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Progress of Soft-x-ray Absorption Endstation for Environmental Samples

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Abstract

A new endstation was developed at beamline 9.3.1 of the Advanced Light Source (ALS), Berkeley, CA, USA, to perform x-ray absorption experiments with soft x-rays on environmental samples such as liquid and hydroscopic solid samples at atmospheric pressure. The sample stage is separated from the vacuum of the beamline by a thin beryllium (Be) window which is 0.05 mm thick and 0.64 cm in diameter. A Si-photodiode is used to measure fluorescence from the sample. The experiments are conducted in an enclosure (mini-hutch) to protect users from x-ray radiation, to prevent ambient light from hitting the detector, and to allow running experiments with a background of another gas rather than air. Here we report on fluorescent-mode x-ray-absorption measurement at the chlorine K-edge of KCl and CCl₃F in liquid and solid phases, illustrating the capabilities of the instrument and the technique.

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Keywords: soft-x-ray; x-ray absorption; liquid sample; environmental sample; ambient pressure

1. Introduction

Synchrotron-based x-ray absorption spectroscopy (XAS) has proven to be a versatile structural probe for studying the local environments of cations in a variety of materials ranging from crystalline solids, glasses, and high-temperature liquids to aqueous sorption systems which involve metal complexes associated with (or sorbed at) solid/water interfaces. The structural information provided by XAS includes

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average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species. In many cases including short-range ordering of cations in crystalline solids, cation environments in poorly ordered materials such as gels, glasses, melts, radiation damaged materials, and the structure and composition of sorbed species at solid/water interfaces of environmental importance, XAS provides unique structural data not duplicated by other methods.

X-ray absorption spectroscopy is the measurement of the x-ray absorption coefficient of a matter as a function of excitation energy. The x-ray absorption spectrum is typically divided into two energy regions: the X-ray Absorption Near-Edge Structure or XANES region, and the Extended X-ray Absorption Fine Structure or EXAFS region, shown in Fig.1. The XANES region is also sometimes referred to as the Near-Edge X-ray Absorption Fine Structure or NEXAFS region. The physics of the processes responsible for XANES and EXAFS spectral features is different, thus these spectral regions provide different types of information about an element and its local environment [1,2].



Fig. 1. X-ray absorption spectrum of FeO with the XANES and EXAFS regions [2].

X-ray absorption spectroscopy in the soft x-ray region is an important technique to investigate environmental and biological samples because the x-ray energy range covers core-electron excitation energies of many light atoms which are the primary atoms in those kinds of samples. However this x-ray technique is difficult to apply when measuring the structural interfaces at the atomic and molecular level for liquid or wet samples. The problem is that soft-x-ray beamlines must be under vacuum: typically with soft-x-ray spectroscopy systems, the samples also must be in vacuum, which means the sample must be contained or behind a barrier such as a thin window. A liquid or wet sample generally cannot be put in a high-vacuum system because the sample will evaporate and the high vapor pressure will not be compatible with the vacuum of the beamline.

2. XAS and liquid samples

During recent years, several techniques to handle liquid samples for XAS experiments have been developed at various levels of complexity. At the beamline 8 of SLRI, Thailand, a rectangular liquid sample cell made of superlene with Kapton tape window is employed in an ambient pressure chamber [3]. M. Freiwald, et al., reported sample cell in which a liquid sample can be circulated through a U-shape tube insert in UHV chamber, soft x-rays are coupled in and out of the sample volume by a silicon nitride membrane window on the tube wall [4]. Kevin Wilson, et al., have developed sophisticated technique to inject microjet of water into the experimental chamber [5]. P. Nachimuthu, et al., placed a plastic straw

filled with liquid samples outside a UHV of beamline port which was separated by a thin window made of Si3N4 membrane [6].

Chlorine was chosen as our primary samples of interest because it is one of the most abundant naturally occurring chemical elements. It also plays an important and significant role in everyday life ranging from drinking water, plants, food, soils to the manufacture of thousands of products we depend on every day. However the behavior and the ultimate fate of chlorine compounds in the environment are not well understood. The study of "formation of stable chlorinated hydrocarbons in weathering plant material" in [7] shows very interested result reflecting the success of XAS technique on biological and environmental samples. The scientific motivation is to look for changes in binding for the same molecule in gas, liquid, and solid phases for the molecules to be studied at ambient pressure (for solid and liquid phases), in the energy range of the chlorine K edge. We expect there to be subtle differences which will shed light on changes in electronic structure with phase of the molecule.

3. Endstation

A new endstation was developed at beamline 9.3.1 of the Advanced Light Source (ALS), Berkeley, CA, USA, to perform x-ray absorption experiments with soft x-rays on liquid samples at atmospheric pressure. The ALS provides high-brightness beams of synchrotron radiation from accelerated relativistic electrons with energy of 1.9 GeV. This beamline is a windowless beamline based on a bending magnet and equipped with a Si(111) double-crystal monochromator which provides x-rays in the 2.2-5.5 keV energy range with an energy resolution of approximately 0.4 eV [8,9]. Beamline 9.3.1 operates extremely well in the energy range of the chlorine K edge (2822.4 eV) [10].

3.1. Design and construction

The endstation was designed and constructed to perform an x-ray absorption experiment on solid and liquid samples at one atmosphere pressure. The endstation consists of two major parts; beam diagnostic and the x-ray absorption experimental station. The beam diagnostic, which is in vacuum, is part of the beamline; while the experimental station, which is in an atmosphere, is located after the end of the beam diagnostic. The beam diagnostic consists of a beam-positioning system, an ion-gauge and an optical shutter and an aluminum-mylar film for I_0 measurement. I_0 is an electric current proportional to the intensity of incident x-rays which can be measured by the aluminum-mylar film due to the photoelectric effect. When x-rays penetrate the film, electrons are ejected from the aluminum surface causing a current flow through the circuit connected to the film. The current measured from the film was monitored by a Keithley (model 6517A) electrometer. Since the film is very thin, soft x-rays can penetrate the film with a minimum of loss. At the exit end of the beam diagnostic is a window made of 0.05 mm thick Beryllium (Be), which was glued on to the surface of a 1.33 inch vacuum flange which has a 6.35 mm diameter aperture, the use of this window results in a x-ray transmission ranging from about 0.6 at 2200 eV to 0.97 at 5500 eV [11].

The experimental station consists of a sample holder and a Si photodiode fluorescent detector as shown in Fig.2. Both the sample holder and the detector were installed on a movable stage. The sample stage position can be adjusted to position the sample as close as possible to the Be-window to reduce the attenuation of beam intensity in a gas atmosphere (typically helium). The sample holder is inclined at an angle of 45° relative to the beam trajectory. At the center of the inclined plane, there is a 5 mm diameter dent on its surface to support the liquid drop of sample, so only a drop of sample is required for an experiment. A drop of sample spreads as a thin layer over an area of about 1 cm diameter over and around the dent. A typical distance from the window to the sample is 1.5 cm. The sample holder was made of

aluminium and contacted with a cooling bath allowing users to cool the sample either with dry ice or liquid nitrogen and to freeze the samples to solid phase. The sample holder together with cooling bath was not permanently attached to the sample stage. A large-area of silicon photodiode is used to measure total fluorescence from the sample. The experimental station was covered with a 6 mm thick aluminum enclosure which has three functions. First, to prevent the detector from observing light other than the fluorescent light from the sample. Second, to protect users from x-ray radiation. To ensure the users safety, a sheet of tungsten, about 0.15 mm thick and 9×13 cm in size, was glued on to the inside wall of the enclosure behind the sample. Finally, an enclosure allows the users to flow other background gases instead of air during the experiment, for example, helium gas.



Fig. 2. Schematic diagram of the liquid /solid sample endstation for x-ray absorption experiments in fluorescent mode.

3.2. Results and discussion

Chlorine K-edge Near-Edge X-Ray Absorption Fine Structure (NEXAFS) spectra for solid KCl sample and KCl+H₂O solution sample were measured in fluorescent mode using the endstation described above. Both spectra are shown in Fig. 3. The Chlorine K-edge NEXAFS spectrum for solid KCl agrees well with that reported in [12] while that of KCl+H₂O solution agrees well with the one reported in [13] for aqueous Cl-.

The Cl K-edge NEXAFS spectra for trichlorofluoromethane CCl_3F in liquid and solid phases were measured in fluorescent mode using the endstation described above. The spectrum for CCl_3F in gas-phase was measured for reference by a gas absorption cell built in the beamline, which was separated from the beamline by the Kapton window. The Kapton window is used to maintain the pressure in a gas cell in order of hundreds of millitorr while allowing the vacuum part of the beamline to be at 10^{-7} torr or less. The Kapton window was also checked to ensure that it did not contain sulfur or chlorine based molecules which would cause background structure. When the x-ray beam goes into the gas cell and was absorbed by a gas molecule in the chamber some molecular ions and electrons were generated. The molecular ions and electrons were collected by electrodes installed inside the gas cell chamber and connected to a current measurement circuit outside the chamber. The amounts of measured currents are proportional to the amount of absorption events in the chamber. Measuring the currents generated from the sample while scanning energy of the incident photon provides information for the spectrum of x-ray absorption of the gas sample. The spectra shown for gas phase were measured at 300 mTorr of gas pressure, and an applied voltage difference between the electrodes of the gas cell was 400 V. The gas-phase spectra were extremely repeatable.





Since the melting point of CCl_3F is -110.5°C which is much lower than room temperature, we used liquid nitrogen to freeze the sample to solid phase. Preparation of samples on the sample holder was conducted in a glove box under an atmosphere of nitrogen gas to prevented condensation of water moisture. After the cooling bath was filled with dry-ice or liquid nitrogen in the glove box, the sample was placed on the inclined surface of the sample holder then quickly moved to the sample stage. Dry-ice was used to cool the sample when being measured in liquid phase to reduce the evaporate rates. The end-station cover was closed and filled with helium gas. The measured NEXAFS spectra for CCl_3F are shown in Fig. 4. The peaks of all spectra of each molecule are not significantly different, but their shapes obviously reflect the structure depending upon their phase. There are fewer structural features on liquid spectra than for solid due to differences in the order of molecular structure between the bulk of liquid and solid. Data were collected between 2800 and 2900 eV, at intervals of 0.2 eV around the absorption edge and at the intervals of 0.5 eV before and after the edge region.

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Fig. 4. Cl K-edge NEXAFS spectra for CCl₃F molecule.

A newly designed sample holder leads to ease of use and less time consumed from sample loading to starting time of measurement, its taking just few minutes to change low-vapor-pressure liquids and slightly longer for high-vapor-pressure liquids due to the pre-cooling process.

4. Conclusion

A new endstation was developed at beamline 9.3.1 of the ALS to perform x-ray absorption experiments with soft x-rays on liquid samples at atmospheric pressure. A newly designed sample holder leads to ease of use and less time consumed from sample loading to starting measurement. These simple and inexpensive cooling methods allow us to conduct experiments on x-ray absorption of relatively high-vapor-pressure liquid samples.

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