

Core-excitation from excited triplet states of organic molecules: X-ray absorption spectra and doubly excited potential curves

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Synopsis Soft X-ray absorption spectra of the lowest excited triplet states of several organic molecules (quinones, benzaldehydes, and other carbonyls) and potential curves of valence- and core- doubly excited states are calculated for the O 1s region.

Resonant core-excitation from valence excited organic molecules has attracted attentions from the view point of the valence and core interactions and dynamics of valence- and core-doubly excited molecules [1].

The x-ray absorption spectrum of the lowest excited triplet state (T_1 -XAS) were calculated by using the similar procedure for that of the ground state (S_0 -XAS) [2] with modifying the initial state of the resonant core-excitation to the lowest excited triplet state. Potential energy curves of the valence- and core- doubly excited states (PEC-VCDES) for a specific bond are calculated by changing the bond distance with fixing other geometrical parameters [3].

T_1 -XAS of para-cyanobenzaldehyde (PCBA) exhibits a lowest energy peak (Fig. 1) of transition to the hole created at the highest occupied molecular orbital (HOMO). PCBA and other mono-carbonyls show almost the same intensity for HOMO and LUMO (lowest unoccupied) peak. However HOMO peaks of quinones, symmetric di-carbonyls, are very weak that would indicate a new type of valence-core interaction.

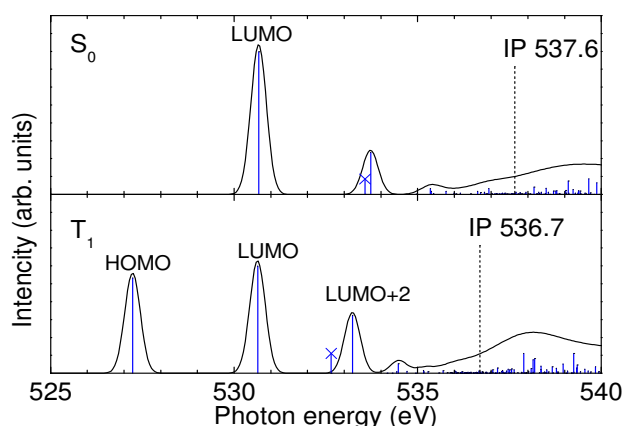


Figure 1. XAS from the S_0 (top) and the T_1 (bottom) of para-cyanobenzaldehyde. Solid vertical lines are calculated transition moments including very weak transitions to the LUMO+1 multiplied by 100 and designated by \times mark. Dotted vertical lines indicates the calculated ionization potential.

The PEC-VCDES from the T_1 have negative gradient for some bonds in several molecules. For the $C\equiv N$ bond of PCBA all PEC-VCDES ($O1s^{-1}$) are repulsive at the equilibrium bond distance in the T_1 state, especially for the $O1s^{-1}$ HOMO¹LUMO² (-77 eV/nm), while all PEC from the S_0 are almost flat regardless of the repulsive nature of the excited orbitals. It is noteworthy that strongly repulsive nature that would result in the site-selective bond scission is found at the most far $C\equiv N$ bond from the core-hole oxygen atom across the benzene ring.

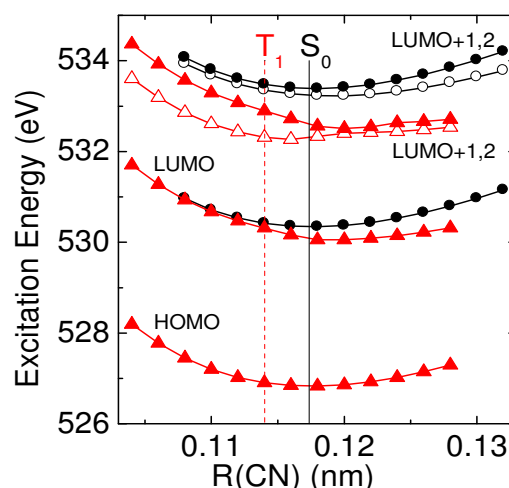


Figure 2. Potential curves along $C\equiv N$ bond of para-cyanobenzaldehyde in the O 1s core-excited states from the S_0 (circle) and the T_1 (triangle). Open symbol designates the states with very weak transition moment. Vertical lines indicate the C-N equilibrium distances in the S_0 (solid) and the T_1 (broken) states.

References

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