









#### Surface-Dependent Hydration of Nanodiamonds in Colloidal Dispersions

T. Petit,<sup>1</sup> H. Yuzawa,<sup>2</sup> M. Nagasaka,<sup>2</sup> H. Girard,<sup>3</sup> J.-C. Arnault,<sup>3</sup> O. Shenderova,<sup>4</sup> N. Kosugi<sup>2</sup> and E. F. Aziz<sup>1,2,5</sup>

<sup>1</sup> Institute of Methods for Materials Development, Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin, Germany

<sup>2</sup> Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>3</sup> CEA, LIST, Diamond Sensors Laboratory, F-91191 Gif-sur-Yvette, France

<sup>4</sup> Adamas Nanotechnologies Inc., 8100 Brownleigh Dr., Raleigh, North Carolina 27617, USA

<sup>5</sup> Freie Universität Berlin, FB Physik, Arnimallee 14, 14195 Berlin, Germany

The organization of water molecules close to solid surfaces or around proteins differs significantly from pure water [1]. Reorganization of solvent molecules is likely to occur around colloidal nanoparticles and its understanding is of outermost importance to better estimate their reactivity and interaction with biological moieties in aqueous environment. Nanodiamonds (NDs) are of particular interest for the investigation of interfacial water since the existence of an ordered water shell ranging from 2 to 4 water layers was recently suggested. In 2014, we have observed that Xray Absorption Spectroscopy (XAS) in pure transmission was particularly efficient to probe water interfacial water around NDs [2].

During this beam time at UVSOR-III, aqueous dispersions of NDs with different surface chemistries prepared from the same initial ND produced by detonation synthesis (diameter ~5nm) by Adamas Nanotechnologies were compared. Carboxylated hydroxylated (NDs-COOH), (NDs-OH) and hydrogenated (NDs-H) were characterized. For comparison, NDs produced by High Pressure High Temperature (NDs-HPHT), with a diameter of 16 nm, were also characterized. By comparing these XA spectra at oxygen K edge to pure water spectra (Fig. 1), the organization of water molecules in hydration layers of NDs could be investigated.

After normalization to the absorption intensity before and after the oxygen edge, strong intensity variations of the signal were observed, which can be interpreted by surface-dependent variation of the water arrangement around NDs. NDs-OH are positivelycharged, like NDs-H and NDs-sp2, but its XA spectrum does not differ from negatively-charged NDs-COOH. This result demonstrates that the water structure is not dependent on the Zeta potential of NDs as previously thought. The strong intensity of the main edge intensity at 538 eV for NDs-H dispersion, although its concentration is half of the other samples, demonstrate that the water organization is extremely different on hydrogenated surface. An enhancement of this feature was previously observed on surfacegraphitized NDs (NDs-sp2), also having hydrogenated surface groups.

During this beam time, we could extend the preliminary results obtained in 2014 to NDs with welldefined surface chemistries. This work demonstrates that hydrogenated surface functional groups are the source of particular water arrangement on NDs. These results will be submitted for publication in the coming months, along with complementary infrared and Raman spectroscopies results.



Fig. 1. (a) XAS of oxygen K-edge from water and aqueous dispersion of detonation NDs with different surface chemistries. Concentration is 1 wt % except for NDs-H (0.5 wt %). Surface-graphitized NDs (NDs-sp2) spectrum is extracted from reference 2.

J.-J. Velasco-Velez *et al.*, Science **346** (2014) 831.
 T. Petit *et al.*, J. Phys. Chem. Lett. **6** (2015) 2909.

BL1U

# Induced Chirality by Circularly Polarized UV Light for Photofunctional Organic/Inorganic Hybrid Materials: Tuning Electrochemical Properties of Artificial Metalloproteins

T. Akitsu<sup>1</sup>, M. Sunaga<sup>1</sup>, M. Takase<sup>1</sup>, T. Konomi<sup>2</sup> and M. Katoh<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Tokyo University of Science, Tokyo 162-8601, Japan <sup>2</sup> UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

In 2015, we have studied on linearly or circularly polarized UV light induced molecular orientation of chiral metal complexes in polymer matrix (synthetic polymers or proteins) and controlled electronic properties of the metal complexes as organic/inorganic hybrid materials. The advantage of using UVSOR facility (BL1U) is to generate wavelength-selective and polarized UV light with high intensity.

We have prepared supramolecular chiral systems as artificial metalloproteins composed of several chiral salen-type Mn(II) and Co(II) complexes in a human serum albumin (HSA) matrix. After linearly polarized UV light irradiation, that anisotropy of molecular orientation of the complexes increased was confirmed by polarized IR spectra. We have observed that the electrochemical behavior of the aligned complexes incorporating diphenyl groups in HSA can be tuned without UV radiation damage of HSA higher structures.

As shown in Fig. 1, we have simulated several organic/inorganic hybrid materials structurally, in other words, artificial metalloproteins composed of chiral salen-type Mn(II) or Co(II) complexes and HSA proteins. We also measured polarized UV-vis spectra or IR spectra after linearly polarized light UV light or CD spectra after circularly polarized light UV light to confirm induced molecular orientation due to Weigert effect. Weigert effect by linearly polarized UV light causes dichroism due to anisotropic aligned metal complexes in a HSA matrix with photochemical reactions as well as interaction with highly polar molecules.

In addition, even strong synchrotron UV linearly polarized UV light irradiation (at 260, 318, and 380 nm of 10<sup>2</sup> mm<sup>2</sup> spot at 10 mW/cm<sup>2</sup> generated with an undulator at IMS UVSOR BL1U [1]) did not damaged higher structure of HSA for the artificial metalloproteins. Little changes from the initial CD spectra in the range of 200-900 nm could be observed after 1, 3, and 5 min irradiation.

As depicted in Fig. 2, the CV measurements revealed the effects of UV light for not only metal complexes but also the artificial metalloproteins. Relatively UV light-resistant metal complexes exhibited CV changes after UV irradiation for 10 min, which may be in agreement with expectation based on the intra-ligand transitions or stable isolation and O<sub>2</sub> oxidation during preparation from Mn(II) source for the analogous Mn(III) complexes. As for diphenyl incorporating metal complexes-HSA hybrids, little CV

changes could be observed significant CV changes (decreasing current) only after 1 min polarized UV irradiation.



Fig. 1. Docking simulation (GOLD) of a chiral metal complex into HSA protein.



Fig. 2. Changes of CV of an artificial metalloprotein after polarized UV light irradiation.

#### [1] UVSOR, UVSOR Activity Report 41 (2014).

BL1U

# Photoionization of Helium Atoms by Photon Beams Carrying Orbital Angular Momentum

T. Kaneyasu<sup>1</sup>, Y. Hikosaka<sup>2</sup>, M. Katoh<sup>3</sup>, H. Iwayama<sup>3</sup> and E. Shigemasa<sup>3</sup>

<sup>1</sup>SAGA Light Source, Tosu 841-0005, Japan

<sup>2</sup>Graduate School of Medicine and Pharmaceutical Sciences, University of Toyama, Toyama 930-0194, Japan <sup>3</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

Light beam characterized by helical wavefront and annular intensity distribution carries orbital angular momentum (OAM). Since the pioneering work by Allen *et al.* [1], the OAM photons have been attracting interests in a variety of research fields such as quantum information, manipulation of micro particles and highresolution microscope. Until now application of the OAM photons has been limited to the visible and infrared wavelength region because it is generally difficult to produce helical wavefront at short wavelengths using optical elements.

Recently it was found that the *n*th harmonic radiation from a helical undulator carries OAM of  $(n-1)\hbar$  per photon [2,3]. This accelerator-based method directly and efficiently produce circularly polarized OAM photon beams in a wavelength range covering from VUV to hard X-rays. Following the successful generation of the OAM photon beam in the UVSOR storage ring, we started an experimental study [4] on the interaction of the OAM photon with gas-phase atoms in which violation of the dipole selection rule is predicted [5].

The experiments were performed at the beamline BL1U using the OAM photon beam produced as the harmonic radiation from the APPLE-II undulator. The undulator radiation was collimated by  $\phi$ 1 mm pinhole and transported into the experimental chamber without optical elements. We measured angular distributions of He 1s photoelectron using the imaging method. Although we had experimental problems regarding the photon beam alignment and background subtraction in the image data, some preliminary results are presented in this report.

The left panels in Fig. 1 show the He 1s photoelectron images measured for the circularly polarized fundamental, second and third harmonic radiation, corresponding to the photon beams carrying OAM of  $0\hbar$ ,  $1\hbar$  and  $2\hbar$  per photon, respectively. The peak photon energy of the undulator radiation was roughly set to 30 eV for each harmonic. The right panels in Fig. 1 show the angular distributions of the photoelectrons converted from the projected images using the peeling-analysis. The measured angular distributions are in reasonable agreement with those calculated for the dipole asymmetry parameter  $\beta = 2$ even for the l = 1 and 2 cases. This result implies that the dipole transition dominates the OAM photon-atom interaction under the present experimental condition where the He atoms are uniformly distributed among

the photon beam of 1 mm diameter. For confirming the present observation, we plan to perform the photoionization experiment after the beamline construction scheduled in 2016.



Fig. 1. Left: Images of He 1s photoelectrons. Right: Photoelectron angular distributions converted from the images. Solid curves represent the calculation for  $\beta$ =2. The photoelectron images were measured for the circularly polarized photon beams carrying OAM of *l* $\hbar$  (*l*=0-2) per photon.

- [1] L. Allen et al., Phys. Rev. A 45 (1992) 8185.
- [2] S. Sasaki and I. McNulty, Phys. Rev. Lett. 100 (2008) 124801.

[3] J. Bahrdt *et al.*, Phys. Rev. Lett. **111** (2013) 034801.
[4] T. Kaneyasu *et al.*, UVSOR Activity Report **42** (2014) 110.

[5] A. Picón et al., New J. Phys. 12 (2010) 083053.

#### Local Structure Observation of Aqueous KSCN Solution by Soft X-Ray Absorption Spectroscopy. Part I. O K-Edge XAS for Solvent Water.

H. Yuzawa, M. Nagasaka and N. Kosugi Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Aqueous solution of highly concentrated electrolyte has been studied extensively, where cations and anions in water were not completely hydrated and interact with each other to produce complicate aggregated structures [1]. However, since it is difficult to clarify their structures by a few kinds of spectroscopic observation, more accumulation of spectroscopic insights is required.

Our research group has developed a new liquid cell for the soft X-ray XAS in transmission mode and has applied it to O K-edge XAS measurements of some electrolyte solutions. As a result, we have clarified the hydration structure around the cation [2]. In the present study, we have extended the measurement to both water and electrolyte in aqueous KSCN solutions, and have investigated the concentration dependence from dilute to nearly saturated one. In this part, we report the O K-edge XAS of water in the solutions.

The experiments were carried out at BL3U. First, the (KSCN)<sub>x</sub>(H<sub>2</sub>O)<sub>1-x</sub> solution samples (x values are from 0 to 0.3. x = 0.3 corresponds to 9.1 M.) were prepared and flowed into the liquid cell which is composed of two Si<sub>3</sub>N<sub>4</sub> membranes. Then, the thickness of liquid cell was optimized by controlling the He pressure around the cell and the O K-edge XAS measurement was started. The photon energy was calibrated by the oxygen 1s  $\rightarrow \pi^*$  excitation peak (530.8 eV) of O<sub>2</sub> gas mixture in He.

Figure 1 shows O K-edge XAS spectra of the  $(KSCN)_x(H_2O)_{1-x}$  samples. In the Fig. 1a, the absorption intensity of the post-edge region around 540 eV decreases with increasing the KSCN concentration. Since this region is assigned to multiple scattering in the hydrogen bond network of water [3], this tendency suggests that the more hydrogen bond is broken by KSCN in higher concentration. In the Fig. 1b, the sharp absorption peak at the main-edge region around 537 eV is clearly observed for high concentration comes close to the spectrum of water vapor [4]. Thus, this peak would be derived from the existence of isolated water molecule (or cluster) surrounded by KSCN.

Figure 2a shows magnified figure of the pre-edge peaks around 534.5 eV in Fig. 1. Figure 2b shows the peak energy shift values of these peak tops. The blue shift of the peak top is larger with increasing the concentration. This indicates that the hydration structure between H<sub>2</sub>O and K<sup>+</sup> (K<sup>+</sup> – OH<sub>2</sub> interaction) increases in number, as reported previously [2].

Therefore, the KSCN concentration dependence of

O K-edge XAS spectra for water can give the information about tendency of the breaking of hydrogen bond network and that of the formation of hydration structure between  $K^+$  and  $H_2O$ .



Fig. 1. O K-edge XAS of  $(KSCN)_x(H_2O)_{1-x}$  solutions in various ratios from x = 0 to 0.3.



Fig. 2. (a) Magnified figure of the pre-edge region in the O K-edge XAS spectra of the  $(KSCN)_x(H_2O)_{1-x}$  solutions shown in Fig. 1. (b) The energy shifts of the pre-edge peak top.

[1] Y. Marcus, Chem. Rev. 109 (2009) 1346.

[2] M. Nagasaka, H. Yuzawa and N. Kosugi, J. Spectrosc. Relat. Phenom. **200** (2015) 293.

[3] Ph. Wernet et al., Science 304 (2004) 995.

[4] T. Tokushima *et al.*, Phys. Chem. Chem. Phys. **16** (2014) 10753.

# Local Structure Observation of Aqueous KSCN Solution by Soft X-Ray Absorption Spectroscopy. Part II. C and N K- Edge and K L-Edge XAS for Solute KSCN.

H. Yuzawa, M. Nagasaka and N. Kosugi Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Oxygen K-edge XAS spectra of water in  $(KSCN)_x(H_2O)_{1-x}$  (x = 0 – 0.3) solutions have revealed that the increase of KSCN induces the breaking of hydrogen bond in water and increases the number of hydration structure (K<sup>+</sup> – OH<sub>2</sub> interaction) [1]. In this part, we report XAS measurements for the solute KSCN (K L-edge, C K-edge and N K-edge) to investigate the interaction around KSCN.

The experiments were carried out at BL3U. The procedure of the XAS measurements for the solution samples is the same as in Part I [1]. In N K-edge XAS, another liquid cell composed of two SiC membranes was used. The photon energy was calibrated by the CH<sub>4</sub> 1s–3pt<sub>2</sub> Rydberg peak (297.99 eV) of CH<sub>4</sub> gas mixture in He or N<sub>2</sub> 1s  $\rightarrow \pi^*$  excitation peak (400.84 eV) of N<sub>2</sub> gas mixture in He. XAS spectra of KSCN solid sample as a reference were also obtained by measuring drain current in a vacuum chamber.

Figure 1a shows K L-edge XAS spectra. Two absorption peaks are assigned to K  $2p_{3/2} \rightarrow 3d$ excitation around 297 eV and K  $2p_{1/2} \rightarrow 3d$  excitation around 300 eV, respectively. These peaks show red shift with the increase of KSCN concentration. Since this tendency means that the electronic state around K<sup>+</sup> comes close to that of KSCN solid (Fig. 1d), the number of interaction between K<sup>+</sup> and SCN<sup>-</sup> in the solution increase in higher KSCN concentration. Considering the results of O K-edge XAS spectra [1], it is suggested that both interactions of K<sup>+</sup> – OH<sub>2</sub> (hydration) and K<sup>+</sup> – SCN<sup>-</sup> (aggregation) increase in number. This conclusion is also supported by a recent report of MD simulation in highly concentrated KSCN solution [2].

Figure 1b shows N K-edge XAS spectra. The obtained peak is assigned to the N 1s  $\rightarrow \pi^*$  excitation. The same tendency (red shift toward the solid state, Fig. 1d) as in the case of K L-edge XAS is obtained. Thus, this can be also explained that the number of interaction between K<sup>+</sup> and N atom in SCN-increases with higher concentration.

Figure 1c shows C K-edge XAS spectra, which is obtained from the C 1s  $\rightarrow \pi^*$  excitation. The peak top energies of the solution samples in C K-edge XAS are almost constant without any dependence on the KSCN concentration (Fig. 1d). The XAS energy shift induced by intermolecular interaction is mainly derived from two factors. The red shift is occurred by the induced dipole interaction (stabilization) between the excited atom and surroundings, while the blue shift is occurred

by the exchange interaction (repulsion) between the excited electron to an unoccupied orbital and the valence and core electrons of surrounding molecules. These influences are stronger when the intermolecular distance is smaller. Based on this discussion, the result of C K-edge XAS suggests that the distance between C atom in SCN<sup>-</sup> and other species is distant, that is, the interaction around the C atom is weaker compared with the interaction around the other atoms.

Therefore, aggregate structure of KSCN in highly concentrated aqueous solution is mainly formed by the  $K^+$ -SCN<sup>-</sup> interaction and the  $K^+$ -NCS interaction, which break the hydrogen bond of water.



Fig. 1. (a) K L-edge, (b) N K-edge and (c) C K-edge XAS spectra of  $(KSCN)_x(H_2O)_{1-x}$  solutions in various ratios from x = 0.002 to 0.3 and KSCN solid sample (x = 1). (d) The energy shifts of the obtained absorption peaks from a to c.

[1] H. Yuzawa, M. Nagasaka and N. Kosugi, UVSOR Activity Report in this volume.

[2] S. Kim et al., J. Chem. Phys. 141 (2014) 124510.

### Development of X-Ray Detecting System Combined with Photomultiplier and Phosphor for Soft X-Ray Absorption Spectroscopy of Dilute Solutions

M. Nagasaka, H. Yuzawa, T. Ohigashi, Y. Okano and N. Kosugi Institute for Molecular Science, Okazaki 444-8585, Japan

Soft X-ray absorption spectroscopy (XAS) is a powerful method to study local structures of liquid. We have developed a liquid flow cell for XAS in transmission mode, and studied the local structures of several aqueous solutions [1]. In normal aqueous solution, soft X-ray absorption is optimized to several tens of percent by adjusting the thickness of liquid layers. In dilute solutions, on the other hand, thick liquid samples should be prepared for XAS of solute because soft X-ray absorption of solute is low. However, the absorption of solvent is also increased due to the thick liquid samples. It is necessary to detect low flux (10<sup>5</sup> photons/s) of transmitted soft X-rays at the incident X-rays of 10<sup>9</sup> photons/s. Because the detection limit of photodiode is 107 photons/s, XAS of 100 mM solution is only measured by the photodiode detector. In this study, we have developed a X-ray detecting system combined with photomultiplier and phosphor for XAS of solute in dilute solutions.

The experiments were performed by using a chamber-type XAS measurement system at BL3U [2]. As shown in Fig. 1, the system consists of two chambers in an ultrahigh vacuum condition and in atmospheric helium condition. These chambers are separated by a 100 nm-thick Si<sub>3</sub>N<sub>4</sub> membranes with the window size of  $200 \times 200 \ \mu\text{m}^2$ . The vacuum chamber is connected to the beam line. In the helium chamber, a liquid flow cell and a soft X-ray detector are installed. In the liquid cell, the liquid layer is sandwiched between two 100 nm-thick Si<sub>3</sub>N<sub>4</sub> membranes, and liquid thickness is controllable from 20 nm to several µm. For XAS of liquid samples, transmitted soft Xrays irradiate to phosphor P43 dipped on the inlet of an optical fiber, soft X-rays are converted to visible lights [3], and visible lights are detected by a photomultiplier connected to the outlet of the optical fiber. We have confirmed that soft X-rays with 10<sup>3</sup> photons/s are detected in this system.

Figure 2 shows Fe L-edge XAS spectrum of 8.7 mM [Fe(bpy)<sub>3</sub>] solution by using the present system. The solvent is DMSO. We have confirmed the presence of Fe peak in XAS regardless of the dilute solutions. The photon flux of incident and transmitted soft X-rays are  $10^9$  and  $4 \times 10^5$  photons/s, respectively. The thickness of liquid layer is estimated to be 8 µm. We have succeeded to measure XAS of metal atoms in dilute metal complex solutions below 10 mM. In the future plan, we will investigate the local structures of ligand in dilute metal complex solutions by using C and N K-edge XAS.



Fig. 1. Schematic of a chamber-type XAS measurement system for liquid samples. Soft X-ray transmission through the liquid sample is detected by a system combined with photomultiplier and phosphor dipped on the inlet of the optical fiber.



Fig. 2. Fe L-edge XAS spectrum of 8.7 mM [Fe(bpy)<sub>3</sub>] solutions. The inset shows the schematics of the Fe metal complex.

[1] M. Nagasaka *et al.*, J. Electron Spectrosc. Relat. Phenom. **200** (2015) 293.

[2] M. Nagasaka et al., in preparation.

[3] A. L. D. Kilcoyne *et al.*, J. Synchrotron Rad. **10** (2003) 125.

# X-Ray Absorption Spectroscopy of Aqueous CO<sub>2</sub>: Chemical Shifts of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> Ions in Water Matrix

M. Patanen<sup>1</sup>, M. Huttula<sup>1</sup>, H. Yuzawa<sup>2</sup>, M. Nagasaka<sup>2</sup> and N. Kosugi<sup>2</sup>

<sup>1</sup>Nano and Molecular Systems Research Unit, Faculty of Science, 90014 University of Oulu, Finland <sup>2</sup>Institute for Molecular Science, Okazaki 444-8585, Japan

Increased atmospheric CO<sub>2</sub> emissions after industrial revolution have not only drastic effects for the atmospheric chemistry but lead to acidification of surface water of oceans [1]. The solubility of molecular CO<sub>2</sub> is governed by Henry's law. In water, CO<sub>2</sub> appears in four forms: molecular CO<sub>2</sub>, carbonic acid H<sub>2</sub>CO<sub>3</sub>, bicarbonate ion HCO<sub>3</sub><sup>-</sup>, and carbonate ion  $CO_3^{2-}$ . A total amount of dissolved aqueous  $CO_2$ species thus varies as a function of pH, since the form which CO<sub>2</sub> takes in water depends strongly on pH. Oceanic CO<sub>2</sub> species play an important role in the global carbon cycle not only at liquid-gas interfaces at the oceans' surfaces, but also at liquid-solid interfaces: e.g., carbonated solutions dissolve silicate minerals releasing metal ions into solution [2]. The electronic structure of the aqueous CO<sub>2</sub> species in pure and saline water is essential in order to model the chemical processes they take part in.

In this work we have studied C 1s and O 1s X-ray absorption spectra (XAS) of CO<sub>2</sub> species as a function of pH at UVSOR BL3U. We have used a liquid flow cell enabling a transmission mode soft X-ray absorption spectroscopy thanks to the thin SiN<sub>x</sub> membranes [3]. The solutions were prepared from water solution of Na<sub>2</sub>CO<sub>3</sub> (~2 M solution has a pH of 12.5) by adding different amounts of HCl (aq) in order to achieve the desired pH. Figure 1 a) presents the Bjerrum plot indicating with vertical grey bars the mole fractions of different species present in the studied solutions. Since the solubility of CO<sub>2</sub> species decreases with the lower pH, we were able to probe only the neutral/basic solutions consisting mostly of bicarbonate and carbonate species.

Figure 1 b) presents the water background subtracted C 1s XAS as a function of pH. It is clearly observed that the absorption energies get higher and bands broader, which corresponds well to the increase of the mole fraction of  $HCO_3^-$  and  $CO_2$  species in the solution with decreasing the pH value from 12.5 to 6.4 (Fig. 1 a)). Therefore, the changes in XAS in terms of energy shifts and broadenings evidence clearly different bonding networks for these species.

Figure 1 c) shows the corresponding O 1s XAS of carbonated solutions and pure water. O1s  $\rightarrow \pi^*$  peak from gaseous O<sub>2</sub> is shown for energy calibration. Below the H<sub>2</sub>O pre-edge peak we observe a clear shoulder whose magnitude is the greater the more basic the solution is. This tendency is identical with that of solubility for the total amount of CO<sub>2</sub> species, which decreases with the lower pH.



Fig. 1. a) Bjerrum plot showing the mole fractions of  $CO_2$  species as a function of pH. b) C 1s XAS of aqueous  $Na_2CO_3$  solutions. Grey bars indicate the maxima of the XAS. c) O 1s XAS showing a shoulder before the water pre-edge peak at 534.8 eV.

[1] K. Caldeira and M.E. Wickett, Nature **425** (2003) 365.

[2] A. Putnis, Science 343 (2014) 1441.

[3] M. Nagasaka, T. Hatsui, T. Horigome, Y. Hamamura and N. Kosugi, J. Electr. Spectrosc. Rel. Phen. **177** (2010) 130.

#### **Impacts of Conformational Geometries in Fluorinated Alkanes**

T. Brandenburg<sup>1, 2</sup>, R. Golnak<sup>1,2</sup>, M. Nagasaka<sup>3</sup>, K. Atak<sup>1, 2</sup>, S. S. N. Lalithambika<sup>1,2</sup>, N. Kosugi<sup>3</sup> and E. F. Aziz<sup>1, 2, 3</sup>

<sup>1</sup> Institute of Methods for Material Development, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-

Einstein-Straße 15, 12489 Berlin, Germany

<sup>2</sup> Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany <sup>3</sup> Institute for Molecular Science, Okazaki 444-8585, Japan

Research in blood substitute formulations is gaining more attention in the scientific community in recent years as more pharmaceutical companies start clinical trials on different artificial blood approaches. In general, artificial blood consists of emulsions of different liquid or protein compounds to increase oxygen solubility and transport capabilities as well as to decrease toxicity to biological tissue. Two of the more promising approaches center themselves around hemoglobin-based carriers and fluorinated microemulsions. Despite setbacks regarding clinical tests and medicinal approval of recent formulations, an emulsion containing perfluorodecalin named Fluosol was successfully approved by the U.S. Food and Drug Administration in 1989 (New Drug Application N860909).

The main oxygen carrier in Fluosol, perfluorodecalin, is part of the family of perfluorocarbons. They have a wide range of applications ranging from tissue oxygenation to post-operative treatment. Their wide range of extraordinary properties - high density, high viscosity, high biological and chemical inertness, high gas solubility - offer opportunities for applications in biomedicine and physical chemistry, as well as subsequently leading to a high interest in scientific development.

An inherent feature to all perfluorocarbons is the so called perfluoro effect, which describes the energy shifts of the spectral features due to the stabilization effect of fluorine in the fluorination process. The magnitude of the energy shift can subsequently be used for a classification of a molecular orbital to either bear  $\sigma$ - or  $\pi$ -character delivering an experimental method for the orbital classification. Some experimental studies based on photoelectron and X-ray absorption spectroscopy have already been performed, but the development of more complex theoretical models and new experimental techniques gives opportunities for further investigation of perfluorocarbons.

In liquid emulsions several effects need to be accounted for. Two of the more prominent are the conformation effect and the van der Waals force. The conformation effect affects peak broadenings and is a result of excited orbital interactions with surrounding molecules of different conformations. In the case of nonpolar systems, the acting van der Waals force is the London dispersion force, that is, an attractive force resulting from induced dipoles.

Through the measurements performed at the beamline BL3U in UVSOR we could obtain X-ray absorption spectra of several liquid fluoroalkanes and their respective hydrocarbons, which are subject to weak van der Waals forces and have a high amount of different conformational geometries.

Insight into the energetic shift induced by fluorination, the so-called perfluoro effect, and a comprehensive picture of the electronic structure of liquid fluoroalkanes and their respective parent hydrocarbon molecules was obtained [1]. In addition DFT calculations for the hydrocarbons, fluoroalkanes and stepwise fluorinated hydrocarbon derivatives were performed. We could reveal a strong involvement of the conformation effect with the local electronic structure and relative inertness of liquid fluoroalkanes. We additionally expose a direct association of different conformational geometries to the solubility rates of the presented perfluorocarbons with other liquid compounds like water and possibly gases like oxygen.



Fig. 1. Sketch of the acquired data for fluoroalkanes with an indication of the discovered peak broadening resulting from the conformational effect [1].

[1] T. Brandenburg et al., under review.

101

Ш-З

#### BL4U

### In-situ Soft X-Ray Absorption Spectroscopy Measurements of Liquid Samples by Scanning Transmission X-Ray Microscope

M. Nagasaka, T. Ohigashi, H. Yuzawa and N. Kosugi Institute for Molecular Science, Okazaki 444-8585, Japan

Two different kinds of molecular liquids can be separated as two liquid phases by controlling the temperature due to a phase transition behavior in the mixed liquid. In order to reveal the mechanism of such a phase transition, it is necessary to investigate local structures of liquid-liquid interfaces of two liquids. Soft X-ray absorption spectroscopy (XAS) is an element specific method to study local structures of liquid. Recently, we have developed a liquid flow cell for XAS in transmission mode. In the liquid cell, a liquid layer is sandwiched between two 100 nm-thick Si<sub>3</sub>N<sub>4</sub> membranes, and liquid thickness is controllable from 20 nm to several µm. By using this liquid cell, we have revealed local structures of several aqueous solutions [1]. We have also developed a liquid flow cell combined with scanning transmission X-ray microscope (STXM), and measured spatial resolved XAS of liquid samples [2]. However, the window sizes of Si<sub>3</sub>N<sub>4</sub> membranes ( $0.5 \times 0.5 \text{ mm}^2$ ) are too small to measure liquid-liquid interfaces, which are widely distributed in the liquid layer. In this study, we have developed a liquid flow cell, whose window size is  $2 \times$ 2 mm<sup>2</sup>, to measure spatial resolved XAS of liquidliquid interfaces by STXM. We have measured O Kedge XAS of liquid water for the test of the liquid flow cell.

The experiments were performed at BL4U by connecting a liquid flow cell to the STXM system. The liquid cell is in the atmospheric helium condition. The liquid layer is sandwiched between two 100 nm-thick  $Si_3N_4$  membranes with the window size of 2 × 2 mm<sup>2</sup>. The membranes are supported by Si frames with the thickness of 0.2 mm. In order to adjust the liquid thickness, 20 µm-thick Teflon spacers are included between two Si frames of the membranes. Liquid samples are exchanged *in situ* by using a tubing pump system. Temperature of a liquid sample is controlled by setting a Cu plate connected with a chiller system.

Figure 1 shows a soft X-ray transmission image of liquid water at the incident photon energy of 550 eV. Because the left part of the image is a Si frame, soft Xray is not transmitted. On the other hand, soft X-rays are transmitted in the right part due to the existence of liquid water. We have observed line shape structures, in which thick liquid layer exists, with the distance of  $250 \,\mu\text{m}$  from the edge of the Si frame. Figure 2 shows O K-edge XAS of liquid water. The beam spot of soft X-ray is set to the line shape structures in the liquid laver to obtain appropriate thickness of liquid lavers for XAS in transmission mode. The thickness of a liquid layer is 480 nm. The intensity ratio of pre-edge

(535 eV) and main-edge (538 eV) is 0.39, and is consistent with our previous results [3].

In the future plan, we will measure spatial resolved XAS images of liquid-liquid interfaces by using this liquid flow cell, and revealed the mechanism of the phase transition of two liquid structures.



Fig. 1. Soft X-ray transmission image of liquid water at the incident photon energy of 550 eV.

2.0

1.5

1.0

0.5

0.0

530

Absorbance

O-K XAS

Water



540

Photon Energy / eV

545

[1] M. Nagasaka et al., J. Electron Spectrosc. Relat. Phenom. 200 (2015) 293.

[2] T. Ohigashi et al., AIP Conf. Proc., in press.

535

[3] M. Nagasaka et al., in preparation.

BL4B

### Auger Decay of Condensed Water Investigated with a Magnetic Bottle Electron Spectrometer

R. Mashiko<sup>1</sup>, K. Soejima<sup>1</sup>, E. Shigemasa<sup>2</sup> and Y. Hikosaka<sup>3</sup>

<sup>1</sup>Department of Environmental Science, Niigata University, Niigata 950-2181, Japan

<sup>2</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>3</sup> Graduate School of Medicine and Pharmaceutical Science, University of Toyama, Toyama 930-0194, Japan

Slow electron formation relevant to inner-shell photoionization of gas phase H<sub>2</sub>O was investigated by multi-electron coincidence spectroscopy [1]. It was found that autoionization from O fragment produced by dissociation of Auger final H<sub>2</sub>O<sup>2+</sup> states is the important source of the slow electron formation. Such slow electron formation from the ionization of water molecules has received particular attention, in connection with DNA strand breaks in living cells exposed to ionizing radiations. The DNA strand breaks are largely caused by the impact of electrons emitted from the ionization of water molecules and biomolecules surrounding the DNA. Here, the majority of the electrons have kinetic energies of less than 20 eV, and the efficiency of the DNA strand breaks is known to be strongly dependent on the incident electron energy of the impacting electrons, due to its resonant character. Thus the knowledge of the energy distribution of the slow electrons is important in modeling the radiation damages of living cells. In this study, we have investigated the slow electron emission process of condensed H2O irradiated with soft x-ray.

The experiment was performed at the beamline BL4B under the single bunch operation of the storage ring. The synchrotron radiation from a bending magnet of the strange ring was monochromatized by a grazing incidence monochromator using a varied-line-spacing plane grating. The monochromatized light was focused onto a copper wire. Water molecules were adsorbed on the surface of the wire, by continuously cooling the wire down to the liquid nitrogen temperature, under its exposition to the base pressure (~ $1.8 \times 10^{-8}$  Torr). Electron coincidence measurements were carried out with the magnetic bottle electron spectrometer [2] whose schematic is shown in Fig. 1.

Coincidence datasets were accumulated for electrons emitted from the copper wire on irradiation of 738.2 eV photons. The two-dimensional map in Fig. 2 displays the energy correlation of the coincident electrons included in the coincidence datasets, where the coincidence counts are plotted as a function of faster (horizontal) and slower electron energies (vertical). A clear structure running horizontally is associated with the coincidences between the O1s photoelectrons and the Auger electrons from condensed water.

We have inspected three-fold coincidences among the O1s photoelectron, Auger electron and slow electron, in order to investigate the energy distribution of the slow electrons emitted after the Auger decay. The energy distribution (not shown) does not exhibit any tangible structures ascribable to autoionization from O: fragments. This observation implies that dissociations forming O\* fragments are suppressed in the condensed phase.



Fig. 1. Schematic of the magnetic bottle electron spectrometer.



Fig. 2. Two dimensional plot of energy correlation between photoelectron and Auger electron emitted in the inner shell ionization of condensed water molecules.

[1] Y. Hikosaka et al., J. Chem. Phys. 137 (2012) 191101.

[2] Y. Hikosaka *et al.*, J. Ele. Spectrosc. Rel. Phenom. **192** (2014) 69.

### Improvement of the VMI Spectrometer for Photoelectron Imaging Experiment

T. Kaneyasu<sup>1</sup>, Y. Hikosaka<sup>2</sup>, H. Iwayama<sup>3</sup> and E. Shigemasa<sup>3</sup>

<sup>1</sup>SAGA Light Source, Tosu 841-0005, Japan

<sup>2</sup>Graduate School of Medicine and Pharmaceutical Sciences, University of Toyama, Toyama 930-0194, Japan <sup>3</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

Velocity map imaging (VMI) [1] is one of the powerful methods for measuring the velocity distribution of charged particles emitted in various atomic and molecular processes. We employed a VMI spectrometer for the experimental investigation on photoionization of gas-phase atoms by circularly polarized undulator radiation which carries orbital angular momentum [2]. Since the VMI spectrometer used in our study was originally developed for the negative ion imaging [3], it was found that slight modification of the spectrometer was necessary for improving the electron image quality.

The details of the VMI spectrometer is described in ref. [3]. Briefly, the spectrometer consists of a repeller plate, electrostatic lenses and a drift tube followed by a two dimensional position sensitive detector. The photoelectrons having same initial velocities are focused to the same detector's position independent of the ionization point by applying the inhomogeneous electrostatic filed to the ionization region. When the cylindrical symmetry is assumed, three-dimensional vectors of the photoelectrons can be reconstructed from the projected two-dimensional image.

The improvements of the VMI spectrometer are as follows. Firstly we introduced a magnetic shield around the drift tube for reducing the stray magnetic field in the electron drift space. Next we replaced the repeller electrode with a mesh-type one. This is because secondary electrons are efficiently produced from the electrode surface by photoions colliding with the repeller plate. Finally we constructed a new frame for supporting the experimental chamber, allowing precise positioning of the spectrometer's center with respect to the photon beam axis.

Following the improvements, performance test of the VMI spectrometer has been carried out at BL5B. The images and angular distributions of the He 1s and Ar 3p photoelectrons are shown in Figs. 1 and 2, respectively. The electric vector of the photon beam is parallel to X-axis of the image. The intense ringshaped structures observed in the images correspond to the photoelectrons, while secondary electrons are weakly distributed inside the ring structures. The secondary electron emission is well suppressed compared to the previous setup consisting of the platetype repeller electrode. The image distortion observed in the previous measurements is reduced by introducing the magnetic shield. Photoelectron angular distributions are converted from the raw images without any background subtraction and image corrections. The measured angular distributions are fairly in agreement with the calculation results, confirming that image quality of the VMI spectrometer is sufficiently improved for the photoelectron imaging experiment.



Fig. 1. (a) Projected image and (b) angular distributions of He 1s photoelectrons measured at hv=27.6 eV. Solid curve represents the calculation for  $\beta=2$ .



Fig. 2. (a) Projected image and (b) angular distributions of Ar 3p photoelectrons measured at hv=21.0 eV. Solid curve represents the calculation result for  $\beta=0.84$ .

[1] A. T. J. B. Eppink and D.H. Parker, Rev. Sci. Instrum. **68** (1997) 3477.

[2] T. Kaneyasu *et al.*, UVSOR Activity Report 2014, **42** (2015) 110.

[3] Y. Hikosaka and E. Shigemasa, J. Electron Spectrsc. Relat. Phenom. **148** (2005) 5. Ш-З

### Auger Spectra Measured in Coincidence with the Photofragment Ions Formed after Migration: 3,3,3-Trifluoropropene at the C K-Edge

R. Tateishi<sup>1</sup>, T. Kaneda<sup>1</sup>, H. Iwayama<sup>2, 3</sup>, M. Kono<sup>4, 5</sup>, K. Okada<sup>1</sup> and E. Shigemasa<sup>2, 3</sup>

<sup>1</sup>Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

<sup>2</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>3</sup>School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585,

Japan

<sup>4</sup>Senri International School of Kwansei Gakuin, Minoh 562-0032, Japan <sup>5</sup>RSPE, Australian National University, Canberra, ACT 0200, Australia

Inner-shell excited molecules relax into molecular cations in different states through Auger decays. The cations are in general unstable and dissociate rapidly into fragment ions. In many hydrocarbon molecules a photoexcitation can cause a rapid geometry change in the molecule. Such migration has also been observed for photoexcitation of molecules at the inner-shell level. In the case of the inner-shell excitation and ionization of acetylene, for example, ion yield spectra of  $H_2^+$  and  $CH_2^+$  were observed [1] and the  $C_2^+/H_2^+$  ion pair was detected [2], indicating a proton migration. We have recently concerned ourselves with the Augerfinal states connecting to particular dissociation channels [3]. This report focuses on the rapid migration in the 3,3,3-trifluoropropene (TFP) molecule excited at the C K-edge. We have employed the Auger-electron-photoion coincidence (AEPICO) method to obtain information on the correlation between photofragment ions formed after migration and Auger-final states of the molecular ion.

The experiments were performed on the soft X-ray beamline, BL6U. The experimental setup has been described elsewhere [3,4]. Synchrotron radiation was irradiated at right angles to the effusive beam of the TFP sample. The pressure of the main chamber was kept at  $4.0 \times 10^{-4}$  Pa during the measurements. Auger electrons traveling through a double toroidal analyzer tube were detected with a position sensitive detector. The pass energy was set to 400 eV. Photofragment ions produced in the ionization region were extracted toward a time-of-flight mass spectrometer by a pulsed electric field applied just after the Auger electron detection. AEPICO data were obtained as list-mode files, containing a series of a set of the detected electron positions and the ion arrival times. The photon energies of 284.5 and 310.0 eV were used as typical resonant excitation and photoionization, respectively.

A correlation map of kinetic energy of the emitted Auger electrons versus m/z of photofragment ions can be depicted from the coincidence data. A variety of photofragment ions is found, such as  $CH_n^+$ ,  $F^+$ ,  $C_2H_m^+$ ,  $CF_m^+$ ,  $C_2H_mF^+$  and so forth, where n = 0-3 and m = 1-3. They form islands on the map. Auger spectra coincident with particular ions can be obtained by extracting the region of interest on the map. In this study we focus on the  $C_2H_3F^+$  ion, which is produced after a fluorine-atom migration.

Figure 1 gives resonant Auger spectra measured in coincidence with the  $C_2H_3^+$  and  $C_2H_3F^+$  detection. The spectra have been obtained after subtraction of the contribution from photoelectrons. Both ions are produced by the C2–C3 bond rupture, with the only difference being with and without the migration before fission. It can be seen that the spectrum coincident with  $C_2H_3F^+$  has a specific peak at the electron kinetic energy of 265.7 eV, whereas that coincident with  $C_2H_3^+$  spreads widely with two distinct peaks. The result reveals that the migration occurs from such limited Auger-final states.



Fig. 1. Resonant Auger spectra measured in coincidence with detection of the  $C_2H_3^+$  and  $C_2H_3F^+$  photofragment ions. The contribution from photoelectrons has been subtracted.

[1] M. N. Piancastelli *et al.*, J. Chem. Phys. **117** (2002) 8264.

[2] J. Laksman *et al.*, J. Chem. Phys. **131** (2009) 244305.

[3] S. Ishikawa, K. Okada, H. Iwayama and E. Shigemasa, UVSOR Activity Report **42** (2015) 121.

[4] T. Kaneyasu, Y. Hikosaka and E. Shigemasa, J. Electron Spectrosc. Relat. Phenom. **156-158** (2007) 279.

BL6U

# Dissociation of CH<sub>3</sub>OH Dication Studied by an Electron-Ion Coincidence Method

M. Higuchi<sup>1</sup>, H. Iwayama<sup>2</sup>, E. Shigemasa<sup>2</sup> and Y. Hikosaka<sup>3</sup>

<sup>1</sup>Department of Environmental Science, Niigata University, Niigata 950-2181, Japan <sup>2</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan <sup>3</sup>Graduate School of Medicine and Pharmaceutical Sciences, University of Toyama, Toyama 930-0194, Japan

A molecule absorbing a soft x-ray photon undergoes inner-shell photoionization and subsequently Auger decay. Because two electrons are emitted through this sequential process, the molecule with two positive charges, called dication, is produced. The dication often dissociates into ion pairs, due to the Coulomb repulsion. In this work, we have studied the ion-pair dissociation of CH<sub>3</sub>OH dication states by an electronion coincidence method.

The experiment was performed at the undulator beamline BL6U of the UVSOR facility. We used an electron-ion coincidence setup consisting of a toroidal electron analyzer and an ion momentum imaging analyzer [1,2].

Figure 1 shows a time-of-flight spectrum of ions produced after the C1s inner-shell ionization of CH<sub>3</sub>OH. Peaks for H<sup>+</sup> and H<sub>2</sub><sup>+</sup> fragments can be observed in 800-1100 ns. The manifold seen in 1900-2400 ns is allocated to the fragments resulting from the dissociations comparing with the CO bond cleavage. The fragments keeping the C-O framework are observed in 2800-3000 ns. Hereafter, we focused on the dissociation producing H<sub>2</sub><sup>+</sup> fragments. The two hydrogen atoms can come from C side only, but the hydrogen atom originally at the O-side can contribute. In practice, the time-of-flight spectrum measured for CH<sub>3</sub>OD (not shown) exhibits both H<sub>2</sub><sup>+</sup> and HD<sup>+</sup> peaks.

Figure 2 shows C1s Auger spectra filtered by detections of  $H_2^+$  (blue) and HD<sup>+</sup>s (red), compared to the normal Auger spectra (black). While the coincidence Auger spectrum for  $H_2^+$  shows a peak around 43 eV, the HD<sup>+</sup> peak lies around 35 eV. This observation implies that formation of HD<sup>+</sup> fragments is involved by lower dication states which may be longer lifetime and thus allows the exchange of hydrogens of O-side and C-side before dissociation.

Figure 3 shows correlations of ion fragments formed in pair, observed for  $CH_3OD$ . The counterparts of  $HD^+$ fragments are mainly the fragments which keeps CO bond, i.e.  $COH^+$  and  $COH_2^+$ . On the other hand, half of the  $H_2^+$  fragments are formed in pair with the fragments resulting from CO-bond braking, e.g.  $CH_2^+$ and  $CH_3^+$ .



Fig. 1. Time-of-flight spectrum of ions produced after C1s inner-shell ionization of CH<sub>3</sub>OH.



Fig. 2. Coincidence Auger spectra filtered by detections of  $H_2^+$  (blue) and  $HD^+$  fragments (red), compared to the normal Auger spectra (black).



Fig. 3. Correlation map for ion pairs detected in coincidence.

T. Kaneyasu, Y. Hikosaka and E. Shigemasa, J. Electron Spectrosc. Rel. Phenom., **156-158** (2007) 279.
 Y. Hikosaka, Y. Shibata, K. Soejima, H. Iwayama and E. Shigemasa, Chem. Phys. Lett., **603** (2014) 46.

#### **Dissociation Dynamics of Doubly-Ionized Water Molecules**

M. Kikuchi<sup>1</sup>, M. Higuchi<sup>1</sup>, H. Iwayama<sup>2</sup>, E. Shigemasa<sup>2</sup> and Y. Hikosaka<sup>3</sup>

<sup>1</sup>Department of Environment Science, Niigata University, Niigata 950-2181, Japan

<sup>2</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>3</sup>Graduate School of Medicine and Pharmaceutical Sciences, University of Toyama, Toyama 930-0194, Japan

Interaction of a water molecule with high-energy radiation may lead to inner shell ionization, and an inner shell electron is emitted as a photoelectron. Subsequent Auger decay generates a doubly-ionized water molecule which mainly dissociates to an ion pair by the Coulomb repulsion. In this work, we investigated to the dissociation processes of the doubly-ionized water molecule.

The experiment was performed at the beamline BL6U, by using an Auger electron-ion coincidence spectrometer consisting of a double toroidal electron analyzer and an ion time-of-fight (TOF) analyzer. We measured Auger electron-ion coincidences for gas phases D<sub>2</sub>O as well as H<sub>2</sub>O. Soft X-ray was irradiated to the sample gases introduced to the ionization point. Kinetic energies of the Auger electrons were determined by the arrival positions on the position sensitive detector of the double toroidal electron analyzer. On the detection of the individual Auger electron, an electric field was applied to the ionization point so that fragment ions are measured by the ion TOF analyzer. Auger electron energy determined by the double toroidal electron analyzer indicates the binding energy of the formed doubly-charged ion states, and TOFs of the ions observed in coincidences with the Auger electron reveal the resultant ion-pair.

Figure 1 shows the correlations of TOFs of ion pairs observed in coincidence with all Auger electrons. Clear correlations corresponding to the D<sup>++</sup>OD<sup>+</sup> ion pair and the D<sup>++</sup>O<sup>+</sup> ion pair are observed. The former ion pair results from the two-body dissociation of  $D_2O^{2+} \rightarrow D^{++}OD^+$ , and the later from the three-body dissociation of  $D_2O^{2+} \rightarrow D^{++}OD^+$ , and the later from the three-body dissociation of  $D_2O^{2+} \rightarrow D^{++}OD^+$ . It is estimated that, from the coincidence counts of these two structures in Fig. 1, the two-body dissociation is about 4.5 times more probable than the three-body dissociation.

The black curves in Fig. 2 are the Auger spectra of (a)  $D_2O$  and (b)  $H_2O$ , which show a band structure in 35-50 eV. The coincidence Auger spectra filtered for the two-body dissociation are represented in red, and those filtered for the three-body dissociation is in blue. In both water samples, the two-body dissociation accounts for the majority and yields the peak around 42 eV. In the higher energy side of the band structure, the fraction of the three-body dissociation increases. Comparison between the spectra for  $D_2O$  and  $H_2O$  implies that the contribution from the three-body dissociation is probably because elongation of the O-H bond becomes slower by the deuteration.



Fig. 1. Correlations of TOFs of ion pairs observed in coincidence with all Auger electrons.



Fig. 2. Total Auger spectra (black) of (a)  $D_2O$  and (b)  $H_2O$ , (a)  $D_2O$ , and coincidence Auger spectra filtered for the two-body dissociation (red) and for the three-body dissociation (blue).

#### BL6U

### Site-Specific Production of H<sub>3</sub><sup>+</sup> Ions Following Core Ionization of CH<sub>3</sub>Cl

H. Iwayama<sup>1, 2</sup> and E. Shigemasa<sup>1,2</sup>

<sup>1</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>2</sup>School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585,

Japan

Trihydrogen cation  $H_3^+$  is one of the most interesting molecules in diverse fields from chemistry to astronomy because it is the simplest triatomic molecule and plays an important role in the interstellar. While the  $H_3^+$  ions can be mainly generated from the proton transfer reactant ( $H_2 + H_2^+ \rightarrow H_3^+ + H$ ), it was shown that unimolecular reactions of soft x-ray irradiated CH<sub>3</sub>X molecules (X=Cl, OH, CN, etc.) also have small contributions of  $H_3^+$  formation in the interstellar [1].

In this work, we investigate the  $H_3^+$  production mechanism of soft x-ray irradiated  $CH_3Cl$  molecules with using an Auger-electron-ion coincidence technique, which allows us to correlate Auger final dicationic states with product ions. From coincidence Auger spectra, we reveal dicationic states which form the  $H_3^+$  ions.

The Auger-electron-ion coincidence measurements were performed on the undulator beamline BL6U at UVSOR. The electron ejected at 54.7° with respect to the electric vector of the incidence radiation were analyzed in the energy by a double toroidal analyzer (DTA), while ions were extracted from the interaction region into a momentum spectrometer by a pulsed electric field according to the electron detection. Arrival position on the detector and time-of-flight (TOF) of ions and electrons were recorder for every event. The pass energy of the DTA was set to 200 eV for observing the Auger electrons. The corresponding electron energy resolution was about 1.9 eV. All signals from the detectors were recorded with an 8ch TDC board. We used the photon energies of 220 and 302 eV for the Cl 2p and C 1s core-ionized states, respectively. To obtain total ion TOF spectra, we also measured ions in coincidence with the Cl 2p and C 1s photoelectrons instead of the Auger electrons.

Figure 1 shows total ion TOF spectra following the Cl 2p and C 1s photoionization. Main fragment ions are  $H_n^+$  (n=1,2,3),  $CH_n^+$  (n=0-3),  $CI^+$  and  $CH_nCI^+$  (n=0,1,2).  $CH_3CI^+$  ions were not observed since the parent molecules following the Auger decay are doubly charged. Doubly charged ions such as  $CI^{++}$  and  $CH_nCI^{++}$  (n=0-3) were also observed. The most remarkable difference in fragmentation between the Cl 2p and C 1s photoionization is the relative abundance of  $H_3^+$  ions. The relative intensity of  $H_3^+$  ions for the Cl 2p photoionization is ten times larger than that for the C 1s photoionization.

Figure 2 shows the coincidence Auger spectra with  $H_n^+$  (n=1,2,3) ions in the binding energy scale, in comparisons with the total Auger spectra. It is clearly

seen that the formation of the  $H_3^+$  ions is related to only the lowest band around the binding energy of 32 eV for both the Cl 2p and C 1s photoionization, while the total Auger and coincidence Auger spectra with  $H^+$  and  $H_2^+$ ions are quite different in the two cases. In order to understand the mechanism of such a site-specific production of the  $H_3^+$  ions, theoretical calculations for the Auger final states of the CH<sub>3</sub>Cl molecule are highly desired.



Fig. 1. Time-of-flight spectra of ions taken in coincidence with (a) Cl 2p and (b) C 1s photoelectrons.



Fig. 2. Total and coincidence Auger spectra with Hn+ ions (n=1,2,3) for (a) Cl 2p and (b) C 1s photoionization.

[1] S. Pilling *et al.*, Mon. Not. R. Astron. Soc. **375** (2007) 1488.

BL6U

# Molecular Dynamics of Core Excited N<sub>2</sub> Molecules Studied by an Auger-Electron–Photoion Coincidence Method

H. Iwayama<sup>1, 2</sup> and E. Shigemasa<sup>1,2</sup>

<sup>1</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>2</sup>School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585,

Japan

A core shell electron in a molecule can be promoted to unoccupied orbitals when a photon energy is tuned to resonances. The core excited molecule thus created is highly unstable and relaxes either by radiative decay or Auger electron emission. For light elements (Z < 26), the Auger decay is the dominant process after the core excitation, and various cationic states are formed through the Auger electron emissions. In some cases, core excited molecules become dications by the double Auger decay. The stability and dissociation dynamics of the Auger final states depend on their charge states and electronic states, which can be investigated by using an Auger-electron-photoion coincidence technique. In this work, we investigate the stability and dissociation dynamics of core excited N2 molecules.

The Auger-electron-ion coincidence measurements were performed on the undulator beamline BL6U at UVSOR. The Auger electrons and product ions were measured in coincidence by a double toroidal electron analyzer (DTA) and an ion momentum spectrometer, respectively. The pass energy of DTA was set to 400 eV. All signals from the ion and electron delay-line detectors were recorded with an 8ch TDC board. The photon energy was tuned to 401.1 eV, which corresponds to the resonance energy of the N 1s  $\rightarrow \pi^*$  excitation.

Figures 1(a) and (b) show total and coincidence Auger spectra with  $N_2^+$  and  $N^+$  ions, respectively. The energy scale of the bottom axis is obtained by subtracting the kinetic energy (KE) of Auger electrons from the excitation energy of 401.1 eV. Here this is defined as remaining energy. For cations, the remaining energy corresponds to the binding energy, while it is slightly higher than the binding energy for dications, due to the ejection of a second Auger electron. Below the remaining energy of  $\sim 25$  eV, we observe only  $N_2^+$  ions. This is consistent with the fact that the lowest dissociation limit energy of  $N^+ + N$  is 24.2 eV. On the other hand, we find only  $N^+$  ions above the binding energy of ~25 eV. To identify the contribution of dications resulting from the double Auger decay, we show a coincidence Auger spectrum with  $N^++N^+$  fragment pairs in Fig. 1(c). The spectrum shows the double Auger decay processes can contribute to the Auger final states above the remaining energy of 48 eV.

Figure 2 shows a two-dimensional Auger-electronion coincidence map. The vertical and horizontal axes correspond to the kinetic energy release (KER) of ions and the remaining energy, respectively. We find several diagonal structures, suggesting several dissociation pathways. Dashed lines in Fig. 2 represent lowest dissociation limit energies for N<sup>+</sup> + N and N<sup>+</sup> + N<sup>+</sup>. The horizontal structure at the remaining energy of 48 eV and KER of 0 eV corresponds to metastable N<sub>2</sub><sup>++</sup> ions. Above the remaining energy of 40 eV, the double Auger decay process is dominant. The detail analysis is in progress



Fig. 1. Total (black line) and coincidence Auger spectra (red filled area) with (a)  $N_2^+$  ions, (b)N<sup>+</sup> ions and (c) N<sup>+</sup>+N<sup>+</sup> fragment pairs.



Fig. 2. A two-dimensional Auger-electron-photoion coincidence map. Diagonal dashed lines A and B represent a plot of the KER as a function of the remaining energy for lowest dissociation limits of  $N^++N$  and  $N^++N^+$ , respectively.

#### BL6B

#### **Infrared Microscopy of T- Shape Microfluidics**

M. Nagasaka<sup>1</sup>, H. Yuzawa<sup>1</sup>, M. Nakano<sup>1</sup>, N. Takada<sup>1</sup>, M. Aoyama<sup>1</sup>, E. Rühl<sup>2</sup> and N. Kosugi<sup>1</sup>

<sup>1</sup>Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>2</sup>Physikalische Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin, Germany

Microfluidics is a chemical technique to realize highly efficient chemical reactions in liquids and solutions. The mechanism of such reactions in microfluidics has been studied by thermal lens microscopy [1] and nuclear magnetic resonance methods [2]. It is difficult to apply spectroscopic techniques to microfluidics, especially in the soft Xray regime, since this radiation cannot penetrate a microfluidics cell. Recently, we have developed a liquid cell for soft X-ray absorption spectroscopy (XAS) of liquids in the transmission mode [3]. The liquid layer in the cell is sandwiched between two Si<sub>3</sub>N<sub>4</sub> membranes with the thickness of 100 nm to transmit soft X-rays.

The purpose of this study is to measure XAS and infrared (IR) spectra of structured liquids by developing a microfluidic cell consisting of  $Si_3N_4$  membranes. In the report, we show results from IR microscopy of a T-shaped microfluidics cell during the mixing process of water and ethanol for a proof-of-concept study of a cell that is currently under development.

The experiments were performed by using the IR microscopy IRT-7000 at BL6B combined with a developed microfluidic cell. A T-shape microfluidics setup with a width of 50  $\mu$ m is made from PDMS resin which is covered by a 100 nm Si<sub>3</sub>N<sub>4</sub> membrane (NTT-AT). The adhesion of PDMS to the Si<sub>3</sub>N<sub>4</sub> membrane is realized by pressing a Si frame of the membrane with O-rings. Ethanol and water are mixed in the T-shaped cell with a flow rate of 50  $\mu$ L/min by using syringe pumps. The spatial resolution of 30  $\times$  30  $\mu$ m<sup>2</sup> is reached by using a  $\times$ 16 Cassegrain mirror. IR spectra are taken by detecting the reflected infrared light with an MCT detector.

Figure 1 shows the 2D plot of the IR absorbance in the T-shape microfluidics at 3507 cm<sup>-1</sup>, which is due to the OH stretching mode of water. Ethanol is flowed in the left hand part and water is injected into the right hand part. The ethanol-water mixture is flowed to the lower part after the junction of the liquids. Figure 2 shows IR spectra at different positions of the setup, considering that the absorbance at 3507 cm<sup>-1</sup> of water is larger than that of ethanol. The IR spectra at the positions A, B, and C after the junction of two liquids are similar to each other. The results indicate, however, that the hydrogen bonds between water decrease rapidly after mixing of both liquids.

In subsequent studies, we intend to investigate IR microscopy of chemical reactions using our T-shaped microfluidics setup.



Fig. 1. The 2D plot of the IR absorption at 3507 cm<sup>-1</sup> in the T-shaped microfluidics cell.



Fig. 2. IR spectra at different positions of the microfluidics cell. The positions of data acquisition are shown in Fig. 1. The dashed line indicates the wavenumber of  $3507 \text{ cm}^{-1}$ .

[1] T. Kitamori et al., Anal. Chem. 76 (2004) 53.

[2] T. Tsukahara *et al.*, Angew. Chem. Int. Ed. **46** (2007) 1180.

[3] M. Nagasaka *et al.*, J. Electron Spectrosc. Relat. Phenom. **200** (2015) 293.

# UVSOR User 3









