

INTRODUCTION

Knowledge of an electronic structure is quite important for understanding the properties of materials. Especially, valence electrons play important roles in electric, magnetic and chemical properties. Therefore, valence orbitals/bands of gaseous/solid materials have been commonly and extensively investigated by means of photoemission spectroscopy (PES). Electronic structure is also important for material in liquid state. Large variety of phenomena in liquid state have some connection to variation and dynamics of intermolecular interactions. The origin of intermolecular interactions, such as dipole-dipole interactions and hydrogen bonds, have closely related to the electronic structure of molecule. Hence, information on the valence electronic states of a molecule in liquids is important for understanding of liquids.

However, an ordinary PES is not suitable for the studies of liquid materials since PES is a photon-in electron-out experiment which detects photoelectrons in vacuum condition. In SPring-8 BL17SU, we have used x-ray emission and absorption spectroscopy as an alternative method. Recent advancements in the production of ultra thin films in the order of 100-200nm thickness, which is almost transparent for soft X-rays, enables us to use the thin films as a vacuum tight window for x-ray spectroscopy. Hence the x-ray emission spectroscopy (XES) [1], which is a kind of photon-in photon-out experiment observes the valence electronic structure through energy spectra of emitted photons, can be used as an alternative method

of PES for liquid samples. The first observation of XES for liquid water was reported in 2002[2]. In recent ten years, liquids and solutions have been actively studied using XES [3-19].

Fig.1 shows schematic energy diagrams of x-ray absorption and emission spectroscopy. If incident energy of x-rays is enough to excite core electrons, one can observe electronic transitions between core and valence orbitals as x-ray absorption. X-ray absorption spectroscopy (XAS) measures the

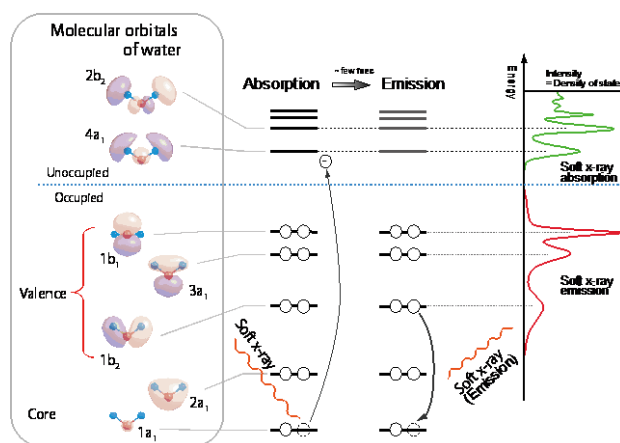


Fig. 1 Schematic energy diagrams of soft x-ray emission and absorption spectroscopy. Relation between spectral feature and molecular orbitals of water molecule is shown as an example.

absorption coefficient of electron transition from core to unoccupied orbitals and provided information on unoccupied states [20]. Since XAS process generates unstable core hole in the system, subsequent relaxation processes occur within a core-hole lifetime (a few fs for light elements). Major relaxation pathways of the core excited state is Auger electron emission. Energy analysis Auger electron provide information on occupied state and is known as Auger electron spectroscopy. One of the minor relaxation pathways is the x-ray emission. Since x-ray emission is energy release of excess energy due to electronic transitions between core and valence orbitals, XES spectra reflect occupied valence electronic states. While Auger electron spectroscopy require vacuum condition to detect electrons for analysing electron kinetic energy, XES is possible to observe emitted soft x-ray photons from sample under atmos pheric pressure through thin film window.

In this text, I'll explain some of basic of x-ray emission study of solution sample.

SELECTIVE XES OBSERVATION OF MOLECULE IN SOLUTION SAMPLES

Fig.2A shows the binding energy of core orbits up to 2200 eV (Data were taken from the table of electron binding energies in the "X-ray Data Booklet"[21]). The binding energy of a core orbital is largely different depending on elements. Core level spectroscopies have thus the unique capability to observe elements separately. Fig.2B shows XES spectra of aqueous Fe(III) chloride, which contains hydrogen, oxygen, iron and chlorine as elements. Owing to difference of binding energy in core orbitals, X-ray emission spectra of oxygen in H₂O and iron of Fe(III)Cl₃ were observed at different energy region.

In general, many solutions contain same element in solute and solvent molecules. Especially, organic molecules consist of limited elements such as carbon, nitrogen and oxygen atoms. In this case, element selectivity of XES is not enough to specify one sort of molecule. Hence, selectivity beyond element selectivity is needed for the research of solution samples using XES.

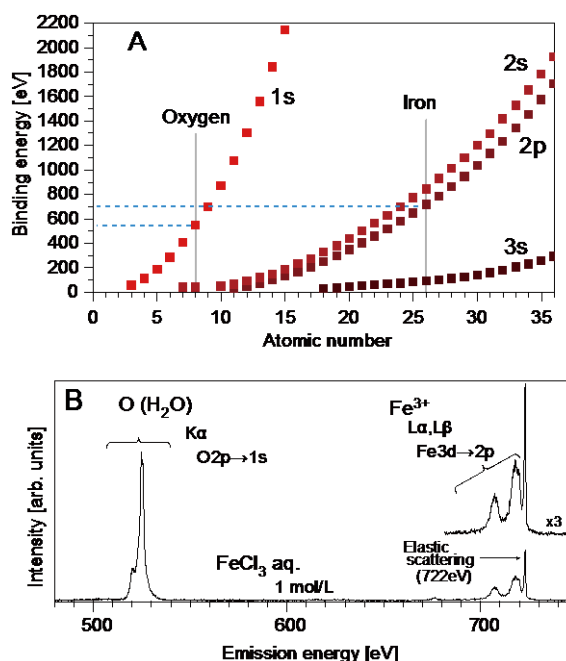


Fig. 2 (A) binding energies of core orbitals up to 2200 eV for the elements of atomic number less than 36. (B) XES spectra of aqueous Fe(III) chloride.

Fig. 3A shows the O1s XAS spectrum of liquid acetone, liquid N,N-dimethylformamide (DMF), liquid acetic acid, aqueous acetic acid and liquid water. It might not be hard to find the connection between molecular structure around oxygen and the peak structure of XAS. The O1s XAS spectrum of liquid acetone shows an intense peak at 531.3eV. This peak structure is also appeared in XAS spectra of DMF and acetic acid with small energy shift. On the other hand, liquid water that has

no C=O type oxygen, then the O1s XAS spectrum shows no peak structure corresponding to the first peak of acetic acid.

Based on XES experiments using BL17SU, the first peak and the second peak in O1s XAS spectrum of acetic acid were assigned to selective excitations of the $O_{C=O}$ 1s and O_{OH} 1s respectively [5, 8]. By tuning excitation energy to such a specific peak corresponding to molecular structure, one can select molecule based on molecular structure as depicted in Fig. 3B.

Fig.4A shows an example of $O_{C=O}$ selective observation for aqueous acetic acid in acid-base equilibrium. In order to perform a selective observation of XES for acetic acid molecules in solvent water, excitation energy was tuned to the $O_{C=O}$ 1s $\rightarrow \pi^*$ resonance excitation, which is absent in water.

As shown in Fig.4A, pronounced changes of XES spectra depend on pH is observed. Since acid dissociation constant, pKa, of acetic acid in aqueous solution is known to be 4.756 at room temperature, acetic acid molecules exist in the neutral form in the acidic solution with pH 0.29. In contrast, for the basic solution (pH 11.44), the anionic form of acetic acid should be dominant species. In the theoretically calculated XES spectra of neutral and anionic acetic acid plotted below experimental spectra in Fig.4A, all peak structures in the experiment are well reproduced. This result indicates that the selective excitation of XES successfully extracts the occupied valence electronic structure of the acetic acid molecules in aqueous solution.

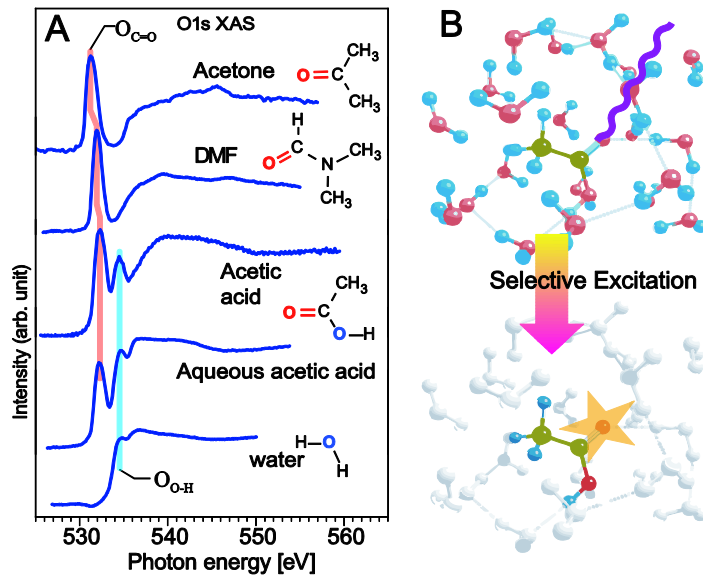


Fig. 3 (A) XAS spectra of acetone, DMF, acetic acid, aqueous acetic acid and water. Molecular structures of each molecule are depicted on right side of the figure. (B) Schematic drawing of selective excitation of XES.

Since acetic acid is a sort of acid, dissociation of hydrogen in OH structure carboxyl group occurs in aqueous solution. However, acetic acid is classified as weak acids. Deprotonation occurs as the pH of its solution decreases as shown in the pH evolution of the valence electronic structure probed by XES (see Fig.4B). Importantly, there are five cross points, i.e. isoemissive points, in XES spectra of the pH evolution at least. Isoemissive points indicate the spectra consist of the overlapping signals of two components; two components are neutral and anionic forms of acetic acid in this case. XES is also useful as analytical tool to monitor the ratio of neutral and anionic forms based on the data in Fig.4B (see ref. [5] for detail).

Such kind of selective observation technique is useful for the study of chemical reaction. Because reactants and products in chemical reactions always contain the same elements, electronic state observation using XES is quite difficult only with element selectivity.

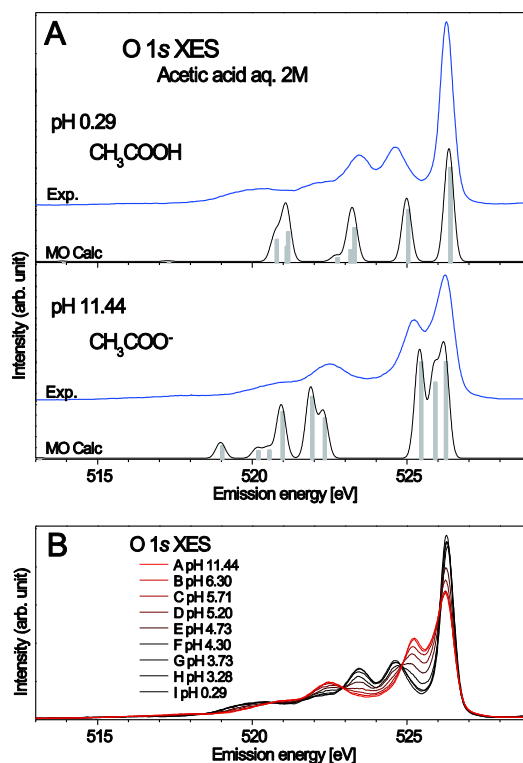


Fig. 4 (A) XES spectra of aqueous acetic acid in acidic and basic solution. Calculated XES spectra based on DFT calculation is plotted in lower part of the plot. The both calculated spectra were shifted by -1.2eV to fit the experimental peak feature with highest intensity. (B) pH dependence of XES spectra.

THE SOFT X-RAY UNDULATOR BEAMLINE BL17SU AND THE EXPERIMENTAL APPARATUS

Soft x-ray beamline BL17SU [22] is constructed to advance the spectroscopic studies for mainly solid state physics and materials science using high brilliant soft x-ray undulator. A novel insertion device called a multi-polarization-mode undulator has been developed for BL17SU[23-26]. The insertion device can be operated as a helical, elliptical, pseudo-linear or pseudo-vertical undulator. Thus, the intense soft x-ray beam of circularly/linearly polarized light of the soft x-ray beam can be obtained at this beamline.

The beamline has branched lines (branch-a and -b) which can be switched by the pre-focusing mirrors and used alternatively. Each branch has high resolution and highly stabilized monochromator [22, 27] and several end-stations. The available energy is ranging between 300 and 1800 eV. Typical resolving power $E/\Delta E$ of the monochromator is higher than 10,000 and the photon flux is of the order of 10^{11} photons/s. End-

stations at BL17SU beamline are actively used for studies using PES, XAS, XES spectroscopies and

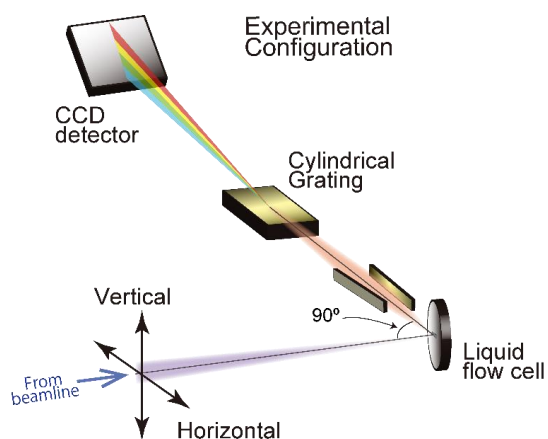


Fig. 5 Schematic drawing of optical configuration of soft x-ray emission spectrometer HEPA 2.5

soft x-ray diffraction.

In the course, the participants will use the end station for liquids and solutions, which is located at the end of branch-a. The apparatus consists of the XES spectrometer, which named High Efficiency Photon Analyzer (HEPA) [28, 29], and the main chamber equipped with the compact flange-mount liquid flow-cell which is designed for the studies of liquids under ambient conditions.

XES spectrometer at BL17SU is a kind of flat-field spectrometer which consists of grating and detector (see Fig.5) with additional optics to increase efficiency [29]. A thinned backilluminated CCD is used as detector. To reduce thermal noise of CCD, detector chip is cooling down around $-100\text{ }^{\circ}\text{C}$ by liquid nitrogen. Fig.6 shows an example of detected O1s x-ray emission from solid Al_2O_3 .

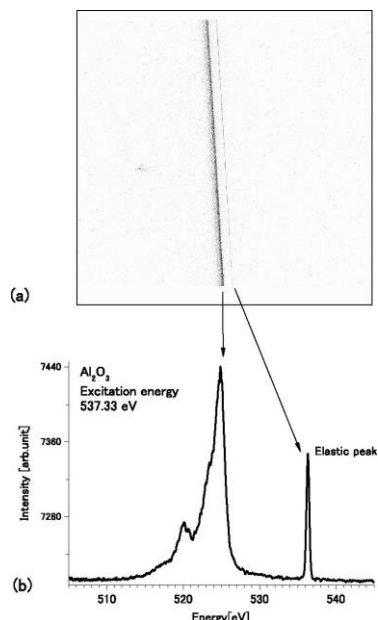


Fig. 6 An example of detected emission lines of CCD image(a) and corresponding x-ray emission spectra (b).

Fig.7 shows liquid flow cell which utilizes ultra-thin film with 150nm thick as a window to separate vacuum and sample under atmosphere. Liquid sample is circulate by pumping through the liquid flowcell. Since ultra-thin film window is quite fragile, liquid flow cell has an emergency pumping out system which detect leak of liquid into the vacuum chamber and stop sample feed by switching valve automatically.

A window material can be chosen according to the element of target material. At the moment, SiN (Silicon nitride) and SiC (Silicon carbide) are available. Since SiN window is cheap to manufacture, we have use SiN window ususally. If a target sample contains nitrogen, nitrogen signal from the SiN window overlap on the nitrogen signal from samples. In this cse, SiC is chosen to observe nitrogen in the sample liquids without contribution of nitrogen in the window material.

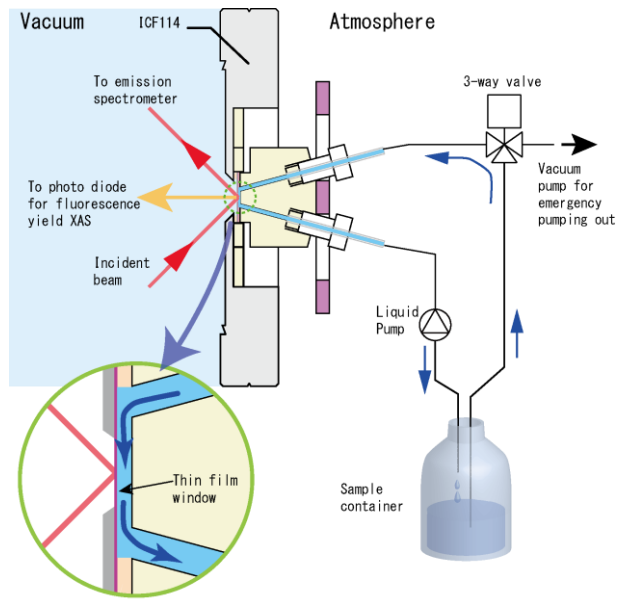


Fig. 7 Schematic drawing of liquid flow cell for soft x-ray spectroscopy

EXPERIMENT PLAN OF THE BEAMLINE PRACTICAL AT BL17SU

In the course, the participants will experience soft x-ray absorption and emission measurements of aqueous solutions under atmospheric pressure. The experiment plan covers standard experimental procedure of XES studies of liquid using selective observation of the molecule.

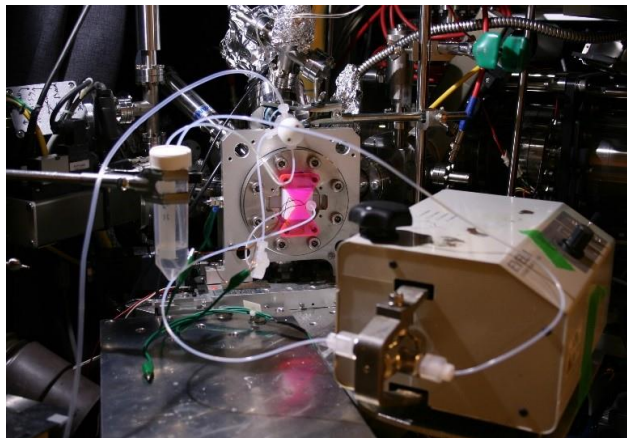


Fig. 8 An overview photo of liquid flow cell setup for soft x-ray spectroscopy

The followings are a plan of the experiment at present.

1. Preparation of samples and setup of the liquid flow cell for soft x-ray spectroscopy
2. X-ray absorption measurements
3. X-ray emission measurements
4. Energy calibration of the beamline monochromator and HEPA spectrometer using a hemispherical electron energy analyzer
5. Data analysis and discussions

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