

X-ray absorption of excited triplet state of quinones

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Pump-probe techniques to characterize electronic structure and dynamics in valence excited states have been extended in probing energy to x-ray regions in these decades. For the measurements of X-ray absorption from UV excited states of organic molecules, we aimed the excited triplet state having longer lifetime than singlet states. Concentration of triplet states was examined by measuring phosphorescence from triplet states. Prior to the UV-pump - X-ray probe measurements suitable molecular system, kind of molecule and its phase such as solid-solution or pure crystal, has been investigated by measuring phosphorescence spectra. Among molecular species and phases examined, anthraquinone (9,10-dioxoanthracene) in micro crystal phase deposited on Au coated Si substrate shows strongest phosphorescence with long lifetime of 73 msec [1]. An UV LED at 380 nm (0.37 W) was used as the UV source with continuous mode.

Total electron yield (TEY) spectra of UV pumped anthraquinone in the C K-edge region and the O K-edge region have been measured. In the C K-edge region, no difference in TEY spectra with and without UV irradiation was observed. Contrary to the C K-edge region, an appreciable enhancement was observed at 532eV peak in the O K-edge region when UV was irradiated. Though the lowest resonant transition from the ground state of anthraquinone is located at the same energy, this UV-induced feature is assigned as a new transition from the excited triplet state of anthraquinone. Since the lowest excited triplet state of anthraquinone is known to be $n\pi^*$ where an electron in the non-bonding orbital (n) localized at oxygen atoms is excited to the lowest π^* orbital, transitions from the O1s to a hole at the n orbital become possible in addition to the transition to the half-filled π^* orbital. In principle two low-lying transitions are expected from the electronic configuration $n^1\pi^{*1}$ of the triplet states, however, only one transition was enhanced by UV irradiation. A possible assignment for this single peak is the transition from the O1s to a UV created hole at the non-bonding orbital. This assignment is based on the fact that appearance of a new peak is observed at the O 1s but not at the C 1s region and is justified by that the n orbital, mainly in-plane 2p orbital, is localized around oxygen atom(s) and has large overlap with O 1s orbital.

X-ray absorption spectra from the lowest excited triplet state of anthraquinone and benzoquinone are calculated at the gradient-corrected DFT level using the StoBe-DEMON program. Both molecules in the triplet state exhibit a new peak (O 1s \rightarrow n) at lower energy side of the lowest absorption peak (O 1s \rightarrow π^*) of the ground states. Difference in the peak position of UV induced peak between experiment and calculation suggest that experimentally observed peak is originated from the $n\pi^*$ triplet excimer [2] not from the monomer. Although our assignment for this new feature appeared by UV irradiation is tentative, our observation is the first examples of soft x-ray absorption spectrum of valence excited organic molecules.

References:

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