

Soft X-ray Emission Spectroscopy of Molecular Adsorbates on Metal Surfaces

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Soft X-ray emission spectroscopy (SXES) is a very powerful tool to investigate chemical bonding of surface-adsorbate system because of its high elemental specificity. It gives direct information on chemical bonds formed by charge transfer between molecules and metals. Besides, soft X-ray emission is governed by the dipole selection rule so that the symmetry of valence orbitals can be identified.

We have constructed a UHV apparatus at BL27SU in order to study surface chemical bonding by means of SXES. An originally developed flat-field spectrometer [1] with high detection efficiency is equipped. Owing to a fine focused beam (10 μ m in vertical) at BL27SU, we can choose an entrance-slit-less type of spectrometer. Furthermore, a Figure-8 undulator supplying horizontally or vertically polarized light enabled us to resolve the symmetry of valence orbitals without rotation of the spectrometer.

Concerning to the performance of the spectrometer, the energy resolution ($E/\Delta E$) of about 1000 has been achieved in the energy range from 280 to 900 eV. The efficiency, which is determined both by the performance

of the spectrometer and the characteristics of the beamline, is considerably high. For example, SXE spectra of c(2x2)O/Ni(100) surface at the O K-edge can be measured within 15min.

Our targets are strong π -bonding systems such as SO₂ and C₄H₄S molecules adsorbed on Ni and Cu substrate. For SO₂/Ni(100) surface, SXE spectra at the O K-edge have been obtained. Owing to the high elemental specificity of this method, there is no obscuring Ni 3d signal in the spectra. The broad structures nearby the Fermi level are clearly observed, and are directly attributable to chemical bonds formed by the charge transfer between Ni 3d and molecular orbitals (MOs) of SO₂. It is revealed that not only the π^* unoccupied MO but also the σ valence MO have strong interaction with Ni 3d and form surface chemical bonds. Excitation energy dependence is also observed suggesting shake processes in SXE at high energy excitation.

Reference

[1] T. Tokushima et al., Surf. Rev. and Lett. **9**, (2002) 503.

Soft X-ray emission spectroscopy of the manganese cluster in Photosystem II at Mn 2p edge with a high flux soft X-ray emission spectrometer.

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Oxygen, indispensable for almost all life on the earth, is produced by plants as a product of water oxidation in photosynthetic processes. The active site of the reaction, the oxygen-evolving center (OEC), is thought to consist of four Mn ions, the so-called Mn-cluster, residing on the lumenal side of Photosystem II(PS II). We have tried to investigate the valence electronic states of the Mn-cluster by the core excitation spectroscopy, however, failed to detect Mn 3d \rightarrow 2p soft X-ray emission from an active Mn cluster in S₁ state of the Kok cycle.

There were four problems to overcome:

1. How to hold a solution in a high vacuum.
2. How to transfer a photosensitive solution from atmosphere to the experimental chamber via the sample introduction chamber, without exposing it to visible light.
3. How to reduce radiation damage as well as possible.
4. How to reduce the data collection time.

1. It is necessary to measure aqueous solutions to keep the activity of the Mn cluster. For this experiment, we have developed an original liquid cell to hold solutions in a high vacuum. It is composed of two Si plates with a 200nm thick SiN membrane, one with six parallel 300 μ m \times 2.5mm \times 380 μ m-depth slits to hold a drop of an aqueous solution for each. It worked well without damage on the membrane.

2. It is necessary to keep the sample in a dark place not to round the S-state in the Kok cycle. We used PS II core complex from the Thermophilic Cyanobacterium *Synechococcus -elongatus* isolated by Dr. M. Sugiura, in

Osaka prefecture University, as a test sample which is well known for its stability in the production of oxygen in photosynthetic processes. At room temperature, it stays in the S₁ state that is thought to be the most stable state. The sample was carefully covered with an aluminum foil prior to the introduction into the sample bank chamber. All the view ports on the experimental chamber were covered with thick dark green films that might decrease the risk of the degeneration of the solution. The aluminum foil was removed by using a transfer rod during the transfer process. This procedure was successfully carried out.

3. The slit window of the liquid cell had to be precisely positioned to the incident beam. Moreover, the sample had to be scanned during measurements in order to avoid the contamination of the soft X-ray emission from those of damaged samples. In this process, we failed to decide an adequate sample position by monitoring a change in photocurrent between the slit (aqueous sample) and base plate positions. It was because of an error in packing the aqueous solution in between the two SiN planes, which caused a charge build-up of the base plate and didn't allow us to measure the photocurrent at all.

4. Also, by some troubles in CCD system, the detection efficiency of soft X-rays was severely decreased from usual conditions so that the attempt to reduce measurement time was discouraged.

We must revise the sample packing process and also prepare an alternative way to position and scan the sample against the incident beam. We also have to stabilize the system for the soft X-ray detection.