







Solvent-Induced Transition of Polymorphological Chiral Supermolecular Architectures in Bent-Core Liquid Crystal Dimer/Nematic Binary Mixtures as Studied by Resonant Soft X-ray Scattering (RSoXS) at UVSOR

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Nano-scaled chiral superstructures, such as tilted lamellar (smectic) structures or helical nanofilaments (HNFs), are often observed in polar (or apolar) softmesophases of achiral bent-core molecules, although their chemical structure has no chiral carbon. The socalled B4 phase is one of such soft-mesophases, in which chirality is macroscopically recognizable as millimeter-sized domains optically segregated under a polarizing microscope. There are two types of B4 domains resembling each other, originated from two different nanoscopic structures; One is filled with bundles of polar HNFs with a pitch of several tens to hundreds nm, and the other is the so-called dark conglomerate (DC) in which concentric polar lamellar structures are interconnected to form bicontinuous pores like a sponge. However, in both cases, the polar tilted lamellar structure is essential and thus almost identical diffraction patterns are obtained by conventional small angle X-ray scattering (SAXS).

Recently, we discovered that these two structures are interchangeable by adding a nematic solvent (ZLI-2293, Merck) to the host bent-core molecule (12OAz5AzO12). Besides, further addition of the nematic solvent induced an unprecedented nano-tubular structure like a "macaroni" as a novel chiral state. This nanoscopic morphological change was first confirmed with scanning electron microscopy (SEM, Fig. 1) - the result suggests that phase separation reduces interfacial free energy and creates spaces to allow the lamellar to be more twisted, leading to the structural transition from DC to macaroni via HNF. However, the SEM technique requires vacuum for electrons to fly, and thus the samples were fractured to expose the internal structure and washed with Hexane to completely remove the solvent nematic molecule. This leaves uncertainty if the bulk structures are surely preserved during the fracturing/washing process or not. Meanwhile, HNF/DC are just morphologically characterized, and hence electron density is basically not spatially modulated by these structures. This means that usual X-ray diffraction/scattering is not very useful to investigate the present system. For these reasons, we performed resonant soft X-ray scattering (RSoXS) measurements using X-ray whose energy is close to the carbon K-edge absorption, which allows us to analyze the nanoscopic structural change in such а morphologically transformable system.

Our RSoXS setup was prepared in BL3U of UVSOR at IMS – A homemade vacuum chamber equipped with a cooled CCD camera (Newton, Andor) was newly designed for small angle detection $(2\theta \sim 1-15^\circ)$. In the present study, the X-ray photon energy was chosen as 284.5 eV, corresponding to the carbon K-edge absorption of the present sample mixtures.

RSoXS patterns for HNF, DC and Macaroni are compared in Fig. 2, which clearly shows transitions due to the morphological change among these states. HNFs, appearing in the middle doping range, show relatively sharp scattering patterns at the scattering angle corresponding to the half-pitch periodicity of the twisting filaments. On the other hand, DCs show broad peaks at the slightly smaller scattering angle region than HNFs, which would be corresponding to the average distances between the lamellar inter-connections. Interestingly, the macaroni state shows just scarce signals in this region, meaning almost no nanoscopic structural periodicity. Needless to say, these confirm that the present RSoXS setup works well for structural investigation for such soft-mesophases.



Fig. 1. Nanoscopic morphological transformation among DC, HNF, and macaroni as observed by SEM.



Fig. 2. RSoXS pattern alteration corresponding to the nanoscopic morphological transformation.

Ш-З

Energy-Dependence of Photoelectron Circular Dichroism of Chiral Molecules

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A simple explanation of the manifestation of photoelectron circular dichroism (PECD), which is measured as forward-backward asymmetry of the photoelectron angular distribution with circularly polarized light, can be that the outgoing photoelectron is affected by a chiral potential originated from the chiral core ion. The intuitive model indicates that the slower photoelectron can exhibit the larger PECD. Actually, most of the PECD measurements so far carried out for various chiral molecules demonstrated decreasing PECD parameters (b_1) as the higher photon energies. However, the b1 parameters of the individual electronic states varied in an independent manner, showing the state-specificity. The energy-dependence and state-dependence of PECD are not simply understood with a simple model but should be examined based on the precise measurements and accurate theoretical calculations, both of which can provide novel pictures for the PECD mechanism.

We have conducted the PECD measurements for S methyl oxirane and other chiral molecules with employment of circular polarized light at BL1U at varied photon energies [1]. Methyl oxirane (propylene oxide) is a typical chiral molecule, whose PECD has been intensively studied. Our results are shown in Fig. 1, where the photon energy-dependence is shown in a series of the image data for (a) 10.3 eV, (b) 11.0 eV, (c) 12.0 eV, (d) 12.7 eV, (e) 13.3 eV, and (f) photoelectron kinetic energy (PKE) scale. Distinct ring structures corresponding to individual electronic states appeared at the higher photon energy than (a) 10.3 eV (close to the ionization threshold) with particular PECD, whose positive and negative b₁ values are represented by red and blue colors. The b₁ value of each ring decreases as the elevated photon energy, but the decreasing behaviors were not monotonic but rather dependent on the states. The strongest PECD observed in the 2 eV PKE region at (c) hv = 12.0 eV rapidly disappeared at an only slightly larger photon energy of (d) hv = 12.7eV, while other bands kept the contrast of the blue/red color (b₁ PECD parameter) for the wider photon energy variations.

The present results are qualitatively similar to the previous study of methyl oxirane [2]: the sign of the b_1 parameters of the three electronic states were well reproduced. We extended our measurements for the finer intervals of the photon energy to examine the

energy-dependence of PECD. A faint feature of the sign change of PECD with the varied photon energy was found in the second band, which is more visible in the polar representation of the observed results (Fig. 1. lower). These results will be verified in comparison with theoretical calculations.



Fig. 1. (Upper) Difference images of photoelectron scattering with left-hand and right-hand circularly polarizations and (Lower) the polar plot presentations of PECD of S-methyl oxirane at varied photon energies.

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BL1U

Photoionization of Atoms by Double-pulsed Radiation from a Tandem-Undulator

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Recently, we have shown a new ability of a tandemundulator in a synchrotron to perform wave packet interferometry using double-pulsed light wave packets. This has enabled the quantum manipulation of the atomic system, so-called coherent control, by synchrotron radiation. The potential of this method has been demonstrated in the proof-of-principle experiments on gas-phase atoms [1-3]. In these experiments, we used a double-pulsed light wave packet to produce a pair of electron wave packets (superposition of eigenstates) that interfere in the single atom. The quantum phase difference between the interfering electron wave packets determines the behavior of the quantum state to be controlled or probed, and is precisely controlled by varying the time delay between the double-pulsed components of light wave packet in the attosecond level.

Here, we extend this approach to the electron wave packets produced in an ionization continuum. The experiment was carried out at the undulator beamline BL1U. The double-pulsed light wave packet was generated by a tandem-undulator in the synchrotron ring. The waveform of the light wave packet was characterized by time-separated 10-cycle oscillations. The fundamental radiation wavelength was set to ~40 nm. The double-pulsed light wave packet interacted with a helium atom, leading to the production of a pair of photoelectron wave packets that interfere in free space. To verify the interference between the photoelectron wave packets, we measured a photoelectron spectrum using a hemispherical electron analyzer fixed at an angle of 55° with respect to the polarization axis.

Figure 1 compares the photoelectron spectra measured for the radiation from a single undulator (\mathbf{a} and \mathbf{b}) and tandem-undulator (\mathbf{c} and \mathbf{d}) configuration. The photoelectron spectra in \mathbf{a} and \mathbf{b} show single peaked distributions centered at around 5 eV. This spectral shape simply reflects the spectral distribution of the radiation from the single undulator which is characterized by a Gaussian-like distribution with 10 % width of the central photon energy. In contrast, the photoelectron spectra show clear interference patterns when the tandem undulator is used to ionize the helium atoms. Moreover, the spacing between interfering fringes depends on the time separation between the doublepulsed components of the light wave packet. To interpret the experimentally measured data, we have calculated the photoelectron spectrum (not shown here), and a good agreement between the experimental and calculation results is obtained. Therefore, it is reasonable to conclude that we observed the interference between the photoelectron wave packets in the present study.



Fig. 1. Photoelectron spectra of helium atoms measured by using radiation from (a) upstream undulator, (b) downstream undulator, (c) and (d) tandem undulator. The time delays between the double-pulsed components of light wave packet are (c) 2 fs and (d) 4.5 fs.

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Electronic State Changes of Cu Nanoparticles on Rutile TiO₂(110) by CO Exposure

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For Cu based catalysts, it exhibits strong catalytic activities for the carbon monoxide oxidation, water-gas shift reaction, methanol oxidation and others [1]. However, their performance is not fully understood. In previous study, we have found the growth mode of Cu nanoparticles deposited on the rutile $TiO_2(110)$ surfaces by medium energy ion scattering (MEIS) [2]. As a result, the two-dimensional (2D) islands grow initially up to Cu coverage of ~0.5 ML and then the three-dimensional (3D) island-growth becomes dominant. The electronic state of supported metal particles is also known to play a critical role in determining catalytic activity. Understanding the adsorbate-induced changes in the surface electronic state is therefore important. In this study, we manifest the reaction of Cu nanoparticles supported rutile $TiO_2(110)$ with carbon monoxide by photoelectron and photon-induced secondary electrons emission spectroscopy.

The experiment was performed at beamline BL2B of the UVSOR synchrotron factory at the Institute for Molecular Science. We prepared the oxygen-rich rutile TiO₂(110) surfaces (O-TiO₂) by exposure of O₂ (5 N) onto the reduced surfaces (R-TiO₂), which were formed by sputtering with 0.75 keV Ar⁺ followed by annealing at 870 K for 10 min in UHV. Cu was deposited on the clean surfaces at RT with a Knudsen cell at a rate of 0.08 ML/min under UHV condition. Here, 1 ML means 1.77×10^{15} atoms/cm², corresponding to the areal density of Cu(111).

Figure 1 (a) shows secondary electron spectra taken for Cu(0.2 ML)/O-TiO₂(110) and oxidized Cu(0.2 ML)/O-TiO₂(110) before and after CO exposure, respectively. After O₂ exposure of 500 L, the work function increases. This electronic state changes indicate an upward band bending. The mechanism of this upward band bending may be considered as follows: Cu nanoparticles are oxidized to Cu₂O by oxygen exposure and then the upward band bending is caused by a p-n junction between Cu₂O and TiO₂ substrate. After CO exposure of 15,000 L, the work function slightly decreased, while the valence band spectra and Ti 3p and O 2s lines did not change nor shift significantly (not shown). The change in work function showed the same tendency even for Cu coverage of 1.0 ML [see Fig.1 (b)]. The work function of TiO₂(110) surfaces scatter largely owing to strong dependence upon bulk and surface defect densities. Note that work function consists of bulk and surface dipole terms and the surface term originates from a surface dipole consisting of positive

cores and valence electrons near a surface. Therefore, this result is ascribed to elimination of the electronegative adsorbate oxygen on top of the surface resulting in weakening the surface dipole with a negative polarity on the vacuum side. These results may suggest that presence of Cu nanoparticles on O-TiO₂(110) strongly enhances the reaction between O and CO.



Fig. 1 Secondary electron spectra taken for (a) Cu(0.2 ML)/O-TiO₂(110) and (b) Cu(1.0 ML)/O-TiO₂(110) before and after CO expos

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X-ray Absorption Spectra of Aqueous Cellobiose

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Biomass conversion using water or an ionic liquid as a solvent without using an organic solvent is an important research topic. There have been many studies on biomass-related compounds in solution, but there are few reports on their molecular theory. We have studied the conversion process by dehydration reaction of polyalcohol as models of sugar molecules and found that the solvation structure with water molecules and the interaction with protons are important for the reaction process [1,2].

The purpose of this study is to explore the solvation structure of sugar molecules in aqueous solution, which is important in the conversion process from cellobiose to glucose, that is typical of biomass-derived sugar alcohol conversion using water or ionic liquids. Cellobiose, a disaccharide, is taken up as a model substance for cellulose, which is one of the starting materials in biomass conversion.

XAS measurements for liquid samples were conducted at UVSOR BL3U using facilities developed by Nagasaka et al. [3]. The liquid sample cell with Si₃N₄ membranes was adopted, where the thickness of the liquid layer was controlled by the He gas pressure around the cell.

Figure 1 shows C-K edge XAS spectra for cellobiose aqueous solutions with concentrations specified in the figure. Fig. 2 shows O-K edge XAS spectra for cellobiose aqueous solutions as well as the spectrum for water (0 M). Molecular dynamics calculations for the solutions and the XAS simulations were conducted using CP2K program to interpret the XAS spectra.

In Fig. 1 three peaks were observed at 289.3, 290.7 and 293.6 eV, named as "A", "B", and "C", respectively. A peak at 290.0 eV was defined as "A", which does not appear for the aqueous solution but is expected to appear in the gaseous isolated cellobiose molecule as found by MD and XAS simulation. With the XAS simulation it was concluded that A, B and C correspond to the absorption by carbon atoms of the alcohol group, the hemiacetal group and the both of these groups, respectively. Temperature and concentration dependences of XAS spectra for cellobise aqueous solutions were measured and relative intensity change of three peaks were observed, which can be explained by the change in the number of hydrogen bond between cellobiose and water. These results were published recently [4]. The analysis of O-K XAS spectra for cellobiose aqueous solutions is under way.



Fig. 1. C-K XAS spectra for cellobiose aqueous solutions at 25 °C. Blue : 0.20 M, Green : 0.15 M.



Fig. 2. O-K XAS spectra for cellobiose aqueous solutions at 25° C. Blue : 0 M, Purple : 0.20 M, Green : 0.05 M.

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X-ray Absorption Spectroscopy Study of 4-MBA on Gold Surfaces

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It is important to understand the behavior of biomolecules on solid surfaces for the application to medical device, biosensor and biocompatible material. It is essential to study the adsorption and desorption behavior of molecules and their response to the applied fields. It is of particular importance to analyze the dynamic behavior of biomolecules on surface in electrolyte solutions close to the realistic condition in the body of living creatures [1,2]. However, the number of studies appears to be still quite limited, especially for the investigation of the dependence of the molecular orientation and ionization on the electrolyte solutions.

In this study, potential-dependent adsorption/desorption behavior of 4-mercaptobenzoic acid (4-MBA) on Au(111) and Au membrane surfaces have been investigated using soft X-ray absorption spectroscopy (XAS) in the fluorescence yield mode for the former case, and in the transmission mode in the latter case. The experiments were performed on the soft X-ray undulator beam line at UVSOR-III, BL3U. We used NaClO₄ as the electrolyte solution. For the adsorption of 4-MBA molecules, the samples were immersed in 1mM 4-MBA/ethanol solution for more than 30 min.

In our previous study, we have studied the adsorption/desorption behavior of 4-MBA on Au films using surface differential reflectance spectroscopy (SDRS) combined with cyclic voltammetry (CV) [3]. The key issue was the interaction between functional group (-COOH) and Au films through Coulomb interaction depending on the applied biases and pH conditions. Redox processes involving charge transfer were clearly observed CV and the relation between the change in the reflectance spectra were investigated in detail. Interestingly, we found some precursor phenomena to cause significant changes in the reflectance spectra with no corresponding signal in the cyclic voltammogram. This indicates that the such changes in the reflectance spectra are not related to the charge-transfer-type reactions but rather to the subtle change in the orientation/conformation of 4-MBA molecules.

To our knowledge, there has been no serious effort to study the 4-MBA/Au system using XAS. We, therefore, tried to investigate the possible precursor phenomena addressed above. Firstly, we have tried to observe the effects on Au(111). However, we could not obtain the clear data showing the adsorption/desorption behavior of 4-MBA. This could be understood because of the relatively low signal-to-noise ratio in the fluorescence yield mode, and the amount of the adsorbed 4-MBA might be less than the detection limit. In order to improve the surface sensitivity, we next tried to observe the effects on membrane Au surface.

Our preliminary results showed clear spectral features in the O K-edge region, as shown in Fig. 1. One is due to the π^* component assigned to the C=O double bond, and the other is possibly due to the formation of the hydrogen bond. The investigation of the C K-edge region is underway.

The next step should be the observation of the slight effects due to the change in the orientation/conformation depending on the applied bias to the electrode (Au membrane). Obviously, we have to conduct the surfacesensitive measurements further to elucidate such subtle effects.

It should be noted that more distinct change in the XAS spectra can be envisioned in the case of cysteine molecules, for which two of them can attach to form a cystine molecule [3]. At this point, we have established the measurement set up for the transmission mode. Therefore, we now also plan to re-investigate the reactions of biomolecules, in terms of the ionization of the functional groups (-COOH, -NH₃).



Fig. 1. O K-edge XAS spectrum for 4-MB.

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Resonant Soft X-ray Scattering Equipment Evaluated by Chicken Leg's Collagens and 100-nm Silica Nanoparticles

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Resonant Soft X-ray Scattering (RSoXS) is similar to Small Angle X-ray Scattering (SAXS) and can provide information on the mesoscopic structure $(1 \sim 100 \text{ nm})$ of samples. Due to the resonance process, RSoXS have selectivities of elements, functional groups and molecular orientations. In particular, since soft x-ray region include K-edge energies of light element such as carbon, nitrogen and oxygen, RSoXS will be a powerful tool to investigate soft matter, which mainly consists on light element atoms. In 2020, we started to develop RSoXS equipments and succeeded in characterizing liquid-crystal materials. To improve an accuracy of our RSoXS equipments, we measured chicken collagen and silica nanoparticles as standard substances.

Our RSoXS measurements were performed at UVSOR BL3U. Figure 1 shows a schematic draw of an experimental setup. Samples of chicken leg's collagen and 100nm-silica nanoparticle were fixed on Si_3N_4 membranes. The photon energy is 284 eV. Scattering light were detected by soft x-ray camera (Andor BN940P). This RSoXS equipment covers scattering angles, 2 θ , ranging from 0 to 15°.

Figure 2(a) shows a scattering image of the chicken leg's collagens. We find three weak ring structures. From the image, we obtained a scattering intensity as a function of scattering vector, q, which are shown in Fig. 2(b). Three peaks at $q = 0.105, 0.212, 0.320 \text{ nm}^{-1}$ indicates that the sample of the chicken collagen have periodic structure of 59.3 nm, which is slightly different from the reference value of 63.8 nm.

Figure 3(a) shows a scattering image of 100-nm (diameter) silica nanoparticles. We find striped ring structures. From the image, we also obtained a scattering intensity as a function of scattering vector, q. As shown in Fig. 3(b), we find oscillation structures. By using theoretical equation of a scattering intensity for spherical sample, we fitted experimental curves with those of the 110-nm nanoparticle.

Thus experimental results are slightly different from actual values, suggesting that we need the standard sample for calibrations of our RSoXS equipment.



Fig. 1. Schematic view of our RSoXS equipment.



Fig. 2 (a) Scattering image of chicken leg's collagens. The color scale is a log scale. (b) Scattering intensity as a function of scattering vector, q.



Fig. 3 (a) Scattering image of 100-nm silica nanoparticles. The color scale is a log scale. (b) Scattering intensity as a function of scattering vector, q. Red and blue lines are experimental and theoretical one, respectively.

Oxygen K-edge X-ray Absorption Spectroscopy of Aqueous Dimethyl Sulfoxide Solutions at Different Concentrations

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Dimethyl sulfoxide (DMSO) is a widely used cosolvent, and aqueous DMSO solutions show numerous physical properties that show maxima or minima in the middle concentration region [1]. Several studies determined microscopic structures of aqueous DMSO solutions, where hydrogen bond (HB) structures of S=O groups in DMSO with water are formed and are changed at different molar fractions [2]. However, the mechanism of the HB formation of DMSO with water have not fully understood. In this study, we have studied the concentration dependence of the HB structures of DMSO with water in aqueous solutions by using O K-edge X-ray absorption spectroscopy (XAS).

The experiments were performed at soft X-ray beamline BL3U. O K-edge XAS of aqueous DMSO solutions were measured by using a transmission-type liquid flow cell [3]. Liquid samples are exchanged by a tubing pump without changing the beam positions.

Figure 1 shows O K-edge XAS spectra of aqueous DMSO solutions $(DMSO)_x(H_2O)_{1-x}$ at different concentrations at 25 °C. In O K-edge XAS of neat water (x = 0.0), the pre-edge peak at 535 eV is assigned as the transition of O 1s electron to the 4a₁ unoccupied orbital in water and reflects HB structures among water molecules, as observed in O K-edge XAS of liquid water at different temperatures [4]. On the other hand, the peak at 532 eV corresponds to the transition of O 1s electron to the S=O π^* orbital in DMSO [5]. From the fitting procedures, we have determined the energy shifts of the pre-edge peaks in water and the first peaks of S=O π^* orbitals in DMSO at the different molar fractions of DMSO.

Figure 2 shows the energy shifts of the first peaks of DMSO S=O π^* orbitals from that of neat DMSO (x = 1.0). By increasing the molar fraction of water (1 - x), the S=O π^* peaks show the higher energy shifts, which shows two concentration regions with the border of x= 0.4. In the DMSO-rich region (0.4 < x < 1.0), the slope of the energy shift is 164 meV / (1 - x). In the water-rich region (0.05 < x < 0.4), on the other hand, the higher energy shift of the S=O π^* peak is accelerated (271 meV / (1 - x)). The pre-edge peaks in water also show characteristic concentration dependence, which shows three concentration regions with the borders of x = 0.2 and x = 0.6. For revealing the concentration dependence of the energy shifts in O Kedge XAS, we will perform molecular dynamics simulations and inner-shell quantum chemical calculations of aqueous DMSO solutions.



Fig. 1. O K-edge XAS spectra of aqueous DMSO solutions at different concentrations.



Fig. 2. Energy shifts of the first peaks of DMSO S=O π^* orbitals from that of neat DMSO (x = 1.0) as a function of molar fraction of DMSO.

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II -3. Chemistry

BL3U

Carbon K-edge X-ray Absorption Spectroscopy of Aqueous Ethanol Solutions at Different Concentrations

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Aqueous ethanol (EtOH) solutions show anomalies of thermodynamic and transport properties [1]. These anomalies would be occurred by the intermolecular interactions between EtOH and water (H_2O). In the previous studies, it is suggested that the EtOH- H_2O mixed clusters are formed in the middle concentration region [2] and the hydrophobic hydration of EtOH is formed in the low concentration region [3]. In this study, we have investigated the local structures around the ethyl group in EtOH by using carbon K-edge X-ray absorption spectroscopy (XAS) of aqueous EtOH solutions at different concentrations.

The experiments were performed at soft X-ray beamline BL3U. C K-edge XAS of aqueous EtOH solutions were measured by using a transmission-type liquid flow cell [4]. Liquid samples are exchanged by a tubing pump without changing the beam positions.

Figure 1(a) shows C K-edge XAS spectra of aqueous EtOH solutions at different concentrations at 25 °C. Each spectrum is fitted by four peaks, where peak A is the lowest peak around 287.3 eV. Figure 1(b) shows the energy shifts of peak A relative to that of liquid EtOH (x = 1.0) as a function of the molar fraction of EtOH (x). We have found that the energy shift of peak A shows four concentration regions (I, II, III, and IV). In the region I (1.0 > x > 0.8), peak A shows the lower energy shift by increasing the molar fraction of H₂O. In the region II (0.8 > x > 0.25), peak A shows the slightly higher energy shift by increasing the molar fraction of H₂O. The lower energy shift of peak A is observed in the region III (0.25 > x > 0.15)and is accelerated by increasing the molar fraction of H₂O in the region IV (0.15 > x > 0.05).

From the inner-shell quantum calculations, we have investigated the molecular interaction between EtOH and H₂O at the four concentration regions. In the region I, the hydrogen bond (HB) structure of EtOH – EtOH is simply substituted to that of EtOH – H₂O. In the region II, the EtOH clusters are formed by the hydrophobic interactions of the ethyl group in EtOH, resulting in the enhancement of the HB structure of H2O - H2O as observed by O K-edge XAS [5]. Whereas a phasetransition like behavior is observed in aqueous methanol solutions [6], there is no phase-transition like behavior in aqueous EtOH solutions due to the strong hydrophobic interactions in EtOH. In the regions III and IV, the size of EtOH clusters becomes smaller, resulting in the increase of the hydrophobic hydration of EtOH in the HB network of H₂O.



Fig. 1. (a) C K-edge XAS spectra of aqueous EtOH solutions at different concentrations. (b) Energy shifts of peak A relative to that of liquid EtOH (x = 1.0) as a function of molar fraction of EtOH (x).

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The C–Si Bond Length of Organosilicon Compounds in Organic Solvent Probed by Carbon K-edge X-ray Absorption Spectroscopy

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Although the reactivity of organic compounds is closely related to the bond length at the reactive site, it is difficult to know the bond length in organic solvents experimentally. Soft X-ray absorption spectroscopy (XAS) has a potential to determine the chemical bond since soft X-ray XAS observes electronic structures of light elements such as C, N, O, etc. Recently, we have developed liquid flow cells for XAS in transmission mode [1]. Hydration of cyanopyrazine on titanium oxide catalysts has been studied by C K-edge XAS, but this study only observed the reaction kinetics [2]. It is still difficult to reveal the relation of the bond length at the reactive site with the reactivity by soft X-ray XAS. In this study, we have investigated the C-Si bond lengths of the organosilicon compounds in organic solvents, which are key compounds for the Hiyama cross-coupling reaction [3], by using C K-edge XAS.

The experiments were performed at soft X-ray beamline BL3U. C K-edge XAS of the organosilicon compounds in organic solvents were measured by using a transmission-type liquid flow cell [1]. The liquid samples were prepared in argon filled glovebox and were flown to the liquid cell by using a syringe pump. Liquid temperature was set to 25 °C.

Figure 1 shows the C K-edge XAS spectra of 100 mM trimethoxy(phenyl)silane (1) in tetrahydrofuran (THF), ethylene glycol-derived pentacoordinate spirosilicate (2) in ethylene glycol, and fluorotrimethoxy(phenyl) silicate (3) in THF solution. The peak around 285 eV in silane 1 is assigned as the transition from the C1s orbital to the C=C π^* unoccupied orbital in the phenyl group. This peak is fitted by three peaks: Peak A is the transition from the C atom bonded with Si, peak B is that from the ortho sites, and peak C is that from the meta sites in the phenyl group. It means that peak A reflects the C-Si bond lengths of the organosilicon compounds. The energy position of peak A in silane 1 is 284.56 eV. The peak A in silicates 2 and 3 show lower energy shifts by -0.02 eV and -0.06 eV from that in silane 1, respectively. We have performed the structural optimization of these organosilicon compounds by the quantum chemical calculations and found that the C-Si bond length becomes longer with the order of compounds 1, 2, and 3. C K-edge inner-shell calculations revealed that the peak A shows lower energy shifts by increasing the C-Si bond lengths. These results are consistent with the experiments. Therefore, it is revealed that due to the longer C-Si bond of silicate 2, it showed the higher reactivity in the Hiyama cross-coupling reaction than that of silane 1. On the other hand, the reactivity of silicate 3 was lower than that of silane 1 despite the longest C–Si bond length [4]. The inertness of silicate 3 would be caused by other factors such as a steric barrier, which is now investigating by the quantum calculation of the transition state in the reaction.



Fig. 1. C K-edge XAS spectra of compounds 1, 2, and 3 in THF or ethylene glycol. Dashed lines show the peak positions of silane 1 obtained by curve fitting procedures.

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Direct Observation of a High Valent Oxo Species of a µ-Nitrido-Bridged Iron Phthalocyanine Dimer Deposited on a Graphite Surface in Aqueous Solution by Soft X-ray Absorption Spectroscopy

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Methane is abundant in nature as natural gas or methane hydrate. Therefore, efficient conversion of methane into valuable raw chemicals such as methanol is highly desired in order to use methane as a nextgeneration carbon resource. However, since high chemical stability of methane prevent its efficient C-H bond activation, development of novel catalysts that allow facile C-H bond dissociation of methane under mild reaction condition is indispensable. We recently found that a µ-nitrido-bridged iron phthalocyanine dimer adsorbed on a graphite surface 1 (Fig. 1) efficiently convert methane into methanol, formaldehyde, and formic acid in an acidic aqueous solution containing H₂O₂ at a temperature below than 100 °C. It was demonstrated that 1 showed one of the most potent methane oxidation activity among a variety of molecule-based catalysts and its activity was almost comparable as that of natural particulate methane monooxgenase (pMMO)[1]. Although it's reactive intermediate was confirmed to be a high valent iron-oxo species 1_{0x0} generated by the reaction with H_2O_2 , the electronic structure of 1_{0x0} has never been investigated. In our previous report, we confirmed that it is possible to observe 1_{0x0} directly by XAS under vacuum by using a highly oriented pyrolytic graphite (HOPG) substrate modified with the µ-nitrido-bridged iron phthalocyanine dimer. In this study, we attempted to observe the conversion of 1 into 1_{0x0} in an aqueous solution by using XAS.

We first prepared a SiN membrane tip modified by 1 (Fig. 2a). A SiN membrane tip coated by 20 nm thickness of carbon membrane was dipped in a pyridine solution of the μ -nitrido-bridged iron phthalocyanine dimer. It was confirmed that the μ nitrido-bridged iron phthalocyanine dimer was successfully deposited on the carbon surface of the SiN membrane tip by detecting the Fe L-edge XAS signals.

The SiN substrate modified with **1** was used for the XAS measurement in an aqueous solution by using a beamline equipped with a transmission-type liquid flow cell in BL3U of UVSOR [2]. The O K-edge XAS spectra of **1**_{0x0} formed by the reaction with H₂O₂ were obtained by using the Lambert-Beer law, $\ln(I_0/I)$, where I_0 and I are the transmission signals of **1** in pure water and **1** in a 0.5 % H₂O₂ aqueous solution, respectively.

It was found that the peak at around 532.5 eV was significantly increased after treatment with H_2O_2 (Fig. 2b). DFT calculation suggested that the peak assignable

to the excitation of $O1s - \pi^*$ of Fe=O for 1_{0x0} should be observed at around 529 eV (Fig. 2c), whereas the peaks for 1 having a coordinating H₂O should be observed at higher energy than 534 eV as shown in Fig. 2d (Fig. 2d). Therefore, it is considered that the peak appeared at around 532.5 eV is assignable to the excitation of O1s - π^* of Fe=O for 1_{0x0} . Next, we are going to observe the electrochemically generated 1_{0x0} in H₂O.



Fig. 1. Potent methane oxidation catalyst 1 and its reactive species 1_{0x0} .



Fig. 2. (a) Structure of a SiN tip coated with 1, (b) Comparison of O K-edge XAS spectra of 1 before and after treatment with H_2O_2 . DFT-calculated O K-edge XAS spectra for 1_{0x0} (c) and $1(OH_2)$ (d).

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Soft X-ray Absorption of Photocatalysts for Artificial Photosynthesis: A Feasibility Study under Ultraviolet Light Irradiation

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Sodium tantalate (NaTaO₃) is a semiconductor photocatalysts which produces hydrogen–oxygen mixed bubbles in the overall water splitting reaction, when properly doped with metal cations [1]. We are conducting a series of studies to answer the question of why doping with metal cations raised the quantum yield of the reaction. Here, soft X-ray absorption is applied for characterizing the electronic structure of the photocatalysts in the presence and absence of ultraviolet (UV) light for bandgap excitation.

NaTaO₃ particles doped with and without Sr cations were prepared thorough a solid-state reaction. Oxygen K-edge absorption of the particles was observed in vacuum at room temperature with total electron yield. Figure 1 shows the spectra of the pristine, undoped particles.

The spectrum in the absence of UV light was well fitted with three Gaussian functions peaked at 531.8, 532.8, and 537.2 eV (upper panel). The first and second peaks were assigned to electron transition from oxygen 1s to 2p states which were covalently hybridized with t_{2g} states of Ta 5d orbitals. The third peak present at a larger photon energy was assigned to the transition to oxygen 2p states hybridized with e_g states of the Ta orbitals. NaTaO₃ is a perovskite-structured compound involves TaO₆ octahedra, which provide the 5d orbitals split into t_{2g} and e_g states.

When the photocatalyst particles were irradiated with steady UV light produced by a 200-W Hg–Xe lamp, absorption related to the t_{2g} final states, the first peak at 531.8 eV in particular, weakened relative to the third peak, as presented in the lower panel of Fig. 1. A possible reason of the weakened absorption is the conduction band partially filled with bandgap-excited electrons. The density of vacant states, the final states of the K-edge absorption, should have decreased by the electrons excited from the valence band. Covalent hybridization of the oxygen 2p and Ta 5d orbitals would also be limited to weaken 5d-states character of the final states [2], since the oxidation state of Ta cations decreased from +5 to 4+ by the bandgap excitation.



Fig. 1. Oxygen K-edge absorption spectra of pristine NaTaO₃ photocatalyst particles observed in the absence (upper panel) and presence (lower panel) of UV light for bandgap excitation. The observed spectra (black curves) were fitted with Gaussian functions (red curves). The spectra reconstructed with the functions (blue curves) are shown with residuals (thin black curves at the top).

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III -3. Chemistry

Variation of the Resonance Band of Water in Soft X-Ray Absorption Spectra of Aqueous Acetone Solutions

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Acetone is miscible with water in any ratio. The binary mixture is a typical aprotic-protic solvent system [1]. A role of the acetone molecule acting as a hydrogenbond acceptor adds characteristic properties of water. For instance, the partial molar volume of water in this mixture is 14.25 cm³/mol at 25 °C [2], which is much less than the molar volume of water. Such specific water molecules have a different electronic structure from that of bulk water. The study of the electronic structure of hydrated water is of essential importance because it provides fundamental information on the structure of aqueous solutions in general (e.g., [3]). In this report the O K-edge absorption spectra with various fractions of acetone are recorded for extracting the hydrated water components through an excess function: We expect that there exists some correlation between the hydration and a deviation from Beer's law at some photon energy.

Photoabsorption spectra of the solutions were measured in the oxygen K-edge region on the soft X-ray beamline, BL3U. A pair of windows made of thin silicon nitride membrane was used for the sample cell. The incident photon energy was calibrated to the peak at 530.88 eV of a polymer film [4]. The absorption coefficient was evaluated so as to match the value at 547.85 eV to that tabulated in the database [5]. The sample solutions were prepared by mixing acetone with purified water to give 0–0.50 molar fractions of acetone.

Distinct features are found in the absorption spectra. Figure 1 displays some of the measured absorption spectra of water and aqueous acetone solutions. The π^* resonance peak of acetone located at 531.13 eV for pure liquid is now observed at 531.33 eV for the solution with the molar fraction of acetone of 0.10. The shift depends non-linearly on the molar fraction: The change is larger for a dilute region. The 4a₁ resonance band of water has a peak at 534.56 eV for pure water and at 534.46 eV for the 1:1 molar mixture (not shown in Fig. 1). The change around the molar fraction of 0.25 is noticeable, indicating a greater change in the electronic structure of water around this concentration. Apparent bathochromic shift (or red shift) of the latter resonance peak is reasonable on the basis of chemical shift because the water molecule gets electron-rich if it receives electrons from the carbonyl oxygen of the acetone molecule. One can safely conclude that the absorption component of the hydrated water is embedded in the lower energy side of the band and is

assigned to the resonance transition of water acting as a hydrogen-bond donor.

Further discussion requires a quantitative analysis of the spectra. Additivity of Beer's absorption law is valid for non-interacting mixtures. Conversely, a deviation from the absorption law indicates an extent of interaction between the components. The deviation is expressed as the excess absorbance. The results of the analysis will be published elsewhere.



Fig. 1. The O K-edge absorption spectra of liquid water and aqueous acetone solutions measured for a series of molar fractions of acetone.

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Oxygen K-edge X-ray Absorption Spectroscopy of Molecular Oxygen Adsorbed on Lipid Bilayers

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Some porphyrin complexes, such as the photosynthetic pigment chlorophyll, are known to produce singlet oxygen $({}^{1}O_{2})$ by transferring energy to oxygen molecules that is triplet oxygen $({}^{3}O_{2})$ in the surrounding environment at the photo-excitation and relaxation processes due to light absorption. Singlet oxygen is high-reactive. It can cause damage to biological cells or the sample itself in spectroscopic experiments. In generally, the sample solution is bubbled with argon gas to displace the dissolved oxygen to avoid the generation of singlet oxygen at the measurement of a spectrum in visible right region. On the other hand, the process of singlet oxygen generation accompanying with photoexcitation and relaxation processes of photosensitizers such as porphyrin complexes is applied in cancer treatment as photodynamic therapy [1]. Elucidating the dynamics of singlet oxygen production in such a wet environment is expected to contribute to further research of chemistry and medicine.

We designed the way to measure directly the electric states of singlet oxygen occurred in solution by O Kedge x-ray absorption spectroscopy (XAS). Timeresolved XAS measurement system with synchronized soft X-rays pulse (530 eV, 128 ps) and visible laser pulses (400 nm, 130 fs) have been developed and will be applied. The lifetime of singlet oxygen in liquid is 3 μ s [2], which can be measured with the 128 ps time resolution of synchrotron radiation. In this measurement, a method to measure a dissolved oxygen spectrum was established as a preliminary step for XAS measurements of singlet oxygen.

The XAS spectrum was measured by using the solution XAS measurement system at UVSOR BL3U [3]. The liquid cell consists of a solution layer sandwiched between two Si_3N_4 membranes. Lipid bilayers ware formed on Si_3N_4 membranes by pumping the lipids vesicle aqueous solution to flow into the liquid cell. Then, dissolved oxygen was kept on the lipid bilayers by continuously pumping the buffer solution (NaCl 100 mM, HEPES 25 mM) bubbled with oxygen gas at a flow rate of 100 µl/hr. By increasing the helium pressure in the sample chamber and making the solution layer as thin as possible, the spectrum that has the emphasized peak of dissolved oxygen on the lipid bilayer was measured. In the measurement of singlet oxygen, chlorophyll *a*, added as a photosensitizer to the

lipid bilayer, is photoexcited by visible laser with 400 nm which is SH (second order harmonic) of Ti:sapphire laser. We are planning to measure an O K-edge XAS spectrum of the singlet oxygen produced by the energy transfer at the relaxation process of the photo-excited triplet state of chlorophyll *a*.

Figure 1 shows the O K-edge XAS spectrum of liquid bilayer measured in this experiment. The peak at around 531 eV corresponds to dissolved oxygen absorbed on lipid bilayer which is in the ground state. Since the O K-edge XAS spectrum of water is in higher energy region than 533 eV, the spectrum of dissolved oxygen can be clearly distinguished.



Fig. 1. The O K-edge XAS spectrum of the lipid bilayer. The peak around 531 eV corresponds to a peak of dissolved oxygen absorbed on the lipid bilayer.

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II -3. Chemistry

BL4U

Position-Sensitive Soft X-ray Absorption Spectroscopy of Carbon-based Catalysts for Redox Flow Battery

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Utilization of renewable energy such as solar cell and wind power is indispensable for reduction of CO2 emission and realizing zero emission society. To stably use the renewable energy in practical use, development of large-scale energy storage devices is needed. Redox flow battery (RFB) is one of the candidates [1] as well as Li-ion battery (LIB).

The electrolyte solutions of RFB play a role on the redox reaction as both positive and negative electrodes (i.e., catholyte and anolyte) (Fig. 1), which is different from LIB where the solid-state electrodes (cathode and anode) exhibit the redox reaction. The carbon-based electrodes are soaked in electrolyte solutions and H⁺ in the solutions can move through an ion-exchange membrane between the two electrodes by charge/discharge (Fig. 1). To raise the efficiency of the redox and H⁺ conduction, the performance of carbonbased catalysts combined with the electrodes should be investigated. Electronic-structure analysis using soft X-ray absorption spectroscopy (XAS) is suitable for studying the performance. Then, scanning transmission X-ray microscopy (STXM) provides not only the information of electronic structure, but also its distribution with a high spatial resolution (<100 nm). Thus, we adopted STXM at the C K-edge to carbonbased catalysts for RFB. The STXM measurements were conducted at BL4U, UVSOR.

Figure 2 shows a pinpoint C *K*-edge absorption spectrum (in transmission mode) of a selected area for a graphene sample. The peaks at 285.4 and 291.8 eV in Fig. 2 correspond to π^* and σ^* peaks, respectively [2,3,4]. The weak π^* peak compared to the σ^* peak is similar to the spectrum for graphite with normal incidence [2,3], which suggests that the graphene layers stack along the X-rays. Almost all the area of the graphene particle in the STXM image showed similar XAS line shape. This is important information because the catalytic performance would be dependent on the orientation of stacking. Furthermore, the spectrum shows no peak between the π^* and σ^* peaks, indicating almost no contamination.

In future, we will try *in situ/operando* STXM by constructing a special cell for RFB.



Fig. 1. A schematic picture of RFB using vanadium.



Fig. 2. A pinpoint C *K*-edge XAS spectrum of a specific area (\sim 350 nm × \sim 180 nm) of the graphene sample.

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BL4U

Investigating Electrochemical Reactivity on Ni(OH)₂ Electrocatalyst in Alkaline Electrolytes

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During the electrochemical reaction, the phase transformation of energy storage/conversion materials accompanies intrinsic variation on physico-chemical properties. In particular, the energy conversion materials (catalysts) in aqueous system suffer severe chemical and/or morphological changes during reaction. [1] These changes are governed by the thermodynamics that the material exists as a possible stable phase according to pH or potential. In dynamic condition, the locally generated chemical equilibrium induces the evolution of electrochemical active phase in nanoscale, which are responsible for electro- catalytic activity and stability.

Among various energy conversion materials, Ni(OH)₂, which exhibits superior oxygen evolution reaction (OER) activity, experience multiple phase transformation via dehydrogenation process during OER. [2] Specifically, as hydrogen atom is extracted from the lattice, β -Ni(OH)₂ (Ni²⁺) can convert to more oxidized phase such as β -NiOOH (Ni³⁺) and γ -NiOOH (Ni^{3.6+}), and the OER activity is highly dependent on these high valence state of Ni phases. Additionally, lattice oxygen atoms also play an important role in the OER due to bond formation /breaking process with active metal site. An understanding of the active phase evolution and the coordination of oxygen atom with active metal site is a fundamental prerequisite for designing improved OER catalysts, but it remains a crucial challenge to identify the generation and evolution of nanoscale active phase spatially due to a lack of characterization technique. To investigate the evolution of OER active phase (β -NiOOH or γ -NiOOH), we implemented operando scanning transmission X-ray microscopy (STXM) to track the change in Ni oxidation state that indicates the phase transformation of Ni(OH)2 during OER at the Pohang Light Source STXM beamline 10A1.

Distinctive feature in the phase transformation of β -Ni(OH)₂ is that Ni^{3.6+} phases, γ -NiOOH at 1.70 V versus reversible hydrogen electrode (RHE), are reduced at 1.8 V and 1.9 V versus RHE, where OER is highly occurred. (Fig. 1) From this observation, we speculate that there are two possibilities. First, potassium ion (K⁺) in electrolyte could intercalate into the slab, leading to reduction of the Ni oxidation state owing to the charge neutrality. [2] Second, during OER, oxygen vacancies are generated in the catalyst. [3] To confirm the generation of oxygen vacancies in high anodic potential region, we conducted ex situ STXM measurement of β -

 $Ni(OH)_2$ at UVSOR BL4U for investigating the change in O K-edge absorption spectra.

Figure 2a shows particle-averaged O K-edge spectra of β -Ni(OH)₂ at different potentials, revealing that the pre-peak A (532 eV), assigned to the hybridization of Ni 3d and O 2p orbitals states with e_g orbital symmetry and the d₇ (Ni³⁺) electron configuration, is varied at different potentials. [3] In particular, the intensity of peak A suddenly decreases at 1.65 V, suggesting the return of electrons to Ni site. It can be attributed to the formation of oxygen vacancies and the decreased oxidation state of Ni site. From our results, we conclude that generation of the oxygen vacancy during OER could induce reduction of the active phase (γ -NiOOH), consistent with our operando STXM results.



Fig. 1. Operando chemical composition mapping images of β -Ni(OH)₂ electrocatalyst during OER. (Unpublished)



Fig. 1. a. Voltage-dependent particle-averaged O Kedge STXM-XAS spectra. b. Intensity of peak A at different potentials.

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120

BL4B

Quadruple Auger Decay of the Xe 3d_{5/2} Core-Hole State Investigated by Multielectron–Ion Coincidence Spectroscopy

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Magnetic bottle electron spectrometer is a very efficient electron spectroscopic method, utilizing an inhomogeneous magnetic field to capture all the electrons formed by photoionization. Its use enables us to perform multielectron coincidence spectroscopy very effectively. While the electrons captured over 4π -steradian solid angle are guided to an MCP detector ending a long flight path, ions formed together with electrons can be also detected with the same detector, by applying a pulsed electric field to the photoionization region [1]. To improve the efficiency in multielectron-ion coincidence measurements, an MCP detector with a large open area ratio (nominally 90 %) was recently introduced in our magnetic bottle electron spectrometer [2].

The usefulness of this improved coincidence efficiency is demonstrated by a six-fold coincidence about the quadruple Auger decay of the Xe 3d_{5/2} corehole state. Figure 1 shows energy correlations between the two Auger electrons emitted from $Xe^{3+} 4d^{-2}5p^{-1}$. which was derived from six-fold coincidences including the 3d_{5/2} photoelectron, first-step Auger electron forming 4p⁻¹4d⁻¹, second-step Auger electron forming $4d^{-2}5p^{-1}$, and Xe⁵⁺. The additional coincidence with the product Xe⁵⁺ ions effectively isolates the events associated with the quadruple Auger decay. On the twodimensional map in Fig. 1, remarkable island structures are observed in the area indicated by a square. The faster and slower electrons forming the island structures are assignable to the third-step Auger decay of Xe3+ $4d^{-2}5p^{-1} \rightarrow Xe^{4+} \ 4d^{-1}5p^{-3}$ and the fourth-step Auger decay of $Xe^{4+} \ 4d^{-1}5p^{-3} \rightarrow Xe^{5+} \ 5p^{-5}$, respectively. Essentially the same coincidence structure was observed in a previous multi-electron coincidence measurement [3]. Note that the previous observation was occurred in correlations between two electrons observed in coincidence with the 3d photoelectron and first-step Auger electron, and thus as four-electron coincidences.

One may see that the island structures lie on several diagonal lines defined by x + y = constant. This is because the sums of the two Auger electrons correspond to the energy differences between $Xe^{3+} 4d^{-2}5p^{-1}$ and $Xe^{5+} 5p^{-5}$ levels. Here, the appearance of multiple diagonal lines is due to the contributions from different levels of initial $4d^{-2}5p^{-1}$ and final $5p^{-5}$. The right panel of this figure shows the projection of the island structures toward the y axis of the two-dimensional map. The projection curve exhibits sharp peaks due to the fourth-step Auger decay of $Xe^{4+} 4d^{-1}5p^{-3} \rightarrow Xe^{5+}5p^{-5}$. The kinetic energies of the sharp peaks correspond to

the state energies of the Xe⁴⁺ 4d⁻¹5p⁻³ levels measured from ²P_{1/2} or ²P_{3/2} of 5p⁻⁵, and thus many different Xe⁴⁺ 4d⁻¹5p⁻³ levels are formed through the third-step Auger decay of Xe³⁺ 4d⁻²5p⁻¹ \rightarrow Xe⁴⁺ 4d⁻¹5p⁻³.



Fig. 1. Energy correlation map between two Auger electrons ejected in the quadruple Auger decay of the Xe $3d_{5/2}$ core-hole state, derived from six-fold coincidences including the $3d_{5/2}$ photoelectron, first-step Auger electron forming $4p^{-1}4d^{-1}$, second-step Auger electron forming $4d^{-2}5p^{-1}$, and Xe⁵⁺ ion, and thus it displays the energy correlation between the two Auger electrons emitted in the decay of Xe³⁺ $4d^{-2}5p^{-1}$. The right panel plots the projection of the coincidence counts in the region x = 14-24 eV toward the y axis, which exhibits the structures resulting from the fourth-step Auger decay of Xe⁴⁺ $4d^{-1}5p^{-3} \rightarrow Xe^{5+}5p^{-5}$.

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BL4B

Ion Branching Ratio for the Xe 4p Auger Decay Studied by Photoelectron–Ion Coincidence Spectroscopy

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Photoelectron spectroscopy has revealed an anomalous photoelectron structure of the 4p core-hole state in Xe [1]. In a photoelectron spectrum, the expected $4p_{1/2}$ photoelectron line is dissolved and no longer visible, whereas the $4p_{3/2}$ structure consists of several fine components. These observations imply the breakdown of the independent particle model, resulting from the strong interaction between the $4p^{-1}$ and $4d^{-2}nf/4d^{-2}\varepsilon f$ configurations [2]. In this work, the ion branching ratio associated with the Auger decay of the 4p core-hole state is inspected. A magnetic bottle electron spectrometer with ion detection capability [3,4] was employed in this study, to conduct an efficient photoelectron-ion coincidence measurement. The measurement was implemented at a photon energy of 391.7 eV (bandwidth of ~0.2 eV), i.e. ~240 eV above the 4p threshold.

Figure 1 presents a photoelectron spectrum of Xe and those filtered by coincidences with different Xe^{Z^+} ions (Z = 1-6). Photoelectron structures associated with ejections of electrons from the N and O shells are exhibited in these spectra. The ion detection efficiencies were compensated for the spectral intensities of the coincidence spectra; thus, the relative intensities of individual photoelectron structures in these spectra reflect the ion branching ratios associated with the decays of these core-hole states. The ion branching ratios of the individual core-holes states were already studied by Eland *et al.* with the same coincidence method [5].

The photoelectron spectrum (Fig. 1 top) shows the 4p photoelectron structure consisting of a peak around a kinetic energy of 245 eV and a remarkable shoulder in the lower kinetic energy side. As already pointed out by Eland et al. [5], the determination of the ion branching ratio of the 4p decay is not straightforward, because the determined ratio varies greatly with the photoelectron range considered. When only the peak range around a kinetic energy of 245 eV is considered, the formation of Xe^{3+} is dominant and a sizable Xe^{4+} formation is probably identified. This is consistent with a multielectron coincidence study which reports a dominant Xe^{3+} formation for the main 4p photoelectron peak [6] and also with a recent calculation [7]. On the other hand, the shoulder part of the 4p photoelectron structure mainly produces Xe4+ ion. The shoulder part can be ascribed to double photoionization into the 4d⁻² states, which is enhanced by the virtual super Coster-Kronig transition [2] of $4p^{-1} \rightarrow 4d^{-2}\varepsilon f$ over several tens of electron volts [8]. The formed 4d⁻² states dominantly proceed to sequential fillings of the double 4d core-holes [8], resulting in the dominant formation of Xe⁴⁺ ion.



Fig. 1. Photoelectron spectrum of Xe measured at a photon energy of 391.7 eV, and coincidence spectra obtained by filter with different Xe^{Z+} ions (Z = 1-6). The intensities of the coincidence spectra were corrected by the ion detection efficiencies.

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Electronic Structure Analysis of Ni Complex Bearing *N*-Heterocyclic Carbene Ligand Using Ni L_{2,3}-edge X-ray Absorption Spectroscopy

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Recently, we have synthesized a Ni(0) complex bearing tris(pentafluorophenyl)borane (BCF) as an electron accepting Z-type ligand and N-heterocyclic carbene as an ancillary ligand (1). Single crystal X-ray diffraction (SC-XRD) analysis of 1 revealed that it exhibits a square-planer structure typical of Ni(II) complexes, unlike the tetrahedral geometry that is common for Ni(0) complexes probably due to the sterically demanding BCF ligand. Interested in the electronic structure of 1 which contradicts the ligand field theory, we have performed Ni K-edge X-ray absorption spectroscopy (XAS) of this complex at SPring-8 BL14B2 beamline and found that this complex possessed low-valent Ni(0)-like electronic structure. However, since Ni K-edge XAS basically corresponds to the electron transitions from 1s to a vacant 4p orbital because of the Fermi's golden rule [1], it is difficult to clarify the details of the electronic structure of 3d orbitals which determines the characteristics of metal complexes. In this study, Ni L2,3-edge XAS experiments of the Ni-BCF complex were investigated.

Ni L_{2,3}-edge XAS experiments were performed at the BL4B beamline using partial fluorescent yields (PFYs) method with silicon drift detector (SDD). A stainless-steel sample holder with double-sided conductive carbon tapes was attached to a transfer vessel, which was connected to a glovebox. The inside of the glovebox was evacuated using a rotary pump for at least 30 min, and then, filled with argon gas. The powder sample was applied on a carbon tape, and rubbed with the back of a spatula. After storing the sample holder in the vessel, the gate valve was closed. The vessel was detached from the glovebox, and then, attached to the main chamber. The air in the main chamber was evacuated by a rotary pump, and the gate valve was slowly opened after the pressure level reached in the order of 10^{-3} Pa. A turbo-molecular pump was then activated to create a high vacuum environment. XAS measurements were performed under the pressure less than 5×10^{-5} Pa.

Ni L_{2,3}-edge XAS data of **1**, **2** and **3** are shown in Fig. 1. Although the peak intensity of **1** was different from Ni(II) complex **3**, the peak position of **1** was similar to that of **3** which has octahedral ligand field rather than tetrahedral Ni(0) complex **2**, indicating the intrinsic geometrical similarity between the square-planer and the octahedral. Meanwhile, slightly intense first peak of **1** observed at 852.5 eV was assigned as the electron transition from $2p_{3/2}$ to $3d_{x2-y2}$ orbital. This result indicated the low d-electron occupancy in $3d_{x_2-y_2}$ level due to the σ -backdonation from Ni $3d_{x_2-y_2}$ orbital to vacant p orbital of BCF. In addition, the peak area of **1** (15.5) was closer to **2** (11.5) rather than **3** (25.3) (Table 1). Considering that the peak area reflects the transition probabilities of the electrons [2,3], the d-electron occupancy of **1** would be closer to the Ni(0) state rather than to the Ni(II) state, which is consistent with the Ni K-edge XAS experiment. In addition, the slight increase of the L_{2,3}-edge intensity of **1** would reflect the polarized Ni^{δ+}–B^{δ–} bonding state.



Fig. 1. Ni $L_{2,3}$ -edge XAS data of 1, 2 and 3.

Table 1. Peak area of Ni $L_{2,3}$ -edge XAS data after normalization.

	Peak area		
	L_3	L_2	$L_3 + L_2$
1	10.5	5.1	15.5
2	7.8	3.7	11.5
3	17.3	8.0	25.3

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Evaluation of Absorption Stability of a Hydrogen Absorption Cell

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A hydrogen absorption cell (HAC) is a unique optical filter which enables us to estimate density and temperature distributions and an isotope ratio of hydrogen atoms escaping from a planetary atmosphere by detecting a hydrogen Lyman α emission of a planetary corona. The HAC is especially suitable for a payload of a planetary mission because of its small size and light weight. However, no measurement of a planetary corona by a HAC has been successful so far. Development of a newly designed HAC has been proceeded by the proposers, and it has been decided that the HAC is on board Comet Interceptor which is an ESA mission to investigate an atmosphere of a comet.

Absorption efficiency of the HAC has been improved, but its lifetime has not yet been confirmed. Absorption performance should be highly stable during the mission lifetime of several years. Here we present a result of an experiment in which absorption stability of a protomodel HAC was evaluated using the spectrometer at BL5B of UVSOR.

The HAC and a Kr cell were installed in the beamline. The Kr cell, which contains Kr gas with a pressure of 500 Pa, was used for wavelength calibration of the spectrometer. The grating and mirror combination of "G3M5" was selected. The slit width and the pinhole diameter were 0.01 mm and 1 mm, respectively. Dimension of the HAC is ϕ 35 mm and L40 mm. Pure hydrogen gas filtered by a palladium filter with a pressure of 200 Pa was filled in the HAC. One of the filaments on the HAC was used for this stability test. Filament voltage was fixed at 5.73 V, which heats up the filament at a temperature of approximately 1800 K. A set of data consists of four spectra obtained with combinations of the filament on and off and the beam on and off from 121.1 nm to 122.0 nm with a scan step of 0.01 nm. It took approximately 70 min to acquire a set of data.

Figure 1 shows 8 absorption spectra of hydrogen Lyman α consecutively obtained by the HAC during a beamtime of 12 h. The depth of absorption almost unchanged, though the filament current slightly decreased from 0.170 A at the beginning to 0.167 A at the end. Accordingly, the filament temperature estimated from the voltage and current slightly increased. During the beamtime of four weeks this filament was activated for longer than 30 h, but no significant degradation was observed.

All the absorption spectra show an increasing trend from the shorter wavelength to the longer wavelength. The reason for this trend is unclear, but it might be related to any variation in the environment.



Fig. 1. Absorption spectra of hydrogen Lyman α consecutively obtained by a HAC under the same condition of gas pressure and filament voltage with the same filament.