Possibility of Multi Atom Resonance X-ray Raman Spectroscopy - A new operando low Z-element XAFS method

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X-ray absorption fine structure (XAFS) is a structure appearing at higher energy above the X-ray absorption edge. It provides the useful information about the local structure such as type of coordinating atom, coordination number, bond distance and so on[1]. When XAFS is simultaneously carried with other techniques, one can obtain the valuable structural data of electrode and catalyst under working condition. When it is applied to low Z element, however, the operando measurement is difficult to be carried out owing to the low penetration power. X-ray Raman scattering, however, can be employed in operando XAFS measurement of the low Z elements by using hard X-ray and detect the low Z element XAFS from loss spectra[2]. Nevertheless, the sensitivity is very low. The Raman scattering can be enhanced by tuning the energy of the striking photon to the absorption edge of the sample (resonance X-ray Raman)[3]. The resonance X-ray Raman is limited to the absorption edge of the same compound. In the low Z element, we still have to use soft X-ray in the resonant Raman. If one may use an absorption edge of the metal to which low Z atom is coordinated and if the energy transfer occurs from the X-ray absorbing atom to the coordinating low Z element, one can obtain the X-ray absorption spectrum of the low Z element through the Raman spectra of the hard X-ray enhanced by the resonance conditions of nearest neighbor atom. It is often claimed that the probability of the energy transfer from the central atom to the surrounding ligand must be very little. However, to our knowledge no experimental nor theoretical estimations have been made yet for such probability. In this work we first measured the C K-edge resonance Raman signal in the Tris(cyclopentadienyl)-erbium(III) using X-ray tuned at the excitation of Er L₁ edge white line in order to see such an enhancement occurs or not, qualitatively.

X-ray Raman measurements were carried out in BL36XU of SPring-8. The X-ray emitted from tapered undulator was monochromatized with Si(220) double crystals. The emitted Xrays were analyzed by 4 Johan-typed Ge(660) monochromator located at 820 mm from the sample. Incident X-ray were detected by an ion chamber and emitted X-ray from a sample were detected by two-dimensional pixel array detector (Merlin). The obtained data was processed and analyzed by ImageJ.

Figure 1 is the first evidence for Resonant Raman spectra of C K-edge.



Fig.1 Loss energy (Raman) spectra ($E_{ex} = 9752 \text{ eV}$).

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