cells, and tissues, via the use of spectra from appropriate model complexes.¹⁻⁴ Chemometric analyses can also be used to cluster samples treated with different drugs, or different cells and tissues with the same drug, to examine similarities and differences in biospeciation. This can be complemented by separation of proteins on protein gels and then determining the distribution of an element amongst the proteins by the use of SRIXE (also called μ -XFM, but the latter terminology does not distinguish the synchrotron-based technique from those that use electrons or atoms to induce X-ray fluorescence).⁵ The local atomic environment about the element of interest in each band can then be investigated by XANES and/or XAFS.

Applications of these techniques will be discussed in terms of Ru anti-cancer drugs,² and Cr,³ and V anti-diabetic drugs.¹

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Energy Dispersive XAS: worldwide context

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ESRF

Energy Dispersive X-ray Absorption Spectroscopy (EDXAS) is now a well-established method which has been applied to a broad range of applications. The energy dispersive spectrometer employs a bent crystal to focus and disperse a polychromatic x-ray beam onto the sample. The beam passing through the sample then diverges towards a position sensitive detector, where beam position is correlated to energy. Major advantages of this scheme are: i) an intrinsic stability in focal spot position and in energy scale, since during acquisition there are no moving components ii) a high acquisition speed, where all energy points are acquired rigorously in parallel and iii) a small focal spot, thanks to the focusing properties of the curved crystal.

In this presentation I will try to make an overview of the past, present and planned EDXAS synchrotron radiation facilities worldwide. In this context I will also discuss the fundamental limitations of the technique, which have certainly played a role in the development of EDXAS in the synchrotron radiation community. Finally I would like to stimulate a discussion on how to improve the quality and the quantity of EDXAS data, by posing questions such as: “Which are the experiments that really benefit from the energy dispersive optics?” or “How can we widen the EDXAS user community?”.

Quick XAFS techniques – current status and new challenges at PETRA III

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Using stable double crystal monochromators the Quick-EXAFS (QEXAFS) technique allows time resolved X-ray absorption spectroscopy [1]. XAFS spectra are collected on the fly within time periods ranging from few seconds to some milliseconds. This technique is well suited e.g. for in situ investigations of fast chemical or solid-state reactions, thin film deposition and phase transformations during catalytic processes. Piezo driven tilt tables oscillating the monochromator crystals allow the continuous recording of XANES scans with repetition rates of about 100 Hz, depending on photon flux and sample quality. A dedicated monochromator even enables the acquisition of full EXAFS spectra with a scan range of up to 2.5 keV at a speed of 20 spectra per second, i.e. 50 ms/spectrum [2]. Such a setup employs - for ultimate stability - a channel cut crystal on an oscillating crystal mount. Because a fast sequential energy scanning technique is used the detection of fluorescence radiation or surface sensitive techniques can be directly applied, which is important for dilute samples from biology or catalysis [3, 4]. The fast scanning technique combined with refractive X-ray lenses for beam focusing allows even XANES micro tomography on a short time frame.

Time dependent measurements require very fast high precision detection systems with low noise level, and the photon energy at each instant must be known with high accuracy. Special care is necessary to avoid dynamic distortions of the measured absorption spectra. In addition, the high data acquisition rates make special software developments necessary [5] to store the data streams continuously without losses and to exploit the full flexibility of new monochromator systems [6].

Using cryogenic cooling, the monochromator crystal can cope with the full heat load from insertion devices of third generation synchrotron radiation sources. Currently, a new dedicated setup using an insertion device at the PETRA III storage ring (DESY, Hamburg, Germany) is under development. Initially, a tapered undulator seemed to be the best option to create a wide spectral range for the fast scans. However, it turned out that the spatial intensity distribution of such a source changes significantly within an EXAFS energy range, resulting in distortions of the spectra of inhomogeneous samples. Simulated and real measurements will be presented which convincingly demonstrate those puzzling effects.

Current experimental realizations of hard- and software for QEXAFS measurements are discussed. Experimental factors which are influencing the data quality like the homogeneity of real samples, photon flux and beam stability are evaluated.

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***An advanced beamline for XAS and IR simultaneous time resolved experiments.
A new approach to characterize non equilibrium phenomena.***

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The majority of the physico/chemical processes occur as the interplay between electronic and atomic/molecular structures. The characterization of both collective and individual excitations observed in condensed matter systems including ordered and disordered systems, and biological systems are of great interests for both fundamental and technological researches. Moreover, many low dimensional systems show a rich variety of physical properties pointing out many new technological applications. To characterize these systems and many complex phenomena due to the interplay between localized and delocalized electrons, charge transfers, collective excitations and molecular vibrations, new time-resolved techniques and instruments have to be considered.

Thanks to the unique characteristics such as brilliance and broad spectrum, synchrotron sources offer a unique opportunity to combine X-ray and infrared (IR) beams to investigate many emerging phenomena in materials science, biology, energy and environmental science, etc. A first attempt combining X-ray and IR beams dates back to 1995 at Daresbury. [1] More recently, the capability of a simultaneous analysis has been applied to the study of non-equilibrium processes in mesostructured membranes. [2]

Axiomatic to the construction of a beamline to perform complex concurrent experiments is that they should be the sum of their parts, leading to new unique insight that two techniques applied separately could not achieve. Being straightforward, one has to achieve a level of consistency not achievable by separate experiments made with different instrumental chambers and in a sequence.

The proposal for the first IR and X-ray Simultaneous Spectroscopy beamline has been already submitted in the early 2007 at Diamond and, later, similar projects have been considered in other facilities. An optical design for a conceptually new beamline allowing time-resolved concurrent X-ray and IR experiments has been also published [3]. The advantages, challenges, and future possibilities for combining synchrotron-based X-ray techniques with vibrational spectroscopies have been considered in a recent critical review devoted to catalysis [4]. We will present here the original layout and the expected performances of a beamline for time-resolved experiments designed to combine IR and X-ray radiation from a bending magnet. [5]

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Opportunities and Traps of Hard X-ray photon-in/photon-out Spectroscopy

Pieter Glatzel
ESRF

Energy analysis of the scattered photons ω in addition to control of the incident photon energy Ω (*cf.* Figure 1) extends the range of applications of XAS and addresses some problems that XAS cannot solve [1,2]. The instrumental energy bandwidth in XAS is of the order of the core hole lifetime broadening, which is around 1 eV for 3d transition metal (TM) K edges and as large as 8 eV at the L-edge of actinides. Hard X-ray monochromators are typically based on perfect-crystal Bragg optics for the incident photons and the same principle can be used to analyze the scattered photons. Various geometries using spherical, cylindrical and flat crystals with point-to-point or dispersive geometries have been used at synchrotron radiation beamlines (for references see [1]).

Hard X-ray photon-in/photon-out spectroscopy can thus be defined as detecting the emitted X-rays with an energy bandwidth that is on the order of the core hole lifetime broadening. This observation is relevant because under this condition (i) the emitted x-rays reveal a chemical sensitivity and (ii) the line broadening is no more limited by the XAS core hole lifetime. Despite the rather simple experimental setup some interesting phenomena can be observed that require considerations beyond a standard XAS analysis. The presentation will point to benefits and pitfalls of this technique and will provide an overview of the current status quo of theoretical approaches (see e.g. [3]).

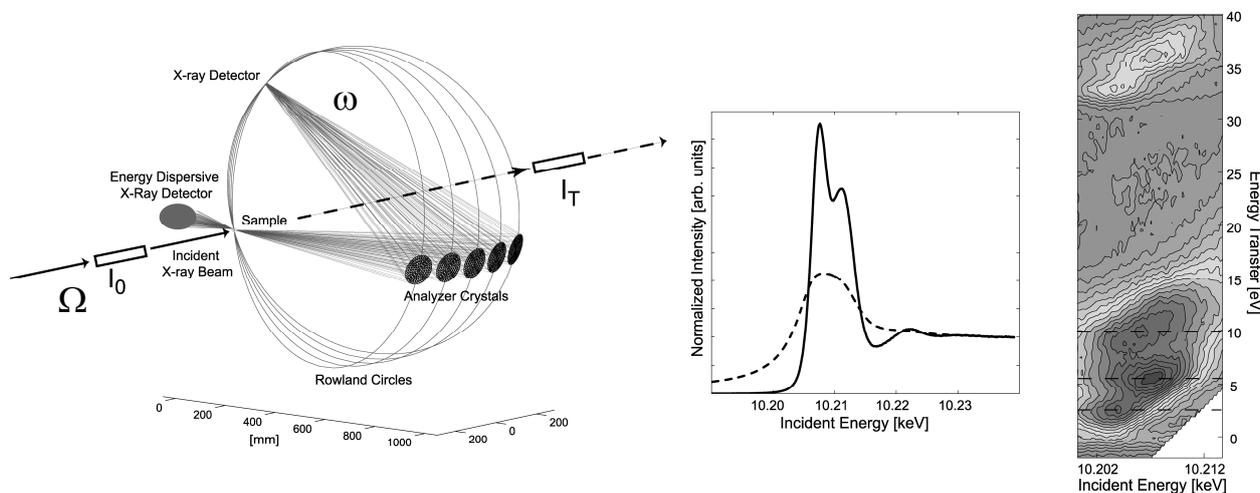


Figure 1: (left) Schematic experimental setup for XAS in transmission (I_T), medium (energy dispersive X-ray detector) and high energy resolution fluorescence detection (HERFD) mode; (center) standard (dashed line) and high resolution XAS of 2 at% W in TiO_2 ; (right) RIXS plane of W in WO_2 ; the dashed lines are a guide to the eye indicating the strongest final states up to 10 eV energy transfer. The features around 35 eV energy transfer are tentatively assigned to W 4f orbitals.

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Ideas for assuring data quality and comparability at the new PETRA III EXAFS beamlines

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Within the next 3 years two new EXAFS beamlines will be build at the PETRA III storage ring (DESY, Hamburg, Germany). They will replace the existing three bending magnet EXAFS beamlines at the old DORIS III storage ring which are in operation today. DORIS III and all the beamlines will be closed end of October 2012. One of the two new beamlines will be optimised for Quick-scanning EXAFS (Q-EXAFS) and highly diluted sample systems. It will be equipped with an additional special fast scanning Q-EXAFS monochromator [1] and a 100 pixel high purity Ge-detector. The second beamline will mainly be used to continue the successful experiments with moderate flux and a beam size of some mm² at the existing beamlines. Both beamlines will be equipped with the necessary infrastructure for all kinds of in-situ experiments.

The most challenging decision with potential severe impact on data quality is which type of source is best suited, especially in the case of the Q-EXAFS beamline. EXAFS spectroscopy in general requires a homogeneous and stable spatial distribution of the intensity during the energy scan especially if inhomogeneous samples are involved. At the same time fast scanning EXAFS with repetition rates of 10 – 20 Hz are not feasible with a scanning undulator, the source must therefore deliver a broad, flat emission spectrum. However, calculations with the *SRW* [2] and *SPECTRA* [3] codes indicate that even hard wigglers ($K > 10$) which are normally supposed to deliver a flat spectrum and a homogeneous intensity distribution might show pronounced interference patterns if they are installed at a 6 GeV machine with 1 nmrad natural emittance.

Other measures to improve the data quality are easier to implement but should already be considered during the design phase of the new beamlines. One important issue is the complete documentation of an EXAFS experiment. Irrespective of the data format which will finally be used at future beamlines it is obvious, that a number of appropriate parameters, which describe the experiment entirely, should be stored together with the actual spectrum. During the design and set-up phase it is necessary to identify these parameters and to integrate means to measure them in a reliable way during the later experiments.

Once being in operation a very important factor will be to use well established procedures to maintain the highest performance in day to day operation, although strict rules how to perform experiments like the *standard operating procedures* used in analytical laboratories might be too inflexible for research applications. However, some basic measures like the use of well characterised standards and standard procedures for instance for the calibration of the monochromator's energy scale etc. are not interfering with the demand for flexible experiments, they are in contrary absolutely necessary to maintain basic experimental standards.

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Insight through in situ XAS studies of Catalytic materials

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Catalysis is the back-bone of chemical industries and they will continue to be essential in numerous applications that are indispensable to enhance quality of our life and society. Although catalysis has been successful in many ways, a positive development of the twenty first century is that we have woken up to the danger to our future - the danger to our environment created by industrial expansion of the last century. Many processes produces unwanted side products which needs to be minimized or completely avoided to produce non-toxic and unwanted side products. To this end, several green chemical processes have been attempted in recent years. More importantly catalysts have been developed that facilitate the production of non-toxic waste products. For example, in oxidation reactions, new approaches have been developed to identify materials that use molecular oxygen or nitrous oxide or hydrogen peroxide as oxidants. For this purpose we require, first an appropriate catalysts and secondly, in the preferred coordination environment to be the active for the catalytic reaction. While catalyst innovation continue to take place through test of several reactions, it is equally important to understand the structure of the catalyst and in particular the coordination environment of the active site. To determine precisely the coordination environment of the catalyst in the active state, X-ray absorption spectroscopy has been used extensively for a variety of systems. With the availability of modern Synchrotron Sources combined with advancements in time-resolved XAS measurements it is possible now to determine precisely the nature of the active sites at a given reaction conditions. Here four types of catalytic materials, as examples of system where X-ray absorption spectroscopy provided the most vital information to resolve both fundamental and issues related to the industry and environment. The examples will include (a) the study of titanium based catalysts that are extensively used for oxidation or alkene molecules in presence of hydrogen peroxide, (b) use of QuEXAFS to develop new convenient process of producing gold nano particles from well defined clusters, (c) use of EXAFS and XANES to determine the speciation in “real” auto-exhaust catalysts and (d) use of XANES and EXAFS to determine the type and ratio of chromium present in industrial, high-temperature shift catalysts. In addition what are the current difficulties in the existing available methods and data analysis procedures for industries to capitalise the facilities will also be discussed.

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***In situ* structural studies of catalysts under high gas pressure environment**

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The talk will be focused on the methodological aspects of structural studies of catalysts under working conditions and under high gas pressure environment using X-ray absorption spectroscopy and complimentary techniques, such as XRD and Raman spectroscopy. The challenges related to the design of dedicated *in situ* reactors and the advantages of multi-technique approach will be discussed. Examples of studies on Fischer-Tropsch catalysts and related high pressure processes will be shown.

Single Crystal XAS Studies on Metalloprotein Intermediates

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Synchrotron based Metal K-edge XAS and EXAFS spectroscopy is a powerful tool for electronic and geometric structure determination of metalloprotein active sites and is dominantly applied to isotropic samples. The combined single crystal XAS and diffraction technique developed at SSRL on beamline 9-3 can be applied to anisotropic protein crystals to obtain direction specific metrical and electronic information about the active site. In addition, important electronic structure information on unstable, trapped intermediate and transient species can be obtained, which can guide the structure determination process or help develop a strategy for diffraction data collection.

Two recent studies on metalloprotein active sites will be presented. In the first study, Single crystal XAS studies on the Ni containing active site of Methyl Coenzyme M Reductase was combined with solution XAS and EXAFS data. The data were used to determine the redox state of a putative Ni(III)-Me intermediate and coupled to structure determination. In the second study, the electronic structure of oxyhemoglobin was explored using both solution and single crystal Fe K-pre-edge and near-edge XAS studies to differentiate between two putative electronic structure descriptions.

SSRL operations are funded by the Department of Energy, Office of Basic Energy Sciences. The SSRL Structural Molecular Biology program is supported by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program, and Department of Energy, Office of Biological and Environmental Research.

T-REX for advanced QEXAFS data analysis

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Quick-scanning EXAFS (QEXAFS) [1,2] is used by many groups to investigate fast processes in physics and chemistry, especially in the field of catalysis [3,4]. Due to recent developments in the QEXAFS technique it is possible to acquire tens of full EXAFS spectra each second in a very accurate and user-friendly way [5,6]. Thereby, huge amounts of data are generated which have to be processed with adequate software tools. On the one hand, these tools have to cover the typical steps of EXAFS analysis, i.e. background subtraction, spline fits, Fourier transformations and atom shell fittings. On the other hand, studying time-resolved data requires additional approaches as e.g. determining the number of independent components with principal component analysis and tracking the weights of sample components by successively fitting the spectra with linear combinations of reference spectra. Valuable approaches are also to determine edge jump, edge position and whiteline intensity as function of time. All these operations have to be performed in an automatized way with thousands of spectra in order to effectively analyze QEXAFS data. Furthermore, with respect to signal processing the large amount of spectra along the time axis provides unique possibilities for the application of digital filters. Thus, it is possible to apply accurate low pass operations or e.g. median filters to achieve the best compromise between time-resolution and noise characteristics.

The new software package T-REX (**T**ime-**R**esolved **E**XAFS analysis software) with a graphical user interface was designed using Microsoft Visual C# in order to provide the mentioned and additional unmentioned operations for QEXAFS data analysis. Thereby, for some of the tools interaction with IFEFFIT [7] is established, which provides a powerful set of methods for the EXAFS data treatment as known from ATHENA [8]. These methods were adapted for the convenient processing of thousands of spectra. The complete data analysis starting with the QEXAFS raw data files in ASCII format can be performed with T-REX. Thereby, each project can be stored making it possible to save progress and to rapidly navigate through the results. The software will be presented along with several typical QEXAFS applications as (i) a Cu/Al₂O₃ catalyst that was periodically reduced and re-oxidized at various temperatures and (ii) Cu layers that were dc sputtered on glass and thereafter oxidized, whereby both surface processes were followed by in-situ QEXAFS measurements in grazing incidence reflection mode.

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In situ time-resolved XAFS study of the formation mechanism of Rh NPs in the presence of quaternary ammonium bromide

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Introduction

Metal nanoparticles (NPs) are getting attention in both fields of fundamental science and engineering. For example, metal NPs have several catalytic activities such as hydrogenation, oxidation or C-C coupling¹. In these days, various scientists' effort enabled us to control NPs' size and/or shape. Their formation mechanisms are also vigorously investigated, but are still under discussion. In this study, we observed the formation of Rh NPs in the presence of quaternary ammonium bromide² in ethylene glycol at elevated temperature by means of in situ time-resolved XAFS technique.

Results and Discussion

Figure 1 shows a series of *in situ* time-resolved EXAFS spectra of Rh NPs formation from RhCl₃·3H₂O with 15 eq. Polyvinylpyrrolidone (PVP, M.W.=24000) and Tetrabutylammonium bromide (TTAB) in ethylene glycol (EG) for 1 hour at 403 K. In the first step, Cl⁻ dissociates from a Rh precursor and the intermediate having Rh-Br bonding was formed. In the second step, the Rh-Rh peak at around 2.3 Å gradually increased in about 20 minutes through an isosbestic point. For the latter 40 minutes, the EXAFS spectra were almost unchanged, which means that the Rh NPs formation stopped under this condition. The TEM observation clarified that the obtained Rh NPs were 6 nm cubic NPs and their size distribution were very small.

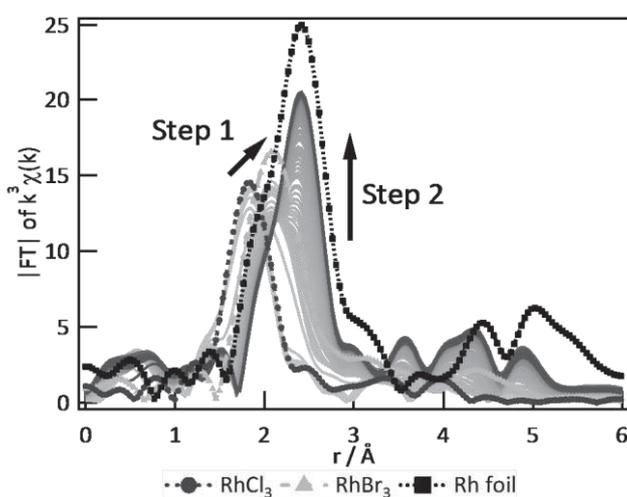


Figure 1 A series of in situ time-resolved Fourier transformed EXAFS spectra for 1 h at 403 K (Additives: PVP and TBAB) Reference spectra: RhCl₃ (Circle), RhBr₃ (Triangle), Rh foil (Square)

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² W. Y. Zhang et al., *J. Am. Chem. Soc.*, **2008**, 130, 5868.

Recent Developments with the LCLS X-ray FEL at SLAC and Prospects for Future Science

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It is now well established that synchrotron radiation produced by electron storage rings is an essential, indeed critical, tool for enabling forefront science in many fields of science and technology. In part this has come from the much higher average brightness provided by the 3rd generation sources, a number of which are in operation or in construction worldwide. Developments in accelerator physics over the past decade or so have provided the underpinning technology to enable a different approach to producing synchrotron radiation based upon linear accelerators rather than storage rings.

Linac-based light sources can have properties that differ significantly from that of storage rings, including much shorter pulses, much higher average and peak (per pulse) brightness and full coherence (in the case of the x-ray free electron lasers - XFELs). The world's first XFEL has now been operational at SLAC serving 5 experimental stations. Exciting scientific results in areas that include AMO physics, x-ray pump probe and coherent x-ray imaging are already providing new scientific insights. This talk provides a brief overview of the LCLS and its recent applications in areas that include x-ray absorption and emission spectroscopy and a perspective on future science opportunities.