

III-3

Chemistry

BL1U

Controlling the Orbital Alignment in Atoms using Circularly Polarized Radiation Wave Packets

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We report on a new application of the circularly polarized radiation provided by a helical undulator at a synchrotron light source - the coherent control of excited state alignment [1]. Our method is based on the use of undulator radiation to create longitudinally coherent wave packets with attosecond-controlled spacing [2]. The performance of our scheme is demonstrated by the photoexcitation of helium atoms in the extreme ultraviolet wavelength region by using the temporal coherent control technique.

The experiment was carried out at the beamline BL1U using the tandem undulator consisted of twin APPLE-II devices. We set the upstream and downstream undulators to provide left-circular polarization (LCP) and right-circular polarization (RCP), respectively. The central photon energy of the fundamental radiation was adjusted to ~ 24 eV, at which the period of the radiation is ~ 171 as. Each relativistic electron in the bunch which passes through the tandem undulator emits a pair of wave packets whose waveforms are well-characterized as time-separated 10-cycle oscillations. The spacing between the wave packets was tuned with attosecond precision by the phase shifter magnet.

Figure 1 illustrates the helium atom interacting with the radiation wave packets from the tandem undulator. As a result of the sequential interaction with the wave packets, helium atom is excited to the $1s6p$ coherent superposition state (transition frequency of ω), which consists of the $M_J = \pm 1$ magnetic substates associated with the first (LCP) and second (RCP) parts of the wave packet pair, following the selection rules for dipole transitions. In an orbital picture, the $6p_{\pm}$ orbitals are coherently superposed, forming a $6p$ orbital aligned in the xy -plane. The orbital alignment is controlled by the delay time, where the tilt angle is set to $\omega\tau/2$ with respect to the x -axis. The detector setup allows us to determine the alignment of the $6p$ orbital because the fluorescence photons are preferentially emitted perpendicular to the alignment axis.

Figure 2 shows the fluorescence yield measured as a function of delay time in decays from the $1s6p$ to the $1s2s$ states, revealing a clear sinusoidal modulation. Reflecting the spatial distribution of the dipole emission as shown in the top panel of Fig. 2, we can expect the signal intensity oscillates at the resonant frequency of the $1s6p$ excited state depending on the

delay time. The observed oscillation shows high visibility and is well reproduced by a sinusoidal curve. This supports the applicability of circularly polarized undulator radiation to control excited state alignment based on the temporal coherent control technique.

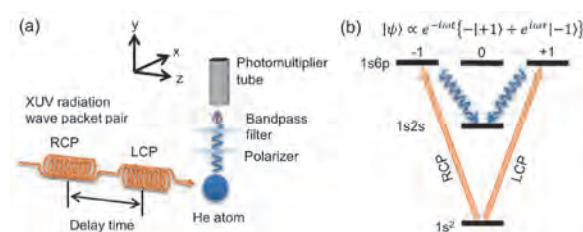


Fig. 1. (a) Interaction between the radiation wave packet pair and helium atom. The fluorescence photons are detected by the photomultiplier tube. (b) The helium atom is excited into the $1s6p$ superposition state which consists of the $M_J = \pm 1$ substates associated with the first (LCP) and second (RCP) parts of the wave packet pair.

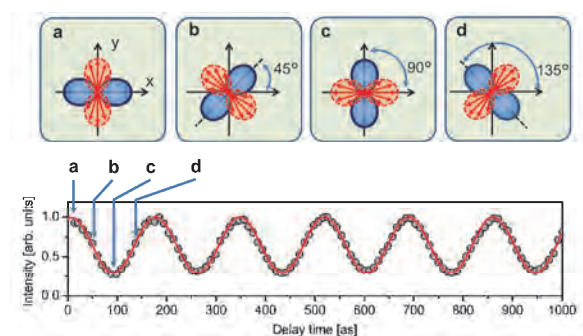


Fig. 2. Fluorescence yield measured as a function of the delay time. The gray circles are measured data and the red line shows the theoretical curve.

[1] T. Kaneyasu *et al.*, Phys. Rev. Lett. **123** (2019) 233401.

[2] Y. Hikosaka *et al.*, Nat. Commun. **10** (2019) 4988.

BL3U

Mechanistic Investigation of Homogeneous Iron-Catalyzed Organic Reactions Based on Solution-Phase L-edge XAS

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We have found that iron complexes of $\text{FeX}_2\text{SciOPP}$ ($\text{X} = \text{Br}$ or Mes) bearing a bulky phosphine ligand SciOPP showed excellent catalytic activities toward the cross-coupling of organometallic reagents of Mg, B, Al, and Zn with various aryl halides [1,2]. Such iron-based catalysts for organic reactions alternative to the conventional precious metal catalysts has been intensively investigated for the development of future sustainable production of chemical compounds. Solution-phase XAS analysis is highly useful for the mechanistic study of iron-catalyzed organic reactions to identify the catalytically active organoiron species with their electronic and molecular structures, because the conventional solution-phase NMR analysis cannot be used due to the paramagnetic nature of organoiron species along with the large paramagnetic shift and peak broadening in NMR spectrum. L-edge XAS of transition-metal catalysts has been expected to be highly useful to investigate the electronic structure of 3d orbitals which provide essential information to elucidate how to work the catalyst. However, solution-phase L-edge XAS measurement is generally difficult because the measurement has to be performed under a vacuum condition where the solution sample is vaporized with vigorous boiling. In this project, we used the specially designed flow-cell for the solution-phase L-edge XAS measurement of homogeneous organic solution of iron complex catalysts. In BL3U, a stainless-steel flow cell has been used for various experiments, but we should carefully avoid contamination of iron species from the environment. For this reason Prof. Nagasaka newly designed and prepared PEEK-made flow cell bearing ultra-thin 100 nm Si_3N_4 membrane X-ray window (Fig. 1. left). The solvent-resistant PEEK made body worked well with an excellent chemical resistance toward the various organic solvents such as THF, CH_2Cl_2 , and benzene, these often used in iron-catalyzed cross-coupling reactions. However, the static electrical charge generated by the frictional interactions between PEEK wall and organic solvents caused undesired baseline shifts in the NEXAFS spectrum. To solve this problem, a gold-made electrode was attached to the Si_3N_4 membrane with earth connection (Fig. 1. right). This flow cell was introduced into the He-filled chamber which inserted into the X-ray optics line, and connected to a syringe pump through a Teflon tube. The THF solution samples of iron catalyst and isolate catalytic intermediates of $\text{FeX}_2\text{SciOPP}$ 1–3 ($\text{X} = \text{Br}$ or Mes) were

prepared in an argon-filled glovebox, because the solution of iron complexes are quite sensitive to oxygen and water, and immediately react to give iron oxide and hydroxide. The XAS measurement was successfully carried out under a flow condition (flow rate: 50–200 $\mu\text{L}/\text{h}$) to give L-edge NEXAFS of 1–3 without the undesired baseline shift by the static electricity (Fig. 2.). However, the penetration of helium gas into the cell causing a bubbling noise could not be perfectly controlled. To solve this problem, Viton O-ring is changed to a fluorosilicone polymer with improving the flow line design and tube connection. This improved cell is testing in 2020 experiment.

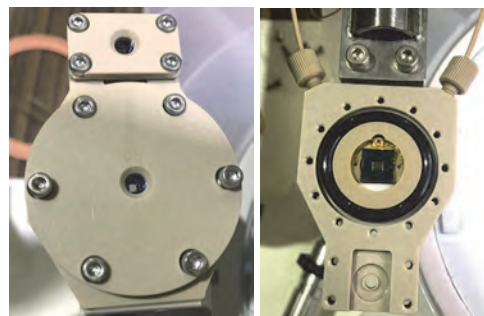
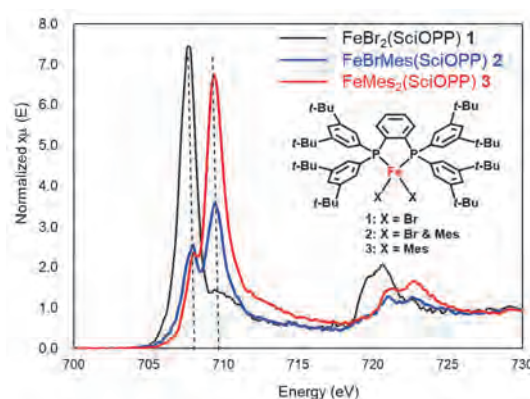


Fig. 1. Photos of the PEEK-made flow cell.

Fig. 2. Solution-phase NEXAFS spectrum of $\text{FeX}_2(\text{SciOPP})$ in THF.

[1] H. Takaya and M. Nakamura *et al.*, Bull. Chem. Soc. Jpn. **88** (2015) 410.

[2] R. Agata, H. Takaya, and M. Nakamura *et al.*, Bull. Chem. Soc. Jpn. **92** (2019) 381.

BLIU

Supramolecular Chirality Induction by Optical Vortex UV Light to Magnetic Azo-metal Complexes

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For several years, we have studied on photochemical materials using optical vortex UV light have attracted attention. In contrast to circularly polarized light (associated with spin angular momentum), a light vortex having a spiral wave front (associated with orbital angular momentum) may provide mechanical torque onto the surface of (photofunctional) materials irradiated. In this context, we attempted molecular orientation control by irradiating linearly and/or circularly polarized (and optical vortex) UV light to polymer films containing (achiral) dinuclear Schiff base metal complexes without photoisomerization moiety in previous study [1,2]. Herein, we have designed new metal complexes having rigid Y-shaped structure with photoisomerization moiety expected to occur Weigert effect to be aligned by polarized UV light. Newly prepared PMMA films from DMF solvent were also employed for enhancing molecular orientation phenomenon induced by several types of UV light irradiation not on the surface but even in the films.

By using laboratory light source, linearly or circularly polarized UV light was irradiated to the PMMA films containing the metal complexes. For example, after linearly polarized UV light irradiation, optical anisotropy of Zn or Cu complexes-PMMA sample was observed as depicted in Fig. 2. Similarly, after circularly polarized UV light irradiation, new CD bands appeared, which suggested chirality attributed not to achiral molecules but to supramolecular arrangement induced by light. Thus, the Zn complex-PMMA was more sensitive to light.

At UVSOR, optical vortex with $l = +1, -1$ orbital angular momentum at 280 nm from linearly polarized light was irradiated to the same sample. CD spectra (Fig. 3) were analyzed with sine curve fitting to extract major linearly polarized light component and minor orbital angular momentum component.

[1] H. Nakatori, T. Haraguchi and T. Akitsu, *Symmetry* **10** (2018) 147.

[2] M. Takase, S. Yagi, T. Haraguchi, S. Noor and T. Akitsu, *Symmetry* **10** (2018) 760.

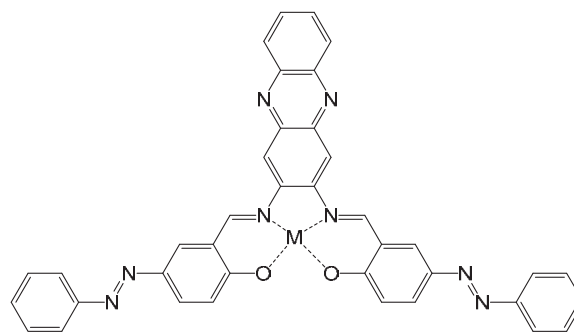


Fig. 1. Molecular structures of metal complexes (M= Cu(II) and Zn(II)).

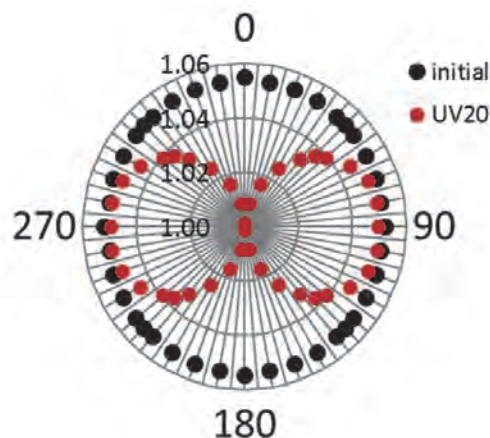


Fig. 2. Angular dependence of absorbance of polarized UV-vis spectra at 385 nm for the Zn complex-PMMA sample.

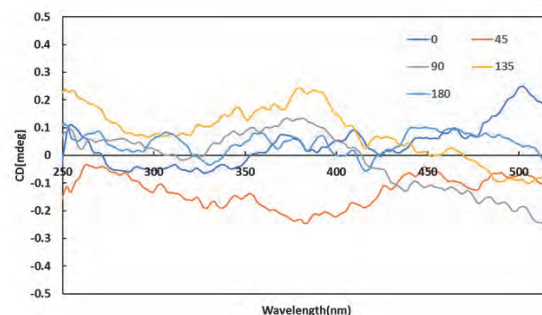


Fig. 3. CD spectra for the Zn complex-PMMA sample after optical vortex irradiation. KBr disk were rotated at five points to cancel artifact CD peaks.

BL1U

Time-Domain Ramsey Interferometry on Rydberg-Electron Wave Packets Generated in Helium Atoms

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Quantum state control of matter by the coherence of light has attracted great interest in various fields such as physics, chemistry, and information processing. The forefront of this coherent control research is rapidly evolving to the extreme ultraviolet wavelength range and attosecond time resolution, thanks to the developments of laser high-harmonic generations and seeded free electron lasers. On the other hand, while synchrotron radiation is high-brightness light covering a wide wavelength range up to X-rays, its longitudinal coherence is significantly lower than that of a laser. Thus synchrotron radiation has not been considered as a tool for coherent control. We demonstrate here the capability of synchrotron radiation to perform coherent control by achieving time-domain Ramsey interferometry on Rydberg wave packets generated in He atoms.

Our scheme for the coherent control by synchrotron radiation uses light wave packet pairs contained in the radiation pulses from two undulators [1,2]. The experiments were performed at the beamline BL1U. The two APPLE-II undulators inserted in series in the U1 straight section of the storage ring were both set to linear polarization mode, and light wave packet pairs of extreme ultraviolet (central photon energy of 24 eV and 10% bandwidth) were emitted. The delay time between the light wave packets was adjusted with an attosecond precision in the range of 2-50 fs, by the three-pole wiggler magnet installed between the two undulators. The central part of the undulator radiation was cut out by an aperture with a diameter of 0.4 mm at 8.2 m

downstream from the downstream undulator, and irradiated with He gases. The bandwidth of the undulator spectrum covers the Rydberg states with principal quantum numbers from 3 to ∞ . Visible/ultraviolet fluorescence emitted in the decays of the populated Rydberg states in He was detected by a photomultiplier tube.

Figure 1 shows the total fluorescence yield measured as a function of the delay time between the light wave packets. It is observed that the fluorescence yield, reflecting the amount of Rydberg states populated by the irradiation, oscillates with a period of about 170 as and its amplitude is modulated. The delay time response of the fluorescence yield is understood in terms of interference of the Rydberg-electron wave packets generated by the light wave packet pair. When the fluorescence from individual Rydberg states was selected in the observation, the relative fluorescence intensities of these states showed remarkable changes depending on the delay time [1]. This observation proves that the populations of the Rydberg states can be controlled by tuning the delay of the light wave packet pair.

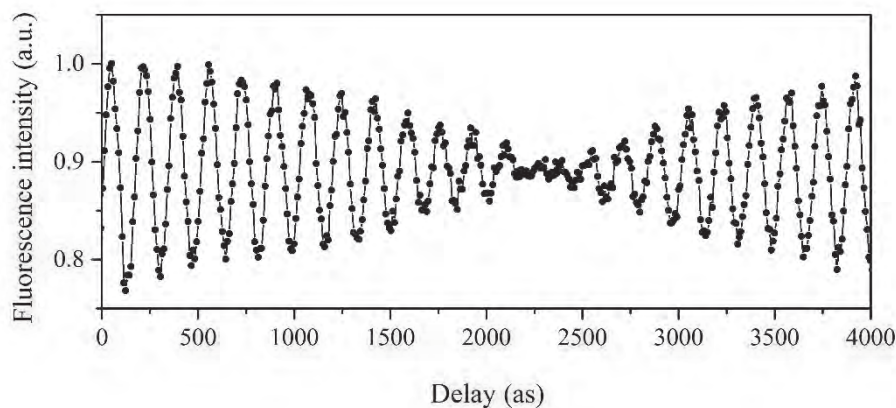
[1] Y. Hikosaka *et al.*, Nat. Commun. **10** (2019) 4988.[2] T. Kaneyasu *et al.*, Phys. Rev. Lett. **123** (2019) 233401.

Fig. 1. Intensities of fluorescent photons from He, measured as a function of the time delay between the light wave packets generated by a tandem undulator [1]. Delay time of the horizontal axis is measured from the original delay (~ 2.1 fs) between the light wave packets.

BL1U

Energy-Dependence of Photoelectron Circular Dichroism of Chiral Molecules

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Photoelectron circular dichroism (PECD) is expected to be a powerful tool for chiral recognition because of the high efficiency due to electric dipole interaction of chiral molecules with radiation. The PECD emerges as forward-backward asymmetry in the photoelectron scattering distribution of enantiomers with respect to propagation of circular polarized light. The origin of PECD has been simply described as an incomplete compensation of the scattering amplitudes of partial photoelectron waves due to the chiral molecular framework. Although a good agreement of the experiments and theoretical model calculations was shown for typical chiral molecules in the previous studies with VUV light, a recent finding of PECD in the higher photon energy region was explained by a different mechanism, indicating the significance of the energy-dependence to understand PECD. In this research project, we have planned to measure PECD in a wide photon energy region to establish an effective model to describe the physical origin of PECD.

We conducted the measurement of PECD at BL1U with a velocity-mapping photoelectron imaging detector [1]. Since this was our first experimental action, detection efficiency and energy- and angular-resolution were carefully inspected based on the comparison with the literature results of typical PECD systems: camphor and methyl-oxirane. Undulator radiation was used to ionize the vapor sample, which was introduced into the vacuum chamber as an effusive beam. Photon energy was varied in the 10 - 20 eV region, which generated photoelectrons with the kinetic energy of 0 - 8 eV. A set of PECD data consisted of the scattering images with circularly polarized radiation. The controllability of the polarization and the photon energy in the BL1U undulator was quite useful for obtaining the difference image data between the right/left-handed circularly polarized radiations under the constant measurement conditions.

Our measurements well reproduced the PECD images of camphor and methyl-oxirane in the previous studies. Examples of the observed results of camphor are shown in Fig. 1. The forward-backward asymmetry with respect to the light propagation direction (vertical in Fig. 1), which is experimental evidence of PECD, exhibited opposite signs for *l*- and

d-camphor enantiomers. The radial distributions indicating the state-specific PECD showed a good agreement with the previous measurements. The photon energy dependence of the PECD images was also confirmed in this measurement (Fig. 1). Further analysis was limited at present by a relatively large photon energy width ($\Delta E/E \approx 10\%$), which smears PECD due to overlapping of the photoelectron bands.

Feasibility of the PECD measurements with BL1U was positively demonstrated in the present study. We found possible modifications to BL1U to improve the quality of the PECD data.

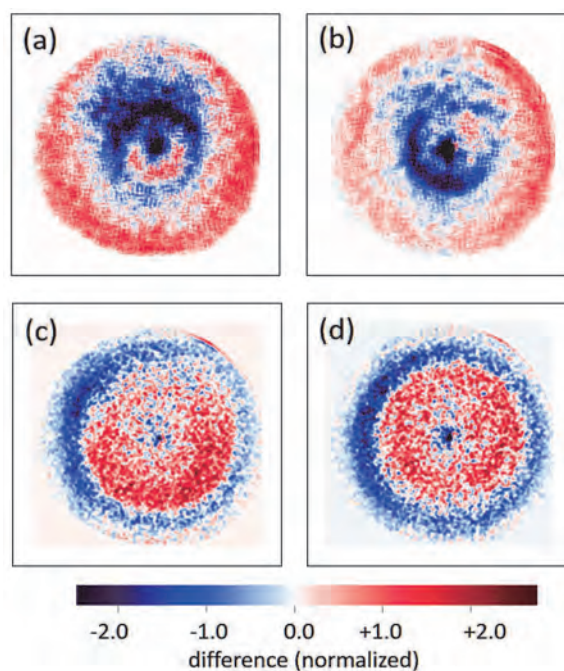


Fig. 1. Photoelectron circular dichroism of *l*- and *d*-camphor enantiomers measured at BL1U. (a) and (c); *d*-camphor, (b) and (d); *l*-camphor. Photon energy-dependence is shown as the difference between the image data with $h\nu = 120$ nm ((a) and (b)) and $h\nu = 60$ nm ((c) and (d)).

[1] T.Kaneyasu *et al.*, Phys. Rev. A **95** (2017) 023413.

BL1B, BL6B

Low-Frequency and THz Region Spectroscopy on Various Organic Molecules to Elucidate Microwave-Enhanced Organic Reactions

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THz and Low-frequency region spectroscopic analysis was performed on various organic compounds to investigate the dynamic behavior of organic molecules under microwave irradiation.

Microwave-enhanced chemical process has been recently focused intensely because the high-speed and high-selective molecular conversion provide a highly efficient chemical process which never accessible by using the conventional heating techniques such as oil bath and electric heater. Prof. Yamada and his colleagues found that axially chiral biaryl compounds such as 1-methyl-6*H*-naphtho[2,1-*c*]chromen-6-one **1** show microwave-enhanced racemization behavior under the irradiation of 2.45 GHz microwave, where the corresponding enantiomerically pure atropisomer efficiently undergoes racemization through the rotation around the biaryl axial linkage [1]. Theoretical simulation demonstrated that the rotation-induced atropisomerism closely corresponds to molecular dynamics coupled with THz to low-frequency vibration modes (5–800 cm⁻¹). We considered that microwave irradiation could excite the internal rotation through such vibration modes and the molecular dynamics under microwave irradiation can be detected by THz and low-frequency region vibration spectroscopy. For this reason, we examined the THz-low frequency spectroscopic analysis of

various biaryl organic compounds including **1**.

All the samples of biaryl compounds were once dissolved into the appropriate solvents such as CH₂Cl₂ and THF and directly dropped onto a THz-transparent diamond window to set the sample stem which insets into the vacuum chamber. The THz-low-frequency measurement carried out under the standard condition of the beamline using HDL-5 Infrared Laboratories I.R detector bolometer in the range of 30–130 and 130–680 cm⁻¹ with appropriate beam splitters of Mylar and KBr/Ge, respectively. The resulting raw spectrum was processed by dividing the reference spectrum of diamond plate for baseline correction. Theoretical simulation of the spectrum was performed by DFT at M06-2x/6-311G+(d,p) level of theory using vibrational frequency scale factor for this level (0.967) [2]. The spectrum of compound **1** is shown in Fig. 1. with the corresponding DFT-simulated spectrum where the spectrum in the Mid-infrared range from 350–680 is qualitatively agreed with the real spectrum.

[1] S. Tashima, K. Nushiro, K. Saito and T. Yamada, *Bull. Chem. Soc. Jpn.* **89** (2016) 833.

[2] Computational Chemistry Comparison and Benchmark DataBase (CCC BDB), <https://cccbdb.nist.gov/vibscalejust.asp>

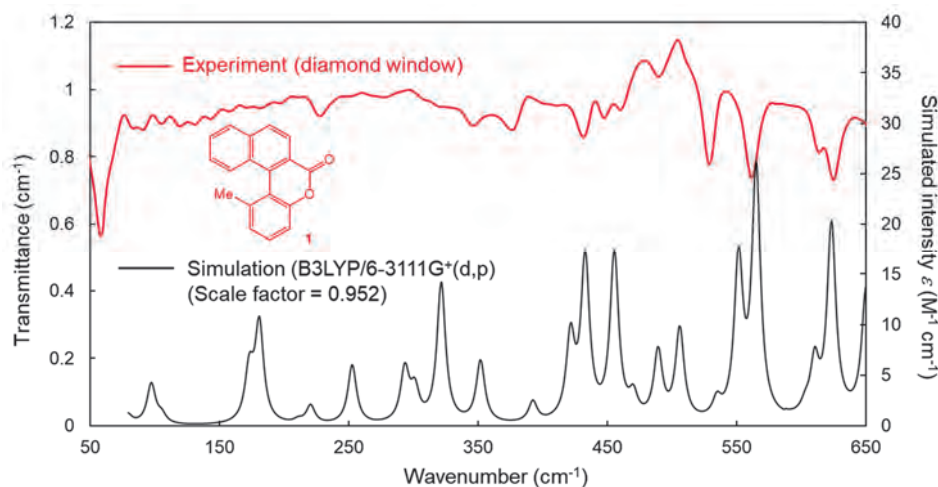


Fig. 1. Low-Frequency IR Spectrum of **1**: Experimental (red solid line) and DFT-simulated with smearing (black solid line).

BL3U

π - π Interactions Between Liquid-Crystal Molecules Studied by *in-situ* X-ray Absorption Spectroscopy

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The liquid crystal is one of the most important materials for display devices. In the case of nematic liquid crystals, the rod-shaped organic molecules have no position order, but they self-align to have long-range directional order with their long axes roughly parallel. Since X-ray absorption spectroscopy (XAS) is sensitive to a local atomic geometry and the chemical state of the atom of one specific element, XAS spectroscopy is suitable to investigate structures of liquid crystal materials. However, XAS measurement of liquid-crystal materials is limited to one in a solid phase due to the requirement of high vacuums of a sample chamber. Considering the fact that they work as display device in a liquid-crystal phase, we need to measure XAS in a liquid-crystal phase. Recently, our colleague, Nagasaka developed a liquid cell, which allows us to measure XAS spectra of liquid samples [1]. In our work, we measure XAS of liquid-crystal materials in the liquid-crystal phase.

Our sample is 4-Cyano-4'-pentylbiphenyl (5cb), which is one of the most popular liquid-crystal materials. A schematic draw of 5cb molecules is shown in Fig. 1. The phase transition temperature of liquid to liquid-crystal and liquid-crystal to solid are 35 and 22.5 °C, respectively. The XAS measurements were carried out at UVSOR BL3U. After liquid-crystal cell which is composed of two Si₃N₄ membranes was filled with the liquid-crystal sample, the thickness of liquid-crystal sample was optimized by controlling the He gas pressure around the cell. The photon energy was calibrated by using the C-K edge XAS spectrum of the proline thin layer.

Figure 2 shows a C K-edge XAS spectrum of 5cb sample at 26 °C, which correspond to the liquid-crystal phase. We observed several peaks and a strong peak at 285 eV. To understand XAS spectrum and perform a peak assignment, we need theoretical calculation. We introduced a quantum chemical calculation software, StoBe, which is based on the density functional theory and can calculate core hole states. A calculated spectrum is also shown in Fig. 2 and reproduces experimental results well. By analyzing the calculation, it is revealed that the strong peak at 285 eV correspond to a core excitation of C 1s to π^* orbitals of phenyl group.

Figure 3 shows peaks at 285 eV for each phase. We observed high energy shift of the peak at the phase transition between solid and liquid-crystal phases. This phase dependence of core excitations reflects the change of molecular alignments between each phase.

Our results show the phase transition between solid to liquid-crystal phases weaken π - π interaction between molecules.

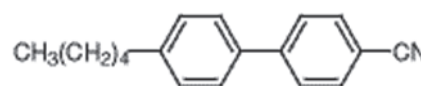


Fig. 1 Schematic draw of 4-Cyano-4'-pentylbiphenyl (5cb) molecules.

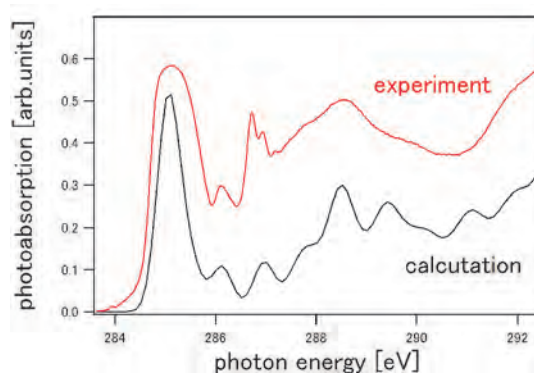


Fig. 2 Experimental and calculated C K-edge spectra of 5cb molecules. Experimental spectra were measured at 26 °C (liquid-crystal phase).

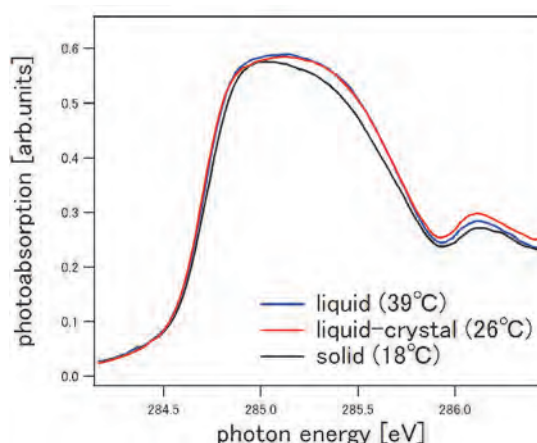


Fig. 3 C K-edge XAFS spectra of 5cb molecules at 18 (solid), 26 (liquid-crystal) and 39 °C (liquid).

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

BL3U

Oxygen K-edge X-ray Absorption Spectroscopy of Aqueous Acetonitrile Solution at Different Concentrations

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Aqueous acetonitrile solution shows microheterogeneity, where two liquids seem to be mixed in a macroscopic scale but are inhomogeneous in microscopic scale [1]. Soft X-ray absorption spectroscopy (XAS) is an effective method to investigate molecular interactions of aqueous acetonitrile solutions since molecular interactions of acetonitrile can be revealed by the C and N K-edge, and the interaction of solvent water molecules is separately revealed by the O K-edge. Recently, several groups measured O K-edge XAS of aqueous acetonitrile solutions. By increasing the molar fraction of acetonitrile, the main-edge peak (538 eV) becomes sharper in profile, which means that isolated water molecules exist in aqueous solutions [2]. However, their studies reported molecular interaction of solvent water only in a limited concentration region. In this study, we have investigated molecular interactions of solvent water in the wide concentration regions by using O K-edge XAS [3].

The experiments were performed at soft X-ray beamline BL3U. XAS spectra of liquid samples were measured by a transmission-type liquid flow cell [4].

Figure 1(a) shows O K-edge XAS spectra of aqueous acetonitrile solutions $(\text{CH}_3\text{CN})_x(\text{H}_2\text{O})_{1-x}$ at different concentrations from $x = 0.0$ to 0.9 by 0.05 step. By increasing the molar fraction of acetonitrile (x), the pre-edge peaks (535 eV) related to the $4a_1$ states show lower energy shifts and the main-edge peaks related to the $2b_2$ states show sharper profile. The sharp profile in the main-edge peak is caused by decreasing molecular interactions among water molecules. This sharp profile starts to grow above $x = 0.2$, which means that water molecules form the dipole (DP) structure with acetonitrile at $x > 0.2$.

Figure 1(b) shows the energy shifts of the pre-edge peaks at different concentrations from those of liquid water ($x = 0.0$). The larger energy shift at higher molar fraction of acetonitrile is caused by the formation of an isolated water molecule enclosed in liquid acetonitrile as shown in the inset. The concentration-dependent energy shift is gentle at $0.7 > x$ but is larger at $x > 0.7$. It suggests that the population of isolated water molecules embedded in liquid acetonitrile is rapidly increased at $x > 0.7$.

We have also measured C and N K-edge XAS of aqueous acetonitrile solution at different concentrations for studying molecular interaction of acetonitrile in aqueous solution [3]. In the middle concentration region, the acetonitrile clusters are fully

surrounded by water with the DP interactions, which is the key structures to emerge the microheterogeneity. The energy shifts of the pre-edge peaks in O K-edge XAS also confirm the DP interactions between acetonitrile and water, which forms isolated water molecules in acetonitrile-rich regions.

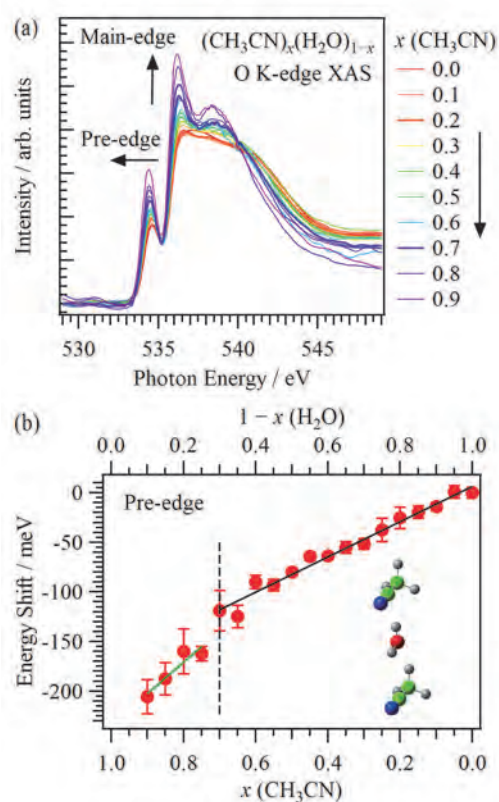


Fig. 1. (a) O K-edge XAS spectra of aqueous acetonitrile solution at different concentrations. The pre-edge and main-edge peaks are changed to the direction of arrows by increasing the molar fraction of acetonitrile (x). (b) Energy shifts of the pre-edge peaks at different concentration from those of liquid water ($x = 0.0$). The inset shows a water molecule enclosed in two acetonitrile molecules.

- [1] Y. Marcus, *J. Phys. Org. Chem.* **25** (2012) 1072.
- [2] N. Huang *et al.*, *J. Chem. Phys.* **135** (2011) 164509.
- [3] M. Nagasaka, H. Yuzawa and N. Kosugi, *J. Phys. Chem. B* **124** (2020) 1259.
- [4] M. Nagasaka *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **224** (2018) 93.

BL3U

Hydrated Water Structure of *N,N*-Dimethylglycine Studied by Soft X-Ray Absorption Spectroscopy

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Living cells protect themselves from external stress such as hydrostatic pressure and drought by regulating the amount of solutes called osmolytes [1]. Several organic osmolytes have a characteristic feature of the form as a zwitterion. Found most commonly in cells are fully *N*-substituted amino acids, although partially- and non-substituted amino acids also take a zwitterionic form. Glycine betaine (also known as *N,N,N*-trimethylglycine or TMG) is among the most common species in cells, and its amount dominates much over *N*-methylglycine (NMG) and *N,N*-dimethylglycine (DMG). Many recent studies have revealed that the higher-order structure of proteins is protected through the indirect interaction between the hydrated proteins and osmolytes. Studying the difference in hydration structure between TMG and DMG gives a clue to understand why biological systems prefer fully *N*-substituted amino acids over partially substituted counterparts. The hydration of DMG has not yet investigated in this sense. We therefore focus in this report on the electronic structure of the hydrated water molecules of DMG compared with that of TMG by soft X-ray spectroscopy.

Photoabsorption spectra at the oxygen K-edge were measured in the transmission mode at room temperature. Aqueous solutions of DMG and TMG with concentrations up to 1.0 M were introduced by means of a tubing pump into a liquid flow cell [2] installed on the soft X-ray beamline BL3U. The flow cell for this study was equipped with a pair of windows made of thin silicon nitride membrane. The incident photon energy was calibrated to the peak at 530.88 eV of a polymer film [3].

Figure 1 shows the O 1s absorption spectra of liquid water, DMG and TMG aqueous solutions enlarged at the water 4a₁ resonance band. The peak top at 534.6 eV is shifted by +0.20 and −0.05 eV for DMG and TMG solutions, respectively. The apparent shift observed for the TMG solution is consistent with our previous measurement [4]. The hydration structure is extracted by deconvolution of the band consisting of the hydrated and bulk water components thanks to the chemical shift present in the inner-shell excitation of molecules under different chemical environments. The second and fourth derivatives (not shown) of the absorption spectra of liquid water suggest that there exist two components in the 4a₁ resonance band. The derivatives for the DMG and TMG solutions indicate that additional components are necessary to reproduce

the spectra. The latter components can be ascribed to the hydrated water acting as a hydrogen-bond donor or acceptor to interact with the solutes. The validity of the present analysis is supported by the fact that the area of the components increases with the concentration.

The apparent blue shift for the DMG solution is reasonably explained by the presence of the hydrated water acting as a hydrogen-bond acceptor. Because its component is placed at the higher energy side of the band, the intensity around it is higher than that of liquid water and of the TMG solution. A further analysis is in progress and the results will be published elsewhere.

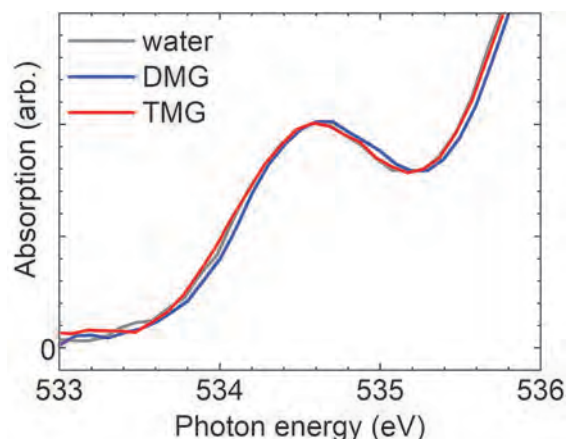


Fig. 1. Enlarged O 1s photoabsorption spectra of liquid water, 1.0-M DMG and 1.0-M TMG aqueous solutions in the 533–536 eV region.

[1] P. H. Yancey, M. E. Clark, S. C. Hand, R. D. Bowlus and G. N. Somero, *Science* **217** (1982) 1214.

[2] M. Nagasaka, T. Hatsui, T. Horigome, Y. Hamamura and N. Kosugi, *J. Elec. Spectrosc. Relat. Phenom.* **177** (2010) 130.

[3] M. Nagasaka, H. Yuzawa, T. Horigome and N. Kosugi, *J. Elec. Spectrosc. Relat. Phenom.* **224** (2018) 93.

[4] S. Ohsawa, N. Fukuda, H. Iwayama, H. Yuzawa, M. Nagasaka and K. Okada, *UVSOR Activity Report* **2018** **46** (2019) 115.

BL3U

X-ray Absorption Measurements Applied to Aqueous Solutions of Carboxylate Ions, in the Vicinity of the O K-edge Ionization Thresholds

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It is well established in organic chemistry that the reactivity of a specific group can be predicted considering several additive or competing effects influenced by the energy position and occupation of the frontier orbitals. In this context, it is interesting to evaluate the role of the molecular skeleton on which a carboxylate group is fixed (R in R-COO⁻), and how its inductive or mesomeric properties might influence the reactivity of the system.

One method to determine the energy position of the unoccupied orbitals of carboxylate is to perform XAS measurements. This was done for instance on aqueous solutions of acetate salts – with the motivation to probe the pairing efficiency of -COO⁻ with different types of positive ions [1].

At the beamline BL3U, and using the liquid cell in transmission mode, we measured XAS in the vicinity of the O K-edge ionization threshold on sodium formate, acetate, propionate, trifluoroacetate and benzoate (R = H, CH₃, C₂H₅, CF₃ and C₆H₅ respectively). See Fig. 1 (C₂H₅ spectrum is not shown but the resonances position is similar to those of CH₃).

The resonance located at $h\nu = 535$ eV is attributed to the O1s excitation of water to its first empty orbital. The O1s $\rightarrow \pi^*_{CO}$ resonances associated with the -COO⁻ group are located between 531.5 eV and 533.5 eV, and the small structure at 530.9 eV is due to surface oxidation of Si₃N₄ membranes. To give a preliminary interpretation of these results, we looked at the inductive and mesomeric properties of R. With R = H taken as a neutral reference, CF₃ and C₆H₅ are electron withdrawing groups (-I), and CH₃ and C₂H₅ are electron donating groups (+I). CF₃ withdraws electrons because of the very strong electronegativity of the fluorine atoms. C₆H₅ is also generally considered as -I compared with hydrogen due to the sp² hybridization of the carbon atom of the phenyl ring bonded to -COO⁻. On the contrary, for CH₃ and C₂H₅, the carbon bonded to the carboxylate has a sp³ hybridization and is considered as electron donating. The sp² hybridized orbitals have a larger s-character than the sp³ ones, and contrary to the 2p-electrons, the 2s-electrons have the property to be more tighten to the nucleus. This leads to less diffuse sp² hybridized orbitals and to an increase of their electronegativity. To explain the strong shift of the C₆H₅ group, one can invoke its mesomeric property (see Fig.

2). Despite more complex and probably weaker, a similar effect might be considered for CF₃ as well due to possible hyperconjugation process [2].

All effects taken into account, it seems that the total charge density located in the vicinity of the oxygens of the carboxylate group plays a crucial role on the resonances position. Induction has an influence on the σ -skeleton of the molecule, and thus might modify the spatial extension of the oxygen lone-pairs carried by -COO⁻, and electron delocalization through the π -system clearly increases the negative charge on the oxygen of carboxylate. These hypotheses need to be confirmed, and their relation with the resonances position will be the subject of theoretical investigations.

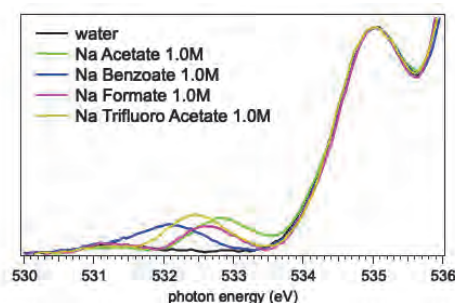


Fig. 1. X-ray absorption spectra of 1 M aqueous solutions of sodium formate, acetate, propionate, trifluoroacetate and benzoate, in the vicinity of the O K-edge ionization thresholds. Normalization is done on the peak maximum at 535 eV.

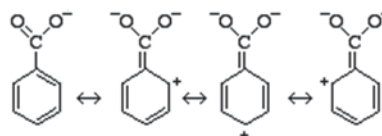


Fig. 2. Resonating forms of benzoate.

[1] J. S. Uejio *et al.*, PNAS **105** (2008) 6809, E. F. Aziz *et al.*, J. Phys. Chem. B **112** (2008) 12567, T. Petit *et al.*, Structural Dynamics **1** (2014) 034901.

[2] L. M. Stock, M. R. Wasielewski, *Progress in Physical Organic Chemistry* 13, chapter 4 (John Wiley & Sons, Inc., 1981).

BL3U

NEXAFS Study of μ -Nitrido-Bridged Iron Phthalocyanine Dimer with Graphite Surface

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Direct C-H activation of light alkanes such as methane and ethane under mild reaction condition is an important challenge in the field of catalytic chemistry because efficient conversion of light alkanes into valuable chemical raw materials can contribute to reduce our dependence on petroleum resources. μ -Nitrido-bridged iron phthalocyanine dimer (**1** in Fig. 1) is one of the most potent molecule-based catalysts for direct C-H activation of methane and ethane [1,2]. It can catalytically convert light alkanes into corresponding alcohols, aldehydes, and carboxylic acids in an acidic aqueous solution at a lower temperature below than 100 °C in the presence of H₂O₂. Recently, we found that the catalytic methane oxidation activity of **1** was significantly enhanced by adsorption on graphite surface. In order to clarify the mechanism of this enhancement, we investigated the structure of **1** on graphite surface, as well as the interaction between **1** and graphite by XAFS study.

1 was adsorbed on a highly oriented pyrolytic graphite (HOPG) to prepare **1**/HOPG as shown in Fig. 1. N K-edge NEXAFS measurements were performed at the soft X-ray beamline BL3U of UVSOR [3]. For these measurements, **1**/HOPG was fixed with double-sided conductive carbon tape onto a stainless sample holder. The holder was fixed on a rotatable linear and installed into a vacuum chamber ($< 1 \times 10^{-5}$ Pa). The N K-edge NEXAFS spectra were obtained in total electron yields by measuring a sample drain current.

Figure 2 (a) shows a comparison of the NEXAFS spectra obtained at three different incident angles ($\theta = 90^\circ$, 55° , and 30° from the HOPG surface). The peaks at around 398 eV are assignable to the excitation of N 1s core electrons to the C=N π^* orbitals of the phthalocyanine. Considering that the C=N π^* transition moment is perpendicular to the p-surface of the phthalocyanine, the high intensity of the π^* peak at $\theta = 30^\circ$ implies that the π -surface was parallel to the HOPG surface. Figure 2 (b) shows incident-angle dependence of the C=N π^* peak intensity at 398 eV with the simulated curve calculated from the tilted angle of the C=N π^* transition moment from the normal of the HOPG surface [4]. As a result of the fitting procedure, the tilted angle of the C=N π^* transition moment is approximately 0 from the surface normal. This indicates that the phthalocyanine π -surface was parallel to the HOPG surface as shown in Fig. 1b.

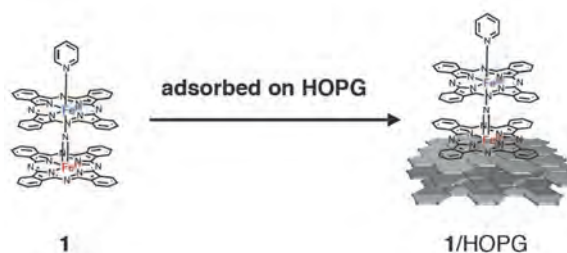


Fig. 1. Adsorption of **1** on a HOPG substrate.

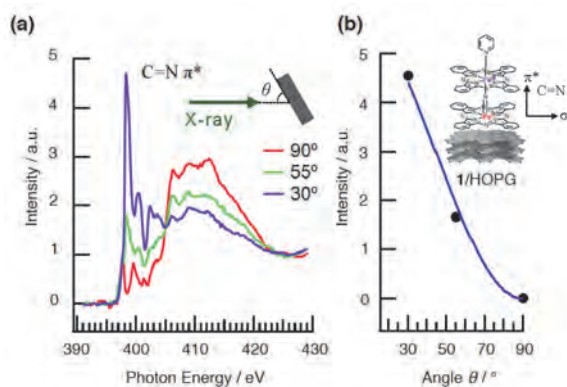


Fig. 2. (a) Comparison of the NEXAFS spectra of **1**/HOPG at three different incident angles ($\theta = 90^\circ$, 55° , and 30°). (b) Dependence of the C=N π^* peak intensity (398 eV) on the incident angle with the simulated curve.

[1] P. Afanasiev and A. B. Sorokin, *Acc. Chem. Res.* **49** (2016) 583.

[2] Y. Yamada, K. Morita, N. Mihara, K. Igawa, K. Tomooka and K. Tanaka, *New J. Chem. M.* **43** (2019) 11477.

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BL3U

Oxygen K-edge X-ray Absorption Spectroscopy of Aqueous Ethanol Solution at Different Concentrations

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Aqueous ethanol (EtOH) solution is a model to explore competition between hydrophilic (namely, HB: hydrogen bond) and hydrophobic interactions and is important to understand several physical, chemical, and biological phenomena [1]. Soft X-ray absorption spectroscopy (XAS) is an effective method to investigate HB with water molecules [2]. Recently, several groups measured O K-edge XAS of aqueous EtOH solutions [3,4], but they reported spectra only in a limited concentration region. In this study, we have investigated HB interaction between EtOH and water in the wide concentration region by O K-edge XAS.

The experiments were performed at soft X-ray beamline BL3U. XAS of liquid samples were measured by a transmission-type liquid flow cell [5]. Liquid samples are exchanged in situ by using a tubing pump without changing the sample position.

Figure 1(a) shows O K-edge XAS spectra of aqueous EtOH solutions at different concentrations at 25 °C. In the XAS spectrum of liquid water ($x = 0.0$), the pre-edge peak at 535 eV corresponds to the transition of O 1s electron to an unoccupied $4a_1$ orbital and reflects HB interaction between water molecules [2]. On the other hand, the pre-edge feature of liquid EtOH ($x = 1.0$) is embedded in the main peak at 538 eV, as observed in the previous study [3, 4]. As observed in the inset of Fig. 1(a), the pre-edge region shows isosbestic points at 534.9 and 535.9 eV. It indicates that the pre-edge region consists of two spectral contributions from EtOH and water, which is also suggested by the previous study [3].

Figure 1(b) shows spectral fractions of EtOH and water in the pre-edge region at different molar fractions of EtOH (x) obtained by fitting the superposition of pure EtOH ($x = 1.0$) and pure water ($x = 0.0$). The spectral fraction of water is decreased and that of EtOH is increased by increasing the molar fraction of EtOH (x). However, these changes show nonlinear features, where the changes of EtOH is crossed with that of water at $x = 0.65$. It is a different trend from O K-edge XAS of aqueous methanol (MeOH) solutions, where the spectral fraction of MeOH is changed linearly and is crossed at $x = 0.5$ [6]. Since the ethyl group is larger than the methyl group, the HB interaction between water molecules would be increased by the stronger hydrophobic interaction in EtOH than in MeOH, resulting the higher ratio of water spectral fraction at the EtOH-rich concentration region.

In the future, we will discuss hydrophobic interactions of the ethyl group in EtOH more directly from the C K-edge XAS spectra.

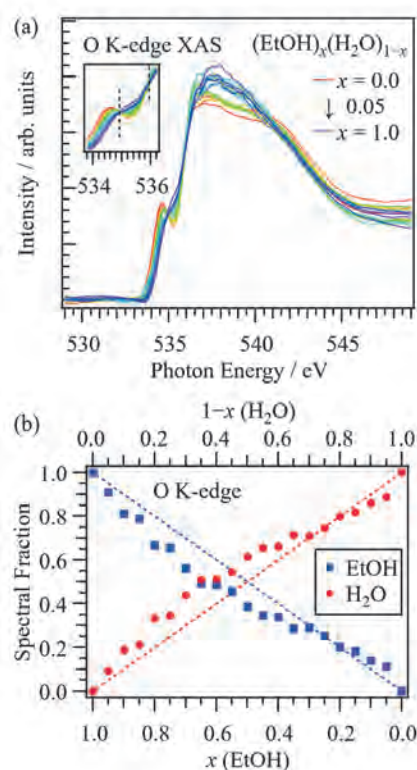


Fig. 1. (a) O K-edge XAS spectra of aqueous EtOH solutions at different concentrations from $x = 0.0$ to 1.0 by 0.05 step. The inset shows the expansion of the pre-edge region. (b) Spectral fractions of EtOH and water in the pre-edge region as a function of the molar fraction of EtOH (x) obtained by fitting the superposition of pure EtOH ($x = 1.0$) and pure water ($x = 0.0$).

- [1] A. Ghoufi *et al.*, J. Phys. Chem. B **120** (2016) 793.
- [2] J. W. Smith and R. J. Saykally, Chem. Rev. **117** (2017) 13909.
- [3] I. Juurinen *et al.*, J. Phys. Chem. B **118** (2014) 8750.
- [4] R. K. Lam *et al.*, J. Chem. Phys. **144** (2016) 191103.
- [5] M. Nagasaka *et al.*, J. Electron Spectrosc. Relat. Phenom. **224** (2018) 93.
- [6] M. Nagasaka *et al.*, J. Phys. Chem. B **118** (2014) 4388.

BL3U

Observations of Micelle Formation in Aqueous Organic Solutions Using Soft X-ray Absorption Spectroscopy

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Amphiphilic compounds in aqueous solutions are known to self-assemble into structures known as micelles above some critical micelle concentration (CMC). The role of amphiphiles in cloud droplet nucleation is still debated, with the specific impact of micelles unaccounted for in cloud formation models [1]. The uncertainties involving the formation of cloud droplets from organic cloud nuclei are some of the largest in the understanding of anthropogenic climate forcing [2].

Aqueous solutions of sodium hexanoate were studied using X-ray absorption spectroscopy (XAS) at the BL3U beamline using the liquid flow cell setup. The range of reported CMC values for sodium hexanoate is 0.53–1.7 M [3]. A value of 0.9 M was assumed and solutions at 0.75 and 3 times the CMC value (i.e. 0.68 and 2.7 M) were made for this study. For each concentration, the solutions were made at the pK_a of hexanoic acid as well as one pH unit above and below the pK_a .

The sensitivity of XAS to chemical environment provides information about the bulk properties of the aqueous components. XAS measurements were made at the carbon K-edge in order to specifically capture the aliphatic $R(CH)R'$ and carboxylic $C(=O)OH$ carbon absorption peaks. The measured photon energy range was from 280 to 300 eV with resolution of 0.02 eV from 285 to 290 eV and 0.1 eV for the rest of the energy range. Measurements were also made on pure water in the liquid cell in order to remove the carbon signal from contamination in the beamline and the liquid cell. The energy of the incident X-rays was regularly calibrated using XAS measurements on a thin polymer film (ProLINE) which has a well-defined absorption peak. The temperature of the liquid samples was controlled to 25 °C.

Measured absorption spectra are shown in Fig. 1. Background absorption has been removed by subtracting the pure water spectrum, and each spectrum has been calibrated using the polymer film spectra taken immediately before and after the sample spectrum. For most of the spectra, a main peak is observed at around 289 eV. In general, the absorption of the sample decreases with increasing sodium hexanoate concentration and decreasing pH value.

Changes in concentration and pH also affect the pre-peak to main peak ratio. A large drop in absorption is observed going from pH ~6 to pH ~5 for both sodium hexanoate concentrations. At low pH values, the absolute absorption values of 0.75 CMC solutions are roughly the same as the 3 CMC solutions. For the 3 CMC sodium hexanoate solutions, the main absorption peak mostly disappears.

Additional analysis of the spectra is ongoing, including comparison to previous measurements at BL3U of similar organic compounds in aqueous solution [4]. Detailed fitting of the spectra will be carried out to identify the underlying absorption peaks. Complementary measurements and theoretical prediction for these systems are also in progress.

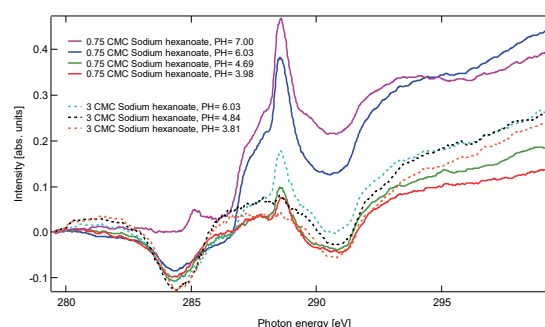


Fig. 1. Preliminary absorption spectra for aqueous sodium hexanoate solutions at 0.75 and 3 times the critical micelle concentration and for various pH values.

[1] N. L. Prisle *et al.*, *Atmos. Chem. Phys.* **10** (2010) 5663.

[2] O. Boucher *et al.*, *Clouds and Aerosols*. In: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge University Press, Cambridge and New York City, 2013).

[3] P. Mukerjee and K. J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems* (U.S. National Bureau of Standards, Washington, D.C., 1972).

[4] J.J. Lin *et al.*, *in prep.*

BL3B

Optical Investigation on Fluoro-olefins in Vacuum-Ultraviolet for New Refrigerant Gas Development

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Chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), and hydrofluorocarbon (HFC) have been used as a refrigerant. These gases have high global warming potential (GWP) over 100. Recently, the hydrofluoroolefin (HFO) gases are expected as new low environmental load refrigerant due to its low GWPs since olefin gas is unstable and easily decompose by ultraviolet light in nature. In order to put HFO into practical use as a refrigerant, it is necessary to clarify the physical characteristics of HFO such as UV absorption and decomposition process. In this study, we measured the vacuum ultraviolet (VUV) absorption and fluorescence of tetrafluoroethylene (TFE). The absorption and fluorescence spectra measurements were carried out in BL3B in UVSOR Synchrotron Facility. TFE gas was filled in the cell having MgF₂ windows at 100 Pa. The optical path length in the cell is 35 mm. The sample-gas filled cell was placed in the vacuum chamber and VUV light was irradiated through the MgF₂ windows and detected by a photodiode. The photoluminescence was measured by the spectrometer at 90 degree from incident beam. Figure 1 shows the photograph of the sample cell and schematics of the experimental setup.

Figure 2 shows the transmission spectra of TFE at 100 Pa. We could clearly observed the absorption at about 145 nm and 190 nm. The absorption at 145 nm is attributed to the stretching and twisting of carbon double band and the 190 nm is the transition from π to π^* , respectively [1].

Figure 3 shows the photoluminescence spectra of TFE at 100 Pa excited by 145 nm. The broad fluorescence from 250 to 350 nm with 276-nm peak was observed. This emission is CF₂ singlet transition [2].

In conclusion, we could observe the optical properties of TFE in VUV region. The results let us know the possibility of the UV- or VUV-induced decomposition dynamics of fluoro-olefins using optical technique such as pump and probe method.

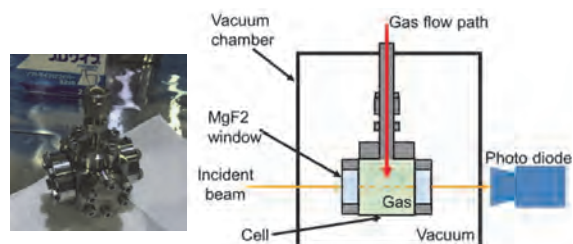


Fig. 1. Photograph of the sample cell and schematics of the experimental setup.

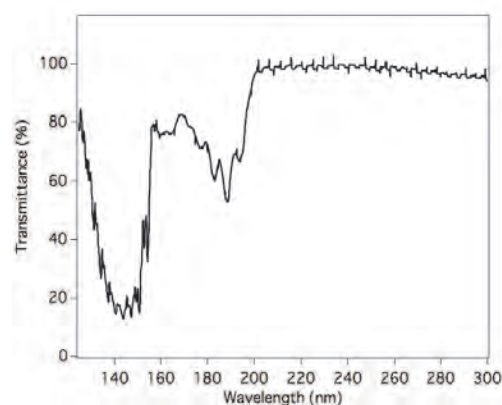


Fig. 2. Transmission spectra of TFE.

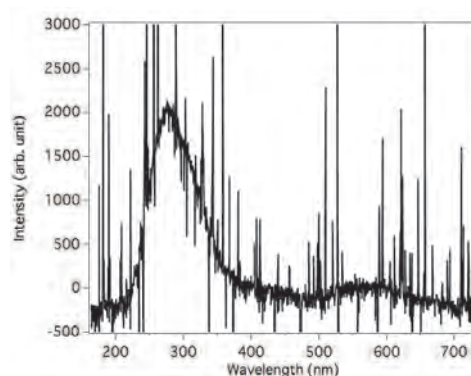


Fig. 3. Photoluminescence spectra of TFE.

[1] G. Belange *et al.*, J. Chem. Phys. **55** (1971) 2055.

[2] B. A. Williams *et al.*, Chem. Phys. Lett. **309** (1999) 75.

BL4B

Electron Coincidence Spectroscopy for Poly(Methylmethacrylate) Thin Film

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Irradiation of soft x-ray to an organic thin film may lead a core electron ejection from a specific atom in the molecular constituent. The core hole thus generated decays mainly by emitting an Auger electron. The spectrum of the Auger electron contains useful information of the valence orbitals relevant to the decay process. In case that the constituent molecule contains the same element at different sites, Auger structures associated with these core holes overlap each other in the conventional Auger spectrum. The atomic site where the core hole has been formed can be identified by the chemical shift of the photoelectron ejected on the core-hole creation. Accordingly, Auger structures associated with individual core holes can be filtered out by coincidence observations with chemical-shifted photoelectrons. Such photoelectron-Auger electron coincidence spectroscopy can be performed with high efficiency by using a magnetic bottle electron spectrometer [1]. The adaptability of the spectrometer to solid samples is already verified [2].

In this study, photoelectron-Auger electron coincidence measurements were made for poly(methyl methacrylate) (PMMA) thin films on a copper wire. The magnetic bottle electron spectrometer employed in this study is equipped with an electrostatic retarder [3], to improve the energy resolving power. PMMA has carbon atoms in different chemical environments within a single unit (see inset of Fig. 1). Figure 1 shows a C1s photoelectron spectrum of PMMA measured at a photon energy of 482.4 eV. At least three photoelectron peaks are identified in the spectrum, and their assignments are indicated with labels of the same colors as used in the chemical formula (inset). The Auger spectra observed in coincidence with the photoelectrons for these three peaks are plotted in Fig. 2, where the colors of the spectra follow those allocated in Fig. 1. Tangible differences in spectral feature are identified among the coincidence Auger spectra. Calculation is under way, to interpret the spectral features.

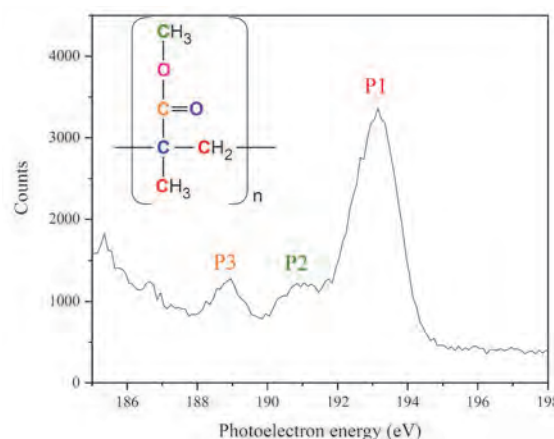


Fig. 1. C1s photoelectron spectrum of PMMA measured at a photon energy of 482.4 eV.

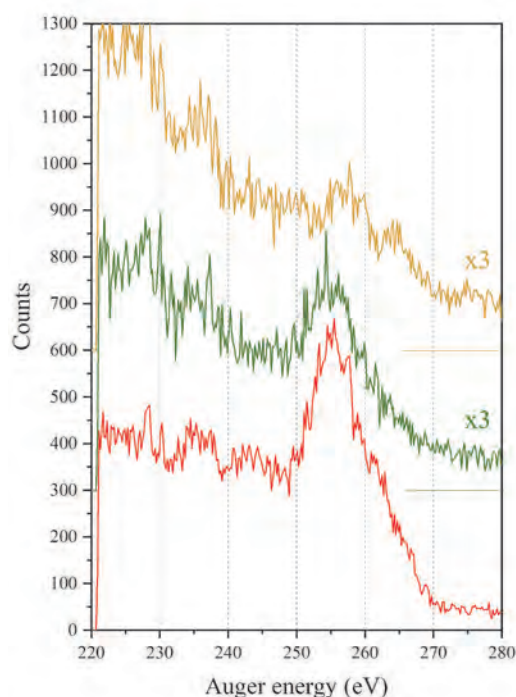


Fig. 2. Auger spectra observed in coincidence with C1s photoelectrons.

[1] J. H. D. Eland *et al.*, Phys. Rev. Lett. **90** (2003) 053003.

[2] Y. Hikosaka *et al.*, J. El. Spectrosc. Rel. Phenom. **213** (2016) 17.

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

BL5B

Evaluation of Polarization Characteristic of Monochromatized Synchrotron Radiation by Observing Zeeman Quantum Beat

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Evaluation of the polarization characteristic of monochromatized synchrotron radiation is an important concern in synchrotron radiation researches. The optical components of monochromators and beamlines modify the original polarization state of the synchrotron radiation. The effect of the modification is pronounced in the extreme ultraviolet (XUV) range, as steeper incidence angles to the optical elements are usually adopted for the monochromatization. The diagnosis of the polarization state of XUV light can be precisely made with an optical method using polarimeters. Such a measurement, however, requires stringent alignments of the polarimeters, and the fabrication and manipulation of an effective polarimeter system are still challenging. Over the optical method, observation of a material process responding to light polarization has an advantage in easy measurement. Angler distribution of photoelectrons emitted from gas samples has been conveniently utilized for evaluating the polarization.

Here we propose that the polarization characteristic of monochromatized synchrotron radiation in the XUV range can be evaluated by observing quantum beat of Zeeman-split Rydberg states in He [1]. A fluorescence decay curve measured at the He 1s→6p excitation energy is presented in Fig. 1 (black dots), where UV fluorescence photons emitted on the 6p→2s decay is detected by a photomultiplier. The photomultiplier was placed at right angles to both the polarization and propagation of the monochromatized synchrotron light, and a magnetic field of 21.1 mT was applied along the light propagation axis.

The fluorescence decay curve exhibits a quantum beat oscillation superposing on the exponential-decay form. This observation manifests the coherent excitation to the Zeeman-split $M_j=\pm 1$ levels. The decay curve can be fitted with the formula

$$I(t) \sim [1 + P \cos \Delta\omega t] \exp(-\gamma t) \quad (1)$$

where P , $\Delta\omega$, and γ are the polarization degree, the transition frequency of the initial excitation, and the lifetime of the excited state, respectively. This equation indicates that visibility of the oscillation superposing on the exponential decay reflects directly the degree of the light polarization. The solid red curve in Fig. 1 is the best fit to the observation, where the temporal resolution of the measurement was assumed as the Gauss function of 2.9 ns FWHM. The fitting indicates the degree of the linear polarization to be $P=0.60\pm 0.05$. The polarization degree may be too poor, even as the light provided by the bending magnet

beamline of the large acceptance in the vertical direction. It is practically anticipated that the fitting result underestimates the actual polarization degree. This is because the fitting does not take into account the large detection solid angle for the present fluorescence observation, while the phase of the quantum beat varies according to the detection angle and the overlap of the quantum beats with different phases in the detection solid angle reduces the visibility of the observed quantum beat oscillation. More accurate estimation of the polarization degree can be achieved by observing fluorescence with a smaller detection solid angle, which is fully feasible considering the favorable count rates in the present investigation.

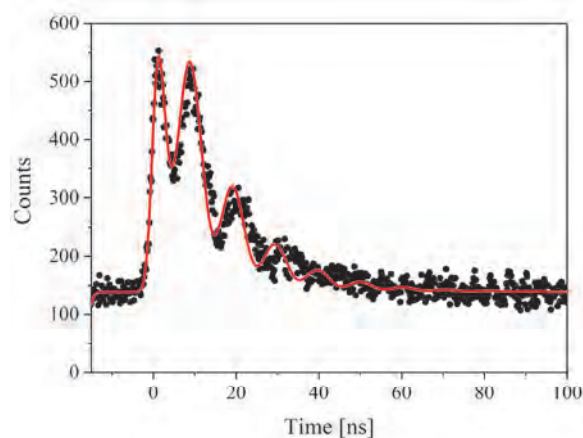


Fig. 1. Fluorescence decay curve (dots) of the 1s6p excited state in helium, measured with a magnetic field of 21.1 mT. It was obtained by an accumulation around 10 min. The red solid curve is the best fit to the observation (see text).

[1] Y. Hikosaka *et al.*, submitted.

BL5B

Visible Fluorescence Studies on the Inner-shell Excitations in Kr and Xe

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The inner-shell excitations of atoms and molecules have been studied in detail along with the development of synchrotron light sources and beamline techniques. Usually the excitation spectra are obtained by detecting the charged particles emitted in the energy relaxation process following the inner-shell excitation. In particular, the ion yield spectroscopy allows one to obtain excitation spectrum which is normally equivalent to the photoabsorption.

We report on visible fluorescence studies on the Kr 3d and Xe 4d excitations. The visible fluorescence photons are emitted in decays of the singly charged ionic states formed by spectator Auger decay of the inner-shell excited state. We show that the fluorescence yield is enhanced at a particular excited state, dependent on the wavelength of the visible fluorescence.

Figures 1 and 2 show the Kr 3d and Xe 4d excitation spectra obtained by the ion and fluorescence yield spectroscopies. The visible fluorescence photons were detected by a photomultiplier tube equipped with a bandpass filter. The assignments of the peaks are indicated in the top panels. It is obvious that the peak structures corresponding to the inner-shell excitations appear more clearly in the fluorescence spectra. This is a consequence of the selective detection of the Auger final states which cannot be populated via valence ionization or normal Auger decay following the inner-shell ionization.

When the wavelength of the fluorescence photon is selected by the bandpass filter, the spectral shapes drastically change. In the Kr 3d excitations, while the $3d^{1/2}5p$ state is enhanced when the 460-nm-wavelength photons are detected, the intensity of the $3d^{1/2}5p$ becomes large in the 450-nm-wavelength spectrum. This spectral feature agrees with the previous measurement [1], and is qualitatively explained by the spectator Auger decay from a specific initial state to a specific final state. Similar behavior is observed in the Xe 4d excitations as in Fig. 2. The measurement approach presented here can be used to investigate the cascade decay following the inner-shell excitation [2]. Additionally, such a detection scheme will allow us to selectively observe the inner-shell excitations even with the use of nonmonochromatized radiation.

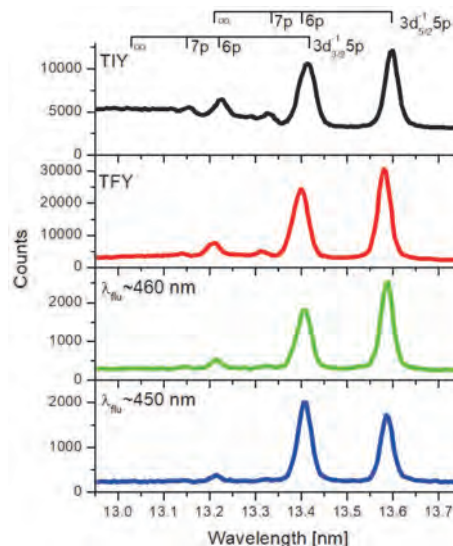


Fig. 1. Total ion yield (TIY), total visible fluorescence yield (TFY) and wavelength-selected fluorescence spectra in the Kr 3d excitation regime.

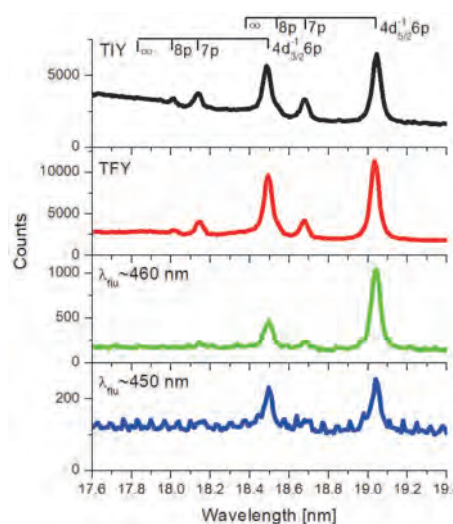


Fig. 2. Total ion yield (TIY), total visible fluorescence yield (TFY) and wavelength selected fluorescence spectra in the Xe 4d excitation regime.

[1] A. Sankari *et al.*, Phys. Rev. A **77** (2008) 032720.

[2] R. Flesch *et al.*, Phys. Rev. A **61** (2000) 062504.

BL6B

Cancellation of Orbital Degeneracy in $\text{Me}_4\text{N}[\text{Pt}(\text{dmit})_2]_2$

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Orbital degrees of freedom and Jahn-Teller effect in the inorganic and organic complex compounds have been investigated by chemists and physicist. Orbital degeneracy in metal-dithiolene complexes has attracted a growing interest since the discoveries of the single-component metal and the photoconductivity. However, only a few efforts have been devoted to revealing the orbital degrees of freedom. We have focused on $\text{X}[\text{Pt}(\text{dmit})_2]_2$ ($\text{dmit} = 1,3\text{-dithiole-2-thione-4,5-dithiolate}$ and $\text{X} = \text{monovalent cation}$) as a candidate of orbital degeneracy. In the past study performed at BL6B and Instrumental center, we revealed that the disproportionation reaction of the $\text{X} = \text{Me}_4\text{Sb}$ and Me_4P salts was ascribed to the cancellation of the orbital degeneracy [1]. However, the behavior of the $\text{C}=\text{C}$ stretching modes of the $\text{X} = \text{Me}_4\text{Sb}$ salt was not always identical to that of the $\text{X} = \text{Me}_4\text{P}$ salt although the crystal structures were isostructural to each other. This result suggested that the inter-molecular interaction depends on the size of counter cation. We moved our focus on the $\text{X} = \text{Me}_4\text{N}$ salt because the cation size is the smallest among three compounds and the transfer integral in a dimer is the smallest. In the present study at BL6B, we analyzed the behavior of the $\text{C}=\text{C}$ stretching modes in the $\text{X} = \text{Me}_4\text{N}$ salt.

Figure 1 shows the infrared spectra obtained by the transmission method. The B mode in the high-temperature phase was changed into the B1 and B2 modes in the low-temperature phase. The C mode was changed into the C1 and C2 modes. The assignments of these vibrational modes are identical to those of the $\text{X} = \text{Me}_4\text{Sb}$ and Me_4P salts [1]. The B and C modes belong to $[\text{Pt}(\text{dmit})_2]_2^{-1}$. The B1 and C1 modes belong to the charge-rich dimer ($[\text{Pt}(\text{dmit})_2]_2^{-1\Delta}$), and the B2 and C2 modes belong to the charge-poor dimer ($[\text{Pt}(\text{dmit})_2]_2^{-1+\Delta}$). This temperature dependence is the evidence for the disproportionation reaction. Similar to the previous results on the $\text{X} = \text{Me}_4\text{Sb}$ and Me_4P salts, the orbital degeneracy at the high-temperature phase of the $\text{X} = \text{Me}_4\text{N}$ salt was canceled in the low-temperature phase.

The intensities of the A1 and A2 modes were inversely proportional to the temperature, which indicates that the A1 mode is assigned to one of the $\text{C}=\text{C}$ stretching modes of a charge-rich dimer. On the other hand, the A1 mode of the $\text{X} = \text{Me}_4\text{Sb}$ salt was negligible in the transmission spectra [1]. The intensity of the $\text{X} = \text{Me}_4\text{P}$ salt was smaller and larger than those of the $\text{X} = \text{Me}_4\text{N}$ and Me_4Sb salts, respectively [1]. Therefore, the

A1 mode belong to the symmetric vibration. Owing to the asymmetric deformation in the charge-rich dimer, the mutual exclusion rule cannot be exactly applicable to both IR and Raman spectra. The difference in the intensities of the A1 modes among three compounds suggests that the degree of deformation of the $\text{X} = \text{Me}_4\text{N}$ salt is larger than those of the $\text{X} = \text{Me}_4\text{N}$ and Me_4Sb salts. This result indicates that the molecular deformation suppresses the instability of the highest occupied orbital arising from the decrease in the transfer integral in the charge-rich dimer.

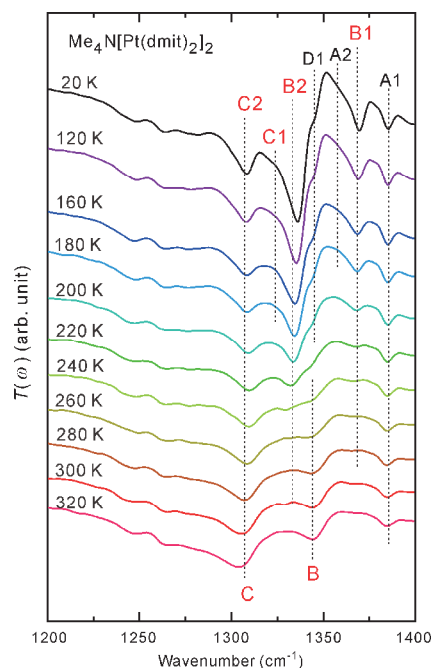


Fig. 1. Transmission spectra of $\text{Me}_4\text{N}[\text{Pd}(\text{dmit})_2]_2$.

[1] T. Yamamoto *et al.*, UVSOR Activity Report 2018 **46** (2019) 126.