BL practice

BL17SU : Selective Observation of Molecules in Solution Under Ambient Condition by Means of Soft X-ray Emission Spectroscopy

Takashi Tokushima and Masaki Oura (RIKEN/SPring-8)

1. 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. Valence orbitals/bands of gaseous/solid materials have been commonly investigated by means of photoemission spectroscopy (PES). However, an ordinary PES is unsuited for studying the electronic structure of liquid materials since PES is a photon-in electron-out experiment which detects photoelectrons in vacuum. Therefore, the soft x-ray emission (SXE) spectroscopy [1], which is photon-in photon-out experiment observing valence electronic structure through energy spectra of emitted photons, has been applied as an alternative method applicable to liquid samples. Since the first observation of SXE for liquid water 2002[2], liquids and solutions has been actively studied using SXE spectroscopy in recent years [3-17].

Fig.1 shows schematic energy diagrams of soft x-ray absorption and emission spectroscopy. Soft x-ray absorption (SXA) spectroscopy [18] measures absorption coefficient of electron transition from core to unoccupied orbitals. Therefore, SXA provided information on unoccupied states. Since SXA process generate unstable core hole in the system, subsequent relaxation processes occurs within core-hole lifetime (few fsec for light element). One of the relaxation pathways is soft x-ray emission (SXE). SXE spectra reflect occupied valence electronic states via electronic transitions between core and valence orbitals.

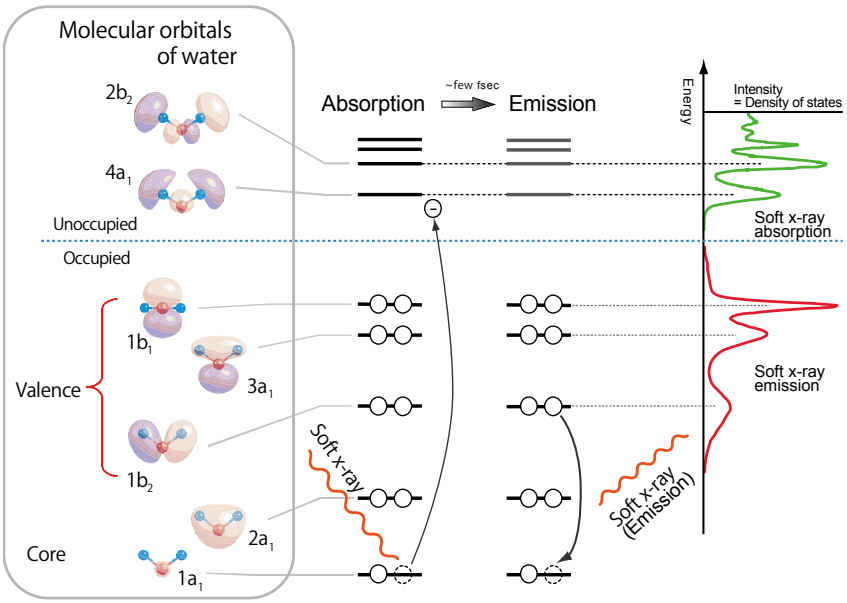

Fig. 1 Schematic energy diagrams of soft x-ray emission and absorption spectroscopy. Relation between spectral feature and molecular orbitals of water molecule is shown as an example.

Fig.2A shows binding energy of core orbitals up to 2200 eV (Data were taken from the table of electron binding energies in "X-ray Data Booklet"[19]). 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 SXE spectra of aqueous Iron(III) chloride, which contains hydrogen, oxygen, iron and chlorine as elements. Owing to difference of binding energy in core orbitals, oxygen of H_2O and iron of Fe(III)Cl_3 is observed at different region of the SXE spectra.

In the course, the participants will experience soft x-ray absorption and emission measurements for the samples in solid state and aqueous solution. The participants will also learn principle of soft x-ray spectroscopy, detail of the soft x-ray beamline and the soft x-ray emission spectrometer.

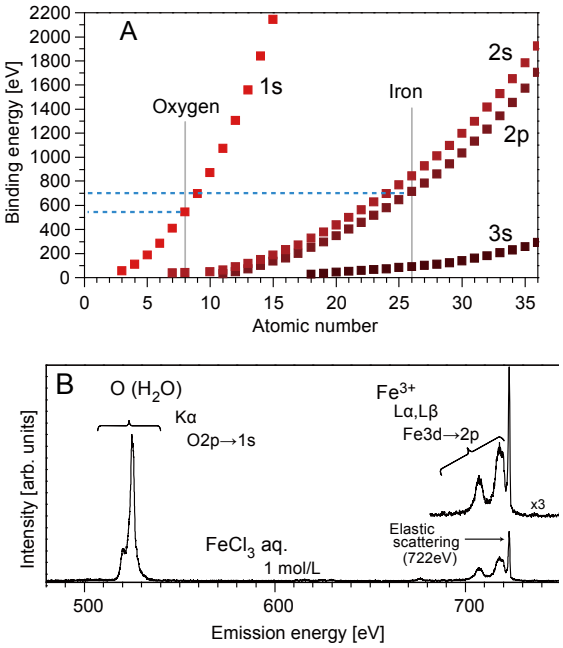

Fig. 2 (A) binding energies of core orbitals for the elements of atomic number less than 36. (B) SXE spectra of aqueous Iron(III) chloride.

2. Outline of the soft x-ray undulator beamline BL17SU and the experimental apparatus

Soft x-ray beamline BL17SU [20] 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[21-24]. 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 [20, 25] and several end-stations. The available energy is ranged between 300 and 1800 eV. Typical resolving power E/ΔE of the monochromator is higher than 10,000 and the photon flux is of the order of

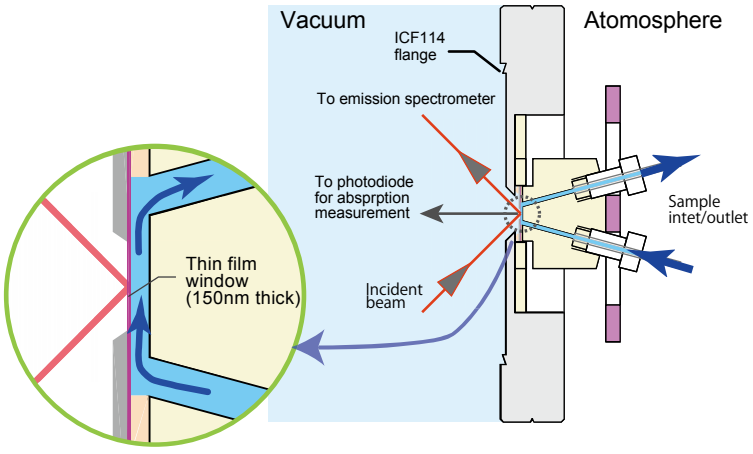

Fig. 3 Schematic drawing of liquid flow cell for soft x-ray spectroscopy

10^{11} photons/s.

End-stations at BL17SU beamline are actively used for studies of surface adsorbates, liquids, solutions and solids using photoemission, photoabsoprtion, SXE 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 SXE spectrometer, which named High Efficiency Photon Analyzer (HEPA) [26, 27], and the main chamber equipped with the compact flange-mount liquid flow-cell which is designed for the studies of liquids under ambient condition. Fig.3 shows liquid flow cell which utilize ultrathin film of SiN or SiC with 150nm thick as a windows to separate vacuum and sample an atmosphere.

3. Experimental procedure

3.1 Preparation of the powdered sample

In the beginning of the course, the participants will be asked to prepare the powdered sample. The sample will be supported by the carbon tape sticked on the sample holder.

3.2 Explanation of the beamline and the SXE spectroscopy

During the evacuation of the chamber, the whole of the beamline as well as the principles of the HEPA spectrometer will be explained to the participants.

3.3 Calibration of the beamline monochromator

After the explanation, calibration of the beamline monochromator will be performed by using a hemispherical electron energy analyzer (SES-2002, VG-SCIENTA) installed at the different station at a-branch. The kinetic energy spectrum of Au 4f electrons will be measured as a function of the exciting photon energy in order to check the relationship between the wavelength of the exciting photons and the setup of the beamline monochromator.

3.4 Soft x-ray absorption (SXA) and SXE measurements for solid powder samples

When the vacuum of the chamber is ready for the measurement, XA spectra of the powdered sample in near O 1s-edge region will be measured by means of the total photon yield (TPY) method. After the XA spectrum measurement, calibration of the HEPA spectrometer will be carried out by measuring the elastically scattered photons from the sample. Resonant SXE measurements will be performed at some energy points where the XA spectrum shows characteristic features.

3.5 Change the setup of the HEPA spectrometer for the measurement of liquid samples

When the SXE measurements for the powdered sample has finished, the participants are asked to change the setup of the HEPA spectrometer to be a setup for the liquid sample measurement. During the evacuation of the chamber, a preparation of the liquid sample will be carried out.

3.6 SXA and SXE measurements of liquid samples

Prior to the SXE measurement, the HEPA spectrometer will be adjusted for the measurements of the liquid sample. When conditions are ready for the measurement, an XA spectrum of the liquid sample in near O 1s-edge region will be performed by means of the TPY method. Resonant SXE measurements will be performed at some energy points as in the case of the

powdered sample.

3.7 Data analysis and discussions

When all the measurements are finished, the spectrum for each sample will be analyzed and compared. The participants are now able to compare the results of the SXE measurements for solid and liquid samples.

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