Soft X-ray emission at the iron *L*-edge of myoglobin solution

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Iron-Porphyrin complexes are known as the basis of heme proteins. The electronic structure of the center irons in the complexes may be responsible for the basic biological function of them. Soft X-ray emission spectroscopy(SXES) is one of the most applicable methods to know the electronic states of center irons. When Fe2*p* core electron is excited enough above its absorption threshold, soft X-ray emission by a transition from a valence state to Fe2*p* core level occurs. This is often called normal SXES (NSXES). In iron compounds, the main emission band is usually derived from Fe3*d* states. When Fe2*p* core electron is excited just above its absorption threshold, it is a resonant process, and the soft X-ray emission is well dependent on the excitation energies including both occupied and unoccupied valence states. This is often called resonant soft X-ray Raman scattering (RSXRS). RSXRS of heme proteins may give information about energies of Fe3*d*-3*d* or charge transfer(CT) excitations, which are almost hidden in optical absorption spectra by a strong absorption band from porphylin π-π transition.

Myoglobin is appropriate for the test measurements because it is stable to the soft X-ray irradiation relative to other heme proteins. Moreover, it includes only one heme site per a molecule. In this study, 8mmol/l met-myoglobin solution was used. To do SXES of solutions, Oura et al. have developed a liquid cell which preserves liquids in a ultra-high vacuum by a thin polyimide window[1]. To reduce the radiation damage as well as possible, the solution was frozen during the experiment using a manipulator with He-refrigerator. The vacuum level of the experimental chamber was kept below $1x10^{-9}$ Torr. The transparency of the polyimide window was found to be about 20% throughout the photon-in and the photon-out process.

Figure 1 shows NSXES of Fe_2O_3, iron-porphyrin powder and met-myoglobin solution excited at 700eV, enough above the threshold. Note that the SXES intensity of iron-porphyrin powder and Fe_2O_3 is devided by 10 and 30, whereas the density ratio of iron ions among 8mmol/l myoglobin, iron-porphyrin powder and Fe_2O_3 powder is roughly 1:200:12000. This means protein chains composed of light elements and H_2O molecules are quite transparent to the soft-x-ray above Fe2*p* resonance, which results in the quite effective emission from buried iron ions. The profiles of the spectra among Fe_2O_3, iron-porphyrin, and met-myoglobin are slightly different even though the iron states of them are commonly the trivalent high spin state. A broad side band structure at higher emission energy is found only in the myoglobin spectrum. In this study, the local configuration of iron-porphyrin and myoglobin around iron center is the same, so that some nonlocal structures around the porphyrin complex or water may affect the profiles of the NSXES spectrum of myoglobin.

Figure 2 shows RSXRS of the iron compounds at the Fe2$p_{3/2}$, 2$p_{1/2}$ edge excitation. As in NSXES, or more clearly, broad structures at higher emission energy and a shoulder at lower side of the main band are observed in RSXRS of myoglobin. In addition, the intensity ratio of the two emission bands at Fe2$p_{1/2}$ edge excitation varies among the samples. These may hold information about ligand environment or valency of iron ions or the lifetime of the core excited state.

References

[1] M.Oura, Y.Harada, K.Kobayashi, M.Watanabe, S.Shin, unpublished..

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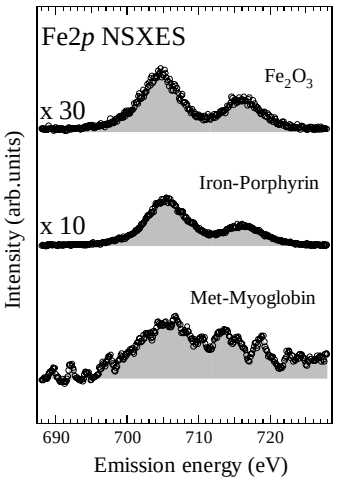

Figure 1 NSXES of Fe_2O_3, Iron-porphyrin powder and Met-myoglobin solution.

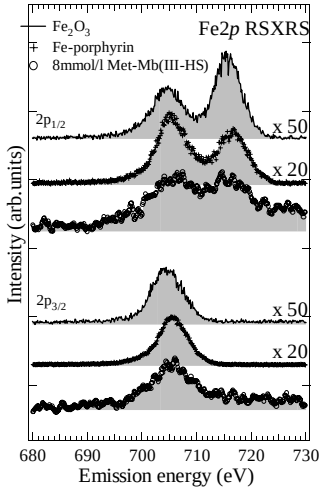

Figure 2 RSXRS of Fe_2O_3, Iron-porphyrin powder and met-myoglobin solution at Fe2$p_{3/2}$, 2$p_{1/2}$ excitations.