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Related Phenomenajournal homepage: [www.elsevier.com/locate/elspec](http://www.elsevier.com/locate/elspec)Reliable absorbance measurement of liquid samples in soft X-ray  
absorption spectroscopy in transmission modeMasanari Nagasaka<sup>a,b,\*</sup>, Hayato Yuzawa<sup>a</sup>, Toshio Horigome<sup>a</sup>, Nobuhiro Kosugi<sup>a,b,\*</sup><sup>a</sup> Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan<sup>b</sup> SOKENDAI (Graduate University for Advanced Studies), Myodaiji, Okazaki 444-8585, Japan

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## ABSTRACT

In soft X-ray absorption spectroscopy in transmission mode (T-mode XAS), it is necessary to optimize the thickness of thin liquid layers for appropriate absorbance around 0.3–0.7 and keep the sample thickness flat within a photon beam. In the present work at the UVSOR Synchrotron Facility, a thin liquid layer is sandwiched between two 100 nm thick Si<sub>3</sub>N<sub>4</sub> or SiC membranes of 2 × 2 mm<sup>2</sup> in a helium chamber with enough working space, and the liquid thickness is optimized by using the elasticity of the membranes under controlling the helium pressure between 0.1013 and 0.12 MPa. The flatness of the liquid sample within a photon beam is investigated with measuring position-dependent O K-edge T-mode XAS spectra of liquid water. In the case of the beam size of 50 μm and the helium pressure of 0.1090 MPa (0.1038 MPa), it is confirmed that the liquid water layer has flat thickness around 200 nm (320 nm) at the center position of 2 × 2 mm<sup>2</sup> sample area with allowance of ±350 μm (±150 μm), where the thickness is ca 900 nm at the brim of the liquid sample area. The pre-edge vs. main edge (Pre/Main) ratio is 0.38 ± 0.01 for the center of the sample area and becomes considerably larger than 0.38 for the off-center position. The deviation from 0.38 is caused by the inhomogeneous thickness and is evaluated in comparison with a model simulation. The Pre/Main ratio can be used to evaluate the flatness in the liquid sample thickness within the beam area of soft X-rays. Positioning of as small a beam as possible on the center of the liquid sample area is essential to obtain reliable T-mode XAS spectra with the present liquid cells.

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## 1. Introduction

X-ray absorption spectroscopy (XAS) is a quite promising method to investigate local structures of liquid samples with the element analysis. Especially, the soft X-ray region below 1 keV has many chemically important absorption edges such as C K-edge (280 eV), N K-edge (400 eV), and O K-edge (530 eV). It is also important that the soft X-ray region covers the L-edge (2p) of 3d transition metals such as Ti L-edge (460 eV), Fe L-edge (700 eV), and Cu L-edge (930 eV), considering that the L-edge is more sensitive to the 3d valence and spin state than the K-edge in the hard X-ray region. XAS in transmission mode (T-mode XAS) of liquid samples can be simply obtained based on the Lambert-Beer law [1–8], though the thickness of liquid samples should be small enough, below a few μm, to allow the transmission of soft X-rays [9]. XAS or XAS-like spectra

have also been measured by detecting secondary or decay processes following the core hole creation, such as fluorescence yields (FY) [10–13], hard X-ray Raman scattering [14–16], and total electron yields [17,18] and inverse partial fluorescence yields [19,20] of liquid microjets. These alternative spectra are compared with the transmission data and the reliability has been discussed from the viewpoint of background subtraction, normalization, saturation effect, and self-absorption effect. In order to reveal detailed local structures of liquid, theoretical simulations of the O K-edge XAS of liquid water [10–13,21–27] should be quantitatively compared with the transmission or absorbance data, based on the calculations of the oscillator strength and electric dipole transition matrix.

The thin liquid layers sandwiched between two Si<sub>3</sub>N<sub>4</sub> membranes have been applied to time-resolved infrared (IR) spectroscopy [28–30] and XAS [30–32] of liquid samples. Nanomaterials in liquid between membranes were measured by transmission electron microscopy [33,34]. Recently, Schreck et al. [5] measured T-mode XAS spectra of liquid samples by developing a new liquid cell. They used 100 nm thick Si<sub>3</sub>N<sub>4</sub> membranes with the window size of 300 × 500 μm<sup>2</sup>, and created inlet and outlet of liquid samples by fabricating the support plate of the membrane. The 250 nm

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thick gold spacers were set between the support plates of the membranes to obtain a thin liquid layer for T-mode XAS. The thickness of the liquid layer was adjusted by evacuating the region around the membranes. It is well known that the uniformity in sample thickness is important to obtain reliable absorbance data from transmission data.

On the other hand, we developed a liquid flow cell for T-mode XAS [4], and applied it to several liquid samples [35–37]. Furthermore, the local structures of water at the solid-liquid interfaces of nanodiamond were studied by the O K-edge XAS [38]. The kinetics of catalytic hydration reactions were studied by successive XAS measurements during the reaction under different temperature [39]. Electrochemical reactions of electrolytes and solid-liquid interfaces of electrodes were studied by using the liquid flow cell with built-in electrodes [40–42]. In our developed liquid cells, the thin liquid layer is assembled by using two 100 nm thick  $\text{Si}_3\text{N}_4$  or SiC membranes with the window size of  $2 \times 2 \text{ mm}^2$ . Teflon spacers of 100  $\mu\text{m}$  thickness are much thicker than the gold spacers used by Schreck et al. [5], and the membrane size  $4 \text{ mm}^2$  is much larger than theirs,  $0.15 \text{ mm}^2$ . The support plates with Teflon spacers are tightly pressed by O-rings outside the liquid layers. A thin liquid layer for the transmission measurement is easily assembled by using commercially standard  $\text{Si}_3\text{N}_4$  and SiC membranes without further fabrication of the membranes. The membranes can be exchanged with no difficulty if necessary.

Although a thin liquid layer is rather easily assembled in our method using affordable size of components, the thickness of a liquid layer may not be flat at different positions within rather large window size of  $2 \times 2 \text{ mm}^2$ . It is well known that O K-edge XAS spectra of liquid water show different pre-edge/main-edge peak ratios when the thickness of the liquid layer is not flat [5]. We have developed a chamber-type XAS measurement system, where the lateral position of the liquid layer can be scanned by using a rather small photon beam and the beam size can be 200, 50, 30, and 10  $\mu\text{m}$  by choosing the membrane size between the helium chamber and the vacuum chamber upstream. In the present study, we have investigated the thickness of the liquid water layer at different positions in soft X-ray transmission measurement by using 200  $\mu\text{m}$  and 50  $\mu\text{m}$  beam size. We have evaluated the influence of the spectral shape caused by the inhomogeneous thickness in comparison with a model simulation. We discuss what condition is necessary to obtain reliable T-mode XAS spectra of liquid samples in our measurement system.

## 2. Experimental methods

The experiments were performed on one of the three soft X-ray in-vacuum undulator beamlines at UVSOR-III Synchrotron, BL3U [43]. Fig. 1(a) shows our chamber-type XAS measurement system that can change the position of a liquid layer sample. This system consists of two chambers in an ultrahigh vacuum condition and in an atmospheric helium condition. The vacuum chamber is connected to the soft X-ray beamline, BL3U. In the helium chamber, a liquid flow cell and some soft X-ray detectors are installed. In the present study of liquid water chosen as a test sample, the two chambers are separated by a 100 nm thick  $\text{Si}_3\text{N}_4$  membrane (NTT AT) with the window size of  $200 \times 200 \mu\text{m}^2$  or  $50 \times 50 \mu\text{m}^2$ , which determines the soft X-ray beam size on the sample. The size  $200 \times 200 \mu\text{m}^2$  is almost the same as the beam size before entering the helium chamber from the monochromator and focusing system at BL3U, and is small enough to endure very different pressures in the two chambers, even larger than 1 atm.

In the present work, the energy resolution of incident soft X-rays at the O K-edge is set to 0.40 eV. When we use a membrane of  $50 \times 50 \mu\text{m}^2$  ( $10 \times 10 \mu\text{m}^2$ ) as a beam spot size, the photon flux is

expected to be reduced by a factor of 1/16 (1/400) or could be more than simply expected if considering the photon beam density is not flat. Assuming the transmitted photon flux after the photoabsorption by samples is  $1 \times 10^8$  photons/s in the case of the beam size of 200  $\mu\text{m}$ , the photon flux in the case of the beam size of 10  $\mu\text{m}$  can be  $2.5 \times 10^5$  photons/s. This assumption is quite reasonable because the incident photon flux in the case of the beam size of 200  $\mu\text{m}$  is  $1 \times 10^{11-12}$  photons/s at BL3U in UVSOR-III, depending on the photon energy resolution. We are using the photodiode detector (IRD AXUV100) which can be used above  $10^5$  photons/s; therefore, the 10  $\mu\text{m}$  beam size is attainable in our system, though we have not yet tested a window size of  $10 \times 10 \mu\text{m}^2$ .

In the atmospheric helium chamber, the flow rate of helium gas is controlled by a mass flow controller (Kofloc), and the pressure can be changed from 0.1013 MPa (1 atm) to 0.12 MPa by adjusting a needle valve in the outlet of helium gas. The sample position of the liquid flow cell can be scanned in  $\mu\text{m}$  scale by using a stepping motor control system. Polarization-dependent XAS spectra can be obtained by rotating the sample cell to change the incident angle of soft X-rays if necessary. The advantage in the chamber-type XAS measurement system is to have a large working space to afford to combine several detection methods. Our system has both a photodiode detector for T-mode XAS and a silicon drift detector (KETEK AXAS-A) for fluorescence-yield (FY) XAS measurement. The XAS spectrum of neat liquid samples is measured in T-mode. The targets, such as solid-liquid interfaces and microfluidic reaction cells, in which soft X-rays are not able to transmit, would be measurable by FY XAS. In the present work on T-mode XAS, we used only the photodiode detector.

Fig. 1(b) shows a schematic of the present liquid flow cell. The helium chamber with a liquid flow cell is also adapted to our own Fourier-transform infrared (FT-IR) and ultraviolet-visible (UV-vis) spectrometers [39]. The structure of liquid samples can be investigated more precisely by the combination of XAS for the inner shell with other photoabsorption for the valence shell (UV-vis) and molecular vibration (IR). The sample cell connected to the manipulator has two types of windows: one is the liquid part to measure the transmission signal of liquid ( $I$ ), and the other is the blank part to obtain the transmission signal without samples ( $I_0$ ). We can easily evaluate the transmission ratio using  $I/I_0$ , and obtain T-mode XAS spectra based on the Lambert-Beer law  $\ln(I_0/I)$ . In order to evaluate the inhomogeneous thickness effect of liquid layer samples at different positions, we have scanned the sample position of liquid water and measured soft X-ray transmission spectra at each position. Liquid samples are easily exchangeable by using a tubing pump system (Cole-Parmer Masterflex L/S) with the liquid flow rate typically of 5 ml/min. The average volume of the present liquid cell is smaller than 10 ml. Temperature of a liquid sample is controllable in the range of  $-5$  to  $80^\circ\text{C}$  by setting a copper plate connected with a chiller and heating system. In the present study, the temperature of liquid water is kept to be  $25^\circ\text{C}$  by using this temperature control system.

The photon energy is accurately calibrated by using a mixed gas in the atmospheric helium chamber, for example, the first peak (287.96 eV) of methanol [44], the first N  $1s \rightarrow \pi^*$  peak (400.84 eV) of  $\text{N}_2$  gas [45], and the O  $1s \rightarrow \pi^*$  peak top (530.80 eV) of  $\text{O}_2$  gas [46], though it takes long time to replace the mixed gas with pure helium. Instead of using such a calibration gas, we also use thin polymer films (ProLINE) with the thickness of 150 nm and 300 nm in the vacuum chamber, as shown in Fig. 1(a). Additional photodiode detectors are set behind the thin polymer film. Fig. 2(a) shows a C K-edge X-ray transmission spectrum of the polymer film with the thickness of 150 nm. The photon energy of the first peak is determined as 285.07 eV. Because the polymer film is in the vacuum chamber, we can calibrate the photon energy quickly, irrespectively of the condition in the helium chamber. Fig. 2(b) shows an

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