Chemistry

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Photon-stimulated ion desorption from sulfur-containing amino acids following sulfur K-edge excitation

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Introduction

Living things exposed to high-energy photons such as ultra-violet light and X-ray are subject to radiolysis resulting in serious transformations such as canceration and transmutation. The cause of such transformations is primarily ascribed to the degradation of fundamental biomolecules due to the core-level photoexcitation and succeeding Auger decays. It is therefore of great importance to clarify the X-ray-induced molecular changes as well as Auger decay processes in fundamental biomolecules in order to know the mechanism of the radiation-induced transformations in living things. Here we present the results for the photon-stimulated ion desorption for some of the biomolecules following the irradiation of monochromatized synchrotron soft X-rays around the core-level ionization thresholds.

Experimental

Experiments were performed at the BL-27A station. The molecules investigated here are sulfur-containing amino acids such as L-cystine, L-cysteine and L-methionine. The samples were pressed into pellets at 1 ton/cm^2. The desorbed ions were detected by a quadrupole mass spectrometer operating in a pulse counting mode. XANES spectra were measured by total electron yield (TEY) which was monitored by sample drain current.

Results and discussion

Fig. 1 shows the mass spectra of the desorbed ions from cystine. The upper spectrum was taken by the irradiation of 14 eV electrons, and the lower one was obtained by the irradiation of 2472.8 eV photons corresponding to the resonance excitation from the S 1s to unoccupied σ^* orbitals. For the electron-irradiated spectrum, we can see various fragment-ions, representing the ionic fragments by the valence excitation. While, the irradiation of 2472.8 eV photons induces only S^+-ion desorption. The result shows that the core-level excitation localized at a sulfur atom is followed by the bond scission only around the excited sulfur atom.

Fig. 2 shows the photon-energy dependencies of TEY and S^+ ion yield for cystine. When we compare the jump ratio (I_{on}/I_{off}) defined as the intensity ratio between off-resonance and on-resonance energies, the I_{on}/I_{off} ratio for the TEY curve is 1.5, but the value for the S^+ yield curve exceeds 20. The results clearly show that the S^+ desorption is caused not by the secondary electrons produced following the Auger decays but by the direct core-to-valence resonant excitation localized at the sulfur atom.

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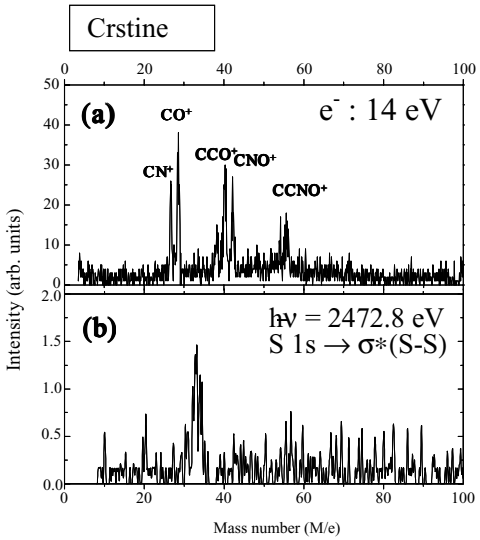

Fig. 1 Mass spectra of desorbed ions from cystine. (a) Irradiated by 14 eV electrons, (b) Irradiated by 2472.8 eV photons.

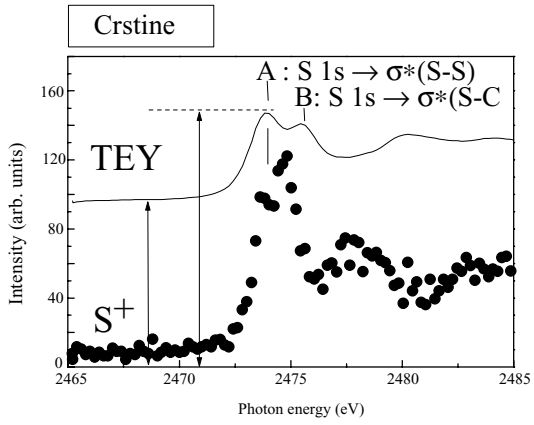

Fig. 2 Photon-energy dependencies of the TEY and S^+ yield around S *K*-edge for cystine.