

X-ray absorption spectra of excited triplet states of organic molecules

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Synopsis X-ray absorption spectra (XAS) have been measured for several organic molecules in the lowest excited triplet states (T_1) prepared by UV irradiation. T_1 -XAS deduced from the UV-ON/OFF difference spectra show good agreement, at least in the lowest peak region, with calculated T_1 -XAS.

Resonant core-excitation from valence excited states of organic molecules in the soft x-ray region has attracted attentions to elucidate details of the core-hole interaction with valence orbitals [1] and of bond dynamics especially bond dissociation in the valence- and core-doubly excited states. However, experimental difficulties in preparation of valence excited states, especially of excited singlet states having very short lifetime, with enough concentration to detect core excitations have prevented realization of measurements on core excitation from valence excited states. We have been trying to measure XAS from valence excited states by using as the initial state of core excitations the excited triplet states that have much longer lifetime than singlet states. Also theoretical investigation have been carried out to search for molecular system exhibiting experimentally favorable x-ray absorption spectra (XAS) [2].

Measurements on X-ray absorption spectra of excited triplet states of organic molecules were carried out at BL-13 of HiSOR (Hiroshima Synchrotron Radiation Center). X-ray absorption spectra are measured as total electron yields (TEY) method. Thin film samples of organic molecule are prepared on platinum coted titan substrate by drop-and-dry method. Phosphorescence life time of samples were measured prior to XAS measurement to insure experimentally detectable triplet formation yields and time averaged concentration. Organic molecules investigated are 4-mercaptobenzoic acid (MBA), 4-cyanobenzaldehyde (CBA), and benzil (BZL). All these molecules are known to produce the lowest excited triplet state (T_1) with high yield and to exhibit long lifetime in ms order.

Figure 1 shows presently obtained TEY spectra of 4MBA and calculated S_0 and T_1 XAS of benzoic acid for comparison. T_1 component in the TEY spectra is deduced from UV On-Off difference spectrum and S_0 (UV OFF) TEY with assuming T_1 concentration of 0.05.

Experimentally deduced T_1 -XAS is in good agreement with calculated XAS especially for the lowest energy peak. Difference between experiment and calculation in the higher energy region is mainly caused by difference of phase, solid for TEY and gas for calculation.

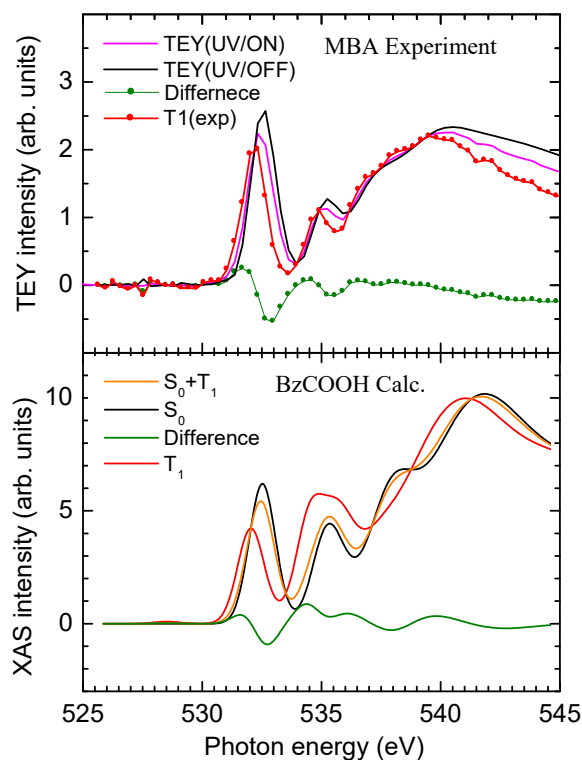


Figure 1. Top: X-ray absorption spectra (top) of 4-mercaptobenzoic acid in low temperature film with (magenta) and without (black) UV irradiation, and UV ON-OFF difference spectrum and T_1 -XAS component deduced from difference spectra. Bottom: Calculated S_0 and T_1 XAS of benzoic acid in gas phase together with S_0 and T_1 mixed XAS and expected difference spectrum (green).

References

- [1] T. Privalov, F. Gel'mukhanov, H. Ågren, 2003 *J. Electron Spectrosc. Relat. Phenom.* **129** 43.
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