

BL17SU : Electronic State Observation of Solute Molecules under Ambient Conditions

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INTRODUCTION

Knowledge of the electronic structure of materials 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 investigated by means of photoemission spectroscopy (PES). 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. Recent advancements in the production of ultra thin films in the order of 100-200nm thickness, which is almost transparent

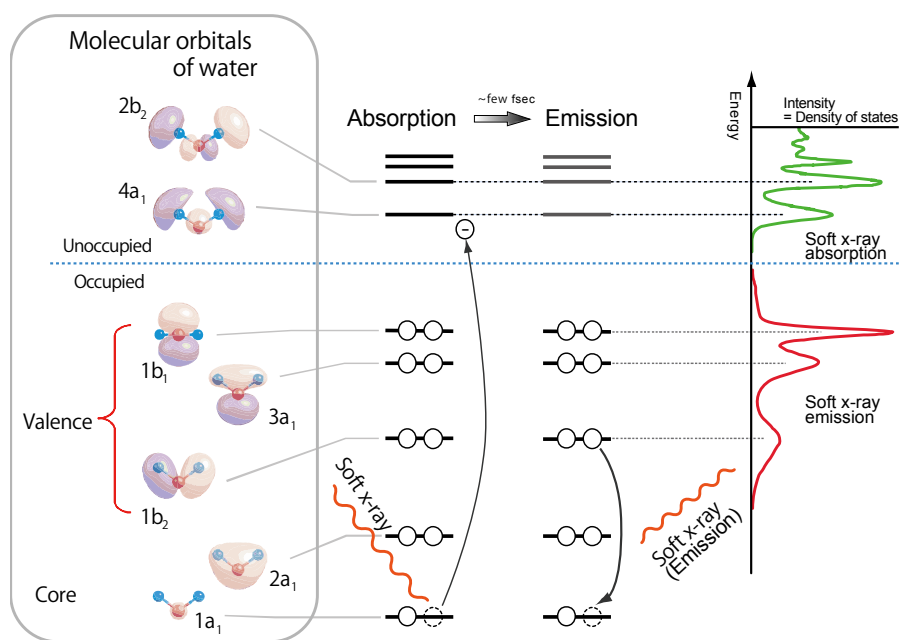


Fig. 1 Schematic energy diagrams of soft x-ray emission and absorption spectroscopy. Relation between spectral feature and molecular orbitals of water molecule is shown as an example.

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]. Subsequently, 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. X-ray absorption spectroscopy (XAS) measures the absorption coefficient of electron transition from core to unoccupied orbitals [20]. Therefore, XAS provided information on unoccupied states. Since XAS process generates unstable core hole in the system, subsequent relaxation processes occur within a core-hole lifetime (a few fsecs for light elements). Major relaxation pathways is Auger electron emission which is related to Auger electron spectroscopy. One of the minor relaxation pathways is the x-ray emission. XES spectra reflect occupied valence electronic states via electronic transitions between core and valence orbitals.

SELECTIVE XES OBSERVATION OF 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.

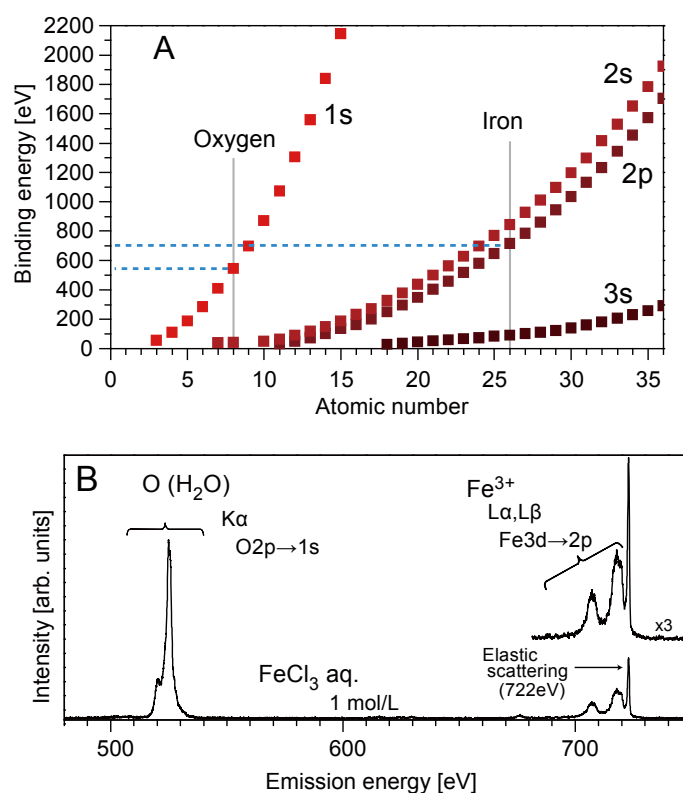


Fig. 2 (A) binding energies of core orbitals up to 2200 eV for the elements of atomic number less than 36. (B) XES spectra of aqueous Fe(III) chloride.

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 with small energy shift. Interestingly, energy positions of the first peak correspond well to the first peak of acetic acid. 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.

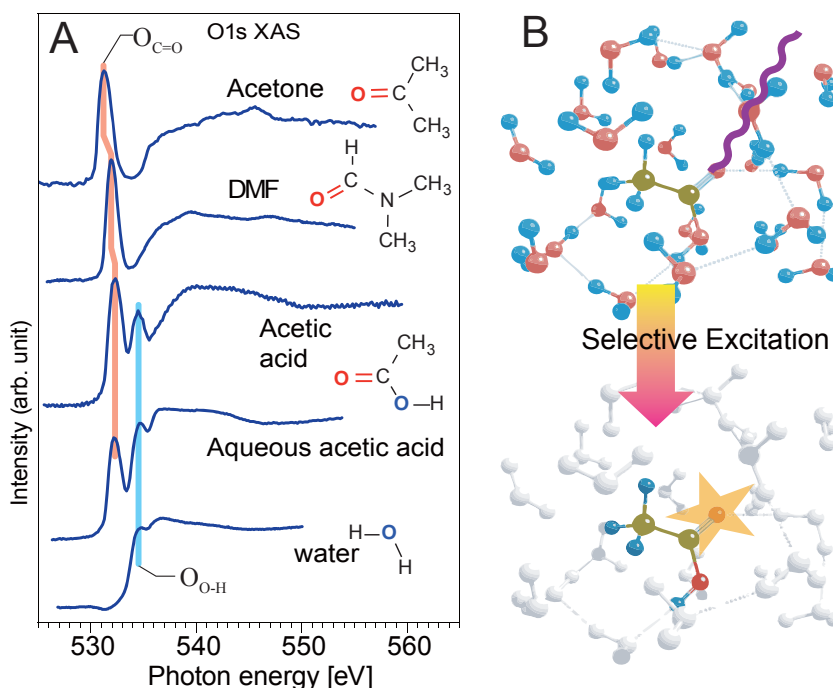


Fig. 3 (A) XAS spectra of acetone, DMF, acetic acid, aqueous acetic acid and water. Molecular structures of each molecule are depicted on right side of the figure. (B) Schematic drawing of selective excitation of XES.

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, pK_a , 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.

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. 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).

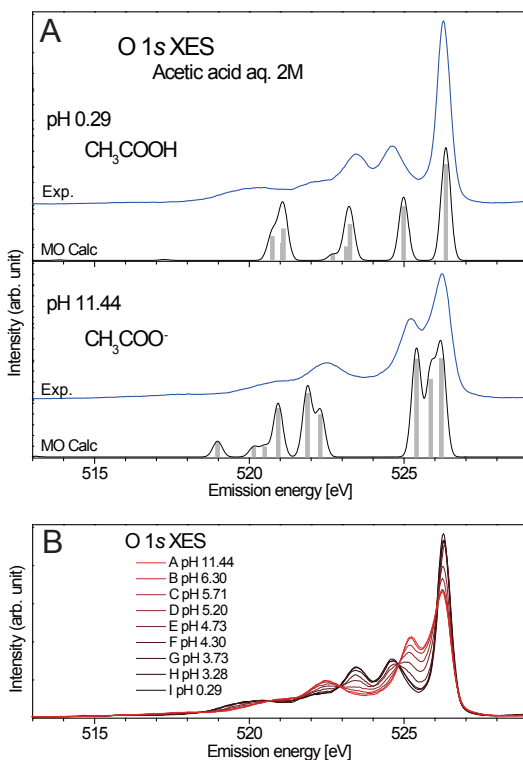


Fig. 4 (A) XES spectra of aqueous acetic acid in acidic and basic solution. Calculated XES spectra based on DFT calculation is plotted in lower part of the plot. The both calculated spectra were shifted by -1.2eV to fit the experimental peak feature with highest intensity. (B) pH dependence

Such kind of technique of selective observation 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.

OUTLINE OF 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]. This 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 ranged between 300 and 1800 eV. Typical resolving power

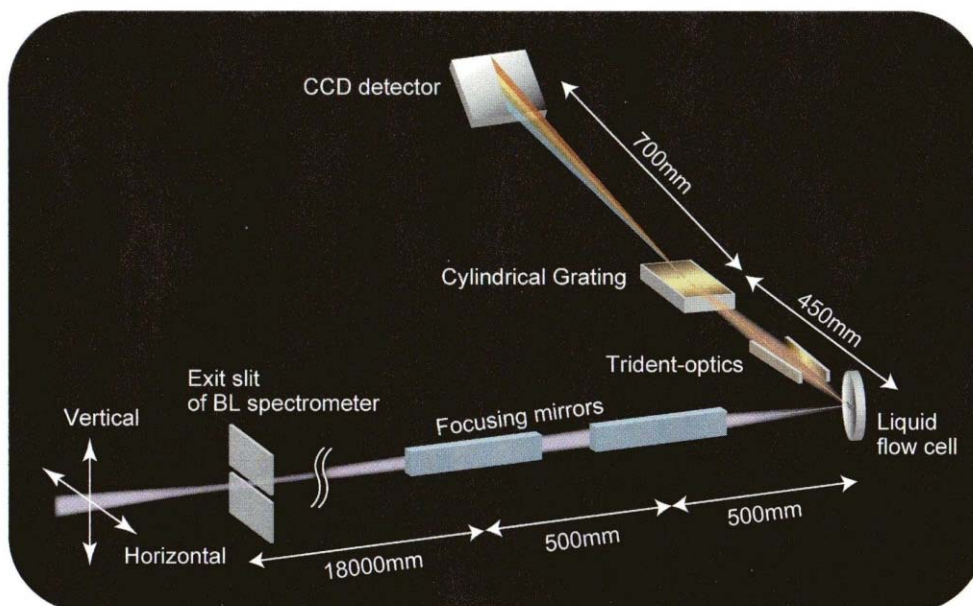


Fig. 5 Schematic drawing of soft x-ray emission spectrometer HEPA 2.5

$E/\Delta E$ 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 of surface adsorbates, liquids, solutions and solids using PES, XAS, XES spectroscopies and soft x-ray diffraction. In the course, the participants will use the end station for liquids and solutions, which is located at the branch-a. The apparatus consists of the XES spectrometer, which named High Efficiency Photon Analyzer (HEPA) [28, 29](see Fig.5), and the main chamber equipped with the compact flange-mount liquid flow-cell which is designed for the studies of liquids under ambient conditions. Fig.6 shows liquid flow cell which utilizes ultra-thin film of SiN (Silicon nitride) or SiC (Silicon carbide) with 150nm thick as a window to separate vacuum and sample under atmosphere.

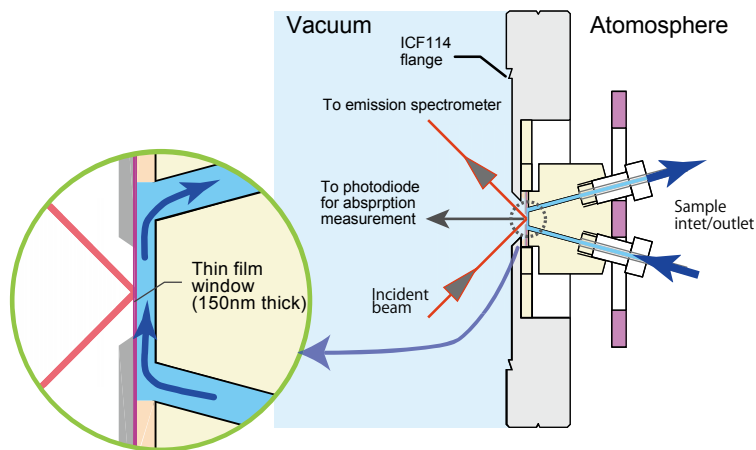


Fig. 6 Schematic drawing of liquid flow cell for soft x-ray spectroscopy

EXPERIMENT OF THE BEAMLIN PRACTICAL AT BL17SU

In the course, the participants will experience soft x-ray absorption and emission measurements for the samples in aqueous solutions under ambient conditions, i.e. room temperature and atmospheric pressure. The participants will also learn the principle of soft x-ray spectroscopy, detail of the soft X-ray beamline and the soft x-ray emission spectrometer. The followings are a plan of the experiment at present.

PREPARATION OF SAMPLES AND SETUP OF THE LIQUID FLOW CELL FOR SOFT X-RAY SPECTROSCOPY

At the beginning of the course, the participants will experience assembly of a liquid flow cell for soft x-ray measurement. During the evacuation of the chamber, a preparation of the liquid sample will be carried out. Detail of soft x-ray spectroscopy including experimental apparatus such as the beamline and HEPA spectrometer will be also explained.

CALIBRATION OF THE BEAMLIN MONOCHROMATOR

Calibration of the beamline monochromator will be performed by using a hemispherical electron energy analyzer (SES-2002, VG-SCIENTA) installed at the different station on a-branch. The absolute energy of monochromatized x-ray will be evaluated by PES measurement of Au 4f electrons using 1st and 2nd order x-ray of beamline monochromator. The

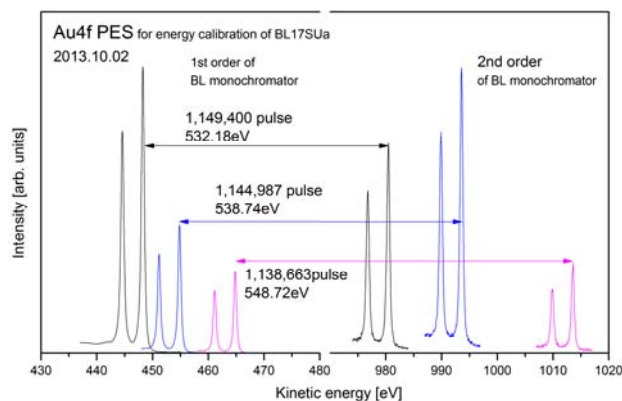


Fig. 7 Example of Au4f PES measurements for energy calibration of beamline monochromator

higher order (harmonics) of x-rays reaches sample location as 2nd order diffraction of beamline monochromator. Since photon energy of 2nd order diffraction is exactly twice of 1st order diffraction, one can obtain absolute value of incident x-rays by means of PES measurements (see Fig.7).

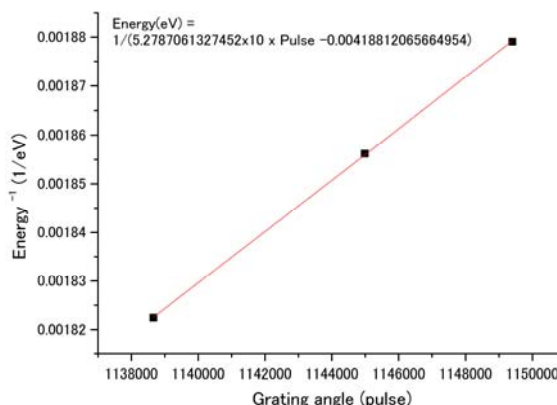


Fig. 8 Example of energy calibration curve for beamline monochromator of BL17SU

Many grating spectrometers use the sine bar mechanism for rotating the grating. The beamline monochromator of BL17SU also use the sine bar mechanism. Hence, linear motion of motor and output wavelength of monochromator becomes as follows,
Wavelength = a × x + b,
where x denote location in linear motion. Since we use a pulse motor for the linear motion, x is pulse count in this case. Photon energy is inversely related to the wavelength of photons. Hence, we can calculate energy like Fig.8.

XAS AND XES MEASUREMENTS OF SOLUTION SAMPLES

When conditions are ready for the measurement, XAS measurement of the sample solution will be performed by means of the total photon yield. Based on the obtained XAS spectra, excitation energy for selective excitation will be determined, and Selective XES observation of solute molecule will be performed.

CALIBRATION OF THE EMISSION SPECTROMETER

In XES spectra, an elastic scattering peak which has exactly same energy of incident beam is

normally observed. Using observed elastic peaks, energy calibration of emission spectrometer is possible. Fig.9 shows elastic scattering peak for three different energy excitation.

Differently from the beamline monochromator, relation between energy and location on the detector is not linear. Calibration curve and the equation of energy vs pixel number on the detector are shown in Fig.10.

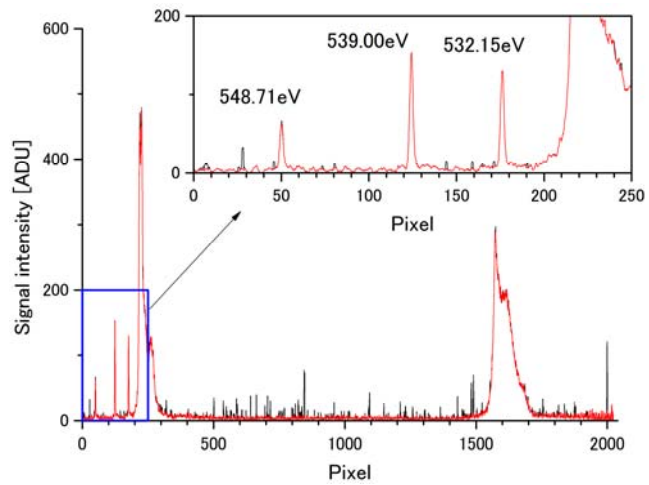


Fig. 9 Example of XES measurements for energy calibration of emission spectrometer. Red line shows spectra after filtering for cosmic rays and environmental radiation. Since solid line is original data, spikes with solid line are cosmic rays or environmental radiation.

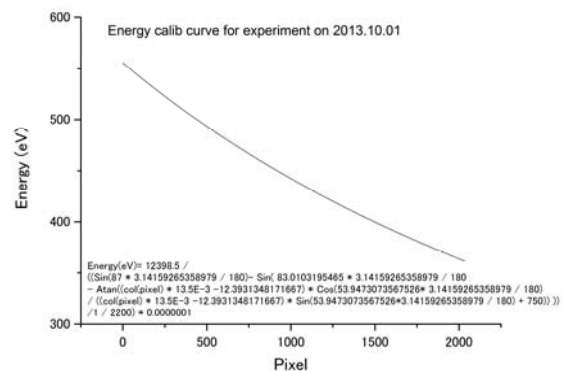


Fig. 10 Calibration curve and the equation of energy vs pixel number on the detector for the

DATA ANALYSIS AND DISCUSSIONS

After completing all the measurements, the spectrum for each sample will be analyzed and compared. The participants are now able to compare and discuss the results of the XES measurements for liquid samples.

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