Theoretical study on X-ray absorption spectra and bond dynamics for core excitation from valence excited benzoic acids

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ABSTRACT

X-ray absorption spectra (XAS) of the lowest excited singlet, triplet, and ground states (S_1, T_1, S_0-XAS) of benzoic acid and methyl benzoate in the O 1s region were calculated. Resonant core transition to a hole at the highest occupied molecular orbital (HOMO) created by valence excitation was predicted about 3 eV below the lowest peak of S_0-XAS but with very weak intensity. A strong peak of the T_1-XAS well separated from S_0-XAS peaks is found for both molecules so that identification of the core-excitations from the T_1 and selective excitation of the T_1 become possible. Bond dynamics of oxygen-containing bonds in the potential energy surface of valence and core doubly excited states are estimated by using molecular dynamics simulation. Enhancement in known state-selective dissociation and new type of state selectiteve dissociation are predicted for the core excitations from valence excited state.

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1. Introduction

Resonant core-excitation in the soft X-ray region from valence excited states of organic molecules has attracted attentions to elucidate details of the core-hole interaction with valence orbitals [1] and bond dynamics including bond dissociation in valence- and core- doubly excited states. In particular, core excitation from an excited triplet state which has long lifetime is desirable for experiment. Benzoic acid and its methyl ester (hereinafter referred as BzA and BzAMe) is known to be produced the excited triplet state in high yields [2] and thus they are suitable for core absorption measurement from the valence excited state.

Theoretical investigation has been carried out to search for organic molecule exhibiting experimentally favourable X-ray absorption spectra (XAS) from the lowest excited triplet state (T_1) and showing unique bond-dissociative nature in the valence and core doubly excited states [3]. Prior to conduct experiments on core excitation from the T_1 of benzoic acids, absorption spectra and bond dynamics associated with the core excitation from excited triplet states are calculated. XAS and molecular dynamics (MD) calculations were carried out also for the core excitations from the ground

(S_0) and the lowest excited singlet state (S_1) for elucidating the effects of different electron configuration and spin multiplicity on XAS and bond dynamics.

2. Computational procedure

Transition energies and intensities of XAS were calculated by using StoBe-deMon [4]. Prior to calculate XAS from S_0, T_1, and S_1 states, molecular geometries in the S_0 and the T_1 were optimized by using Gaussian09 [5] with MP2/cc-pVTZ level, and in the S_1 with CIS/cc-pVTZ level. Small contribution of double excitations in S1 less than 1% was confirmed by CISD (CI singles and doubles) calculation. Dominant single excitations and their coefficients of CIS result for the S_1 of BzA were HOMO → LUMO (0.58) and HOMO−1 → LUMO+1 (0.37). Therefore the S_1 can be described by CIS wavefunction composed of these single excitations. For example, hole-state formed at HOMO is described by linear combination of HOMO (non-bonding orbital localized at carbonyl oxygen) and HOMO-1 (π orbital mainly localized in benzene ring). Orbital characters in the S_1 obtained by using StoBe-DeMon correspond well with those expected from CIS result. For example, HOMO vacancy in the S_1 calculated by StoBe-DeMon is composition of non-bonding orbital at carbonyl and π orbital in benzene ring as shown in Fig. 1. Moreover, slant shape of non-bonding orbitals obtained by StoBe-DeMon can be interpreted in terms of CIS result as the mixing with

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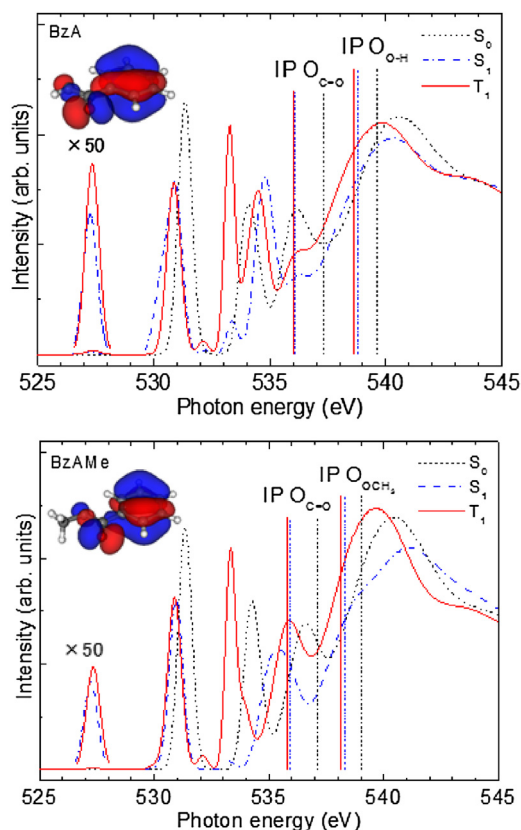 E-mail address: hiraya@sci.hiroshima-u.ac.jp (A. Hiraya).

Fig. 1. Calculated XAS of the S_0, T_1 and S_1 of BzA (upper) and BzAMe (lower). Vertical lines indicate the ionization potentials of two oxygen atoms. Insets show HOMO in the S_1.

sign between in-plane O 2p in HOMO and small out-of-plane O 2p in HOMO-1.

XASs of the lowest excited singlet and triplet states (S_1-XAS and T_1-XAS) were calculated by replacing the electron occupation in the ground state with those in the valence excited states. The ionized center was described by the IGLO-III basis of Kutzelnigg et al. [6] Used basis sets are C(5211/411/1), O(5211/411/1) and H(311/1), auxiliary basis sets are (C5,2;5,2), O(5,2;5,2) and H(3,1;3,1). Perdew and Wang exchange functional (PD86) and correlation functional (PD91) are used. Relativistic correction on the IP of 0.33 eV for the O 1s [7] were added to the transitions. Final XAS were generated by Gaussian convolution of the discrete transition lines. Non-inclusion of two-electron transitions in core-excitation in the present work can be justified at least as an approximation by previously reported weakness of two-electron transitions compared with single excitations in XAS from valence excited states [1].

As the optimum geometry of the core-excited state is different from the ground state, the system will begin to move towards the equilibrium geometry of the core excited state [8]. In order to examine this effect on the core-hole state, the DFT level molecular dynamics (MD) simulations were performed on the potential energy surfaces of the core-excited states of BzA and BzAMe. The MD simulations were started with the non-vibrating molecule in the ground state equilibrium geometry, then evaluated by integrating the equations of motion. The simulations were run for 20 fs, which is sufficiently long for our objective since the short core-hole lifetime of few fs for the second-row elements ensures that most core-excited states will have decayed within this time. Molecular dynamics (MD) simulations were performed in the O1s core-hole excited states (CHES) from the S_0, T_1, and S_1. Time evolution of bond lengths, velocities, and kinetic energies of the motion

between bonded-pair atoms for all oxygen-containing bonds were calculated.

3. Results and discussion

3.1. XAS

The XAS from the S_0, T_1 and S_1 of both molecules are shown in Fig. 1. Transition energy values are summarized in Table 1 for each oxygen site, $O_{(C=O)}$ and $O_{(O-H,O-CH3)}$, together with the orbital character of destination orbital in core excitation. As the designation of destination orbitals commonly applicable for core excitations from S_0, T_1, S_1 states, orbital designation for the S_0 is used also for S_1 and T_1, just as representation of the energetic order. The transitions from $O_{(C=O)}$ 1s to HOMO appear in S_1-XAS and T_1-XAS at about 527.3 eV well below the lowest peak of S_0-XAS. However intensity of these transitions are very weak. Their peak positions are consistent with expectation based on the lower orbital energy of the HOMO than LUMO. Very weak intensities of transitions to HOMO is different from the expectation that their intensities should be strong because the HOMO in valence excited state has non-bonding (n) orbital character being almost pure $O_{(C=O)}$ 2p as shown in insets of Fig. 1. The reason for the weakness of transition intensities from $O_{(C=O)}$ to HOMO both in S_1- and T_1-XAS can be explained as follows. As core-hole created by core-excitation increases effective Coulomb attraction to valence electrons, energy order and wavefunctions are inevitably changed. Actually present XAS calculation shows that the non-bonding character of the HOMO vanishes by the $O_{(C=O)}$ 1s core excitation both from S_1 and T_1. As this resultant orbital in core excitation has no overlap with $O_{(C=O)}$ 1s, transition intensity becomes very week.

From the view point of experiment existence of strong peak in the core excitation from the S_1 and T_1 in the energy region with no peak of S_0-XAS would be desired. Instead, the T_1-XAS of both molecules have strong absorption peak at around 533.3 eV where no absorption from the S_0 exist. It is possible to identify the core-excitations from the T_1 by detecting this peak and to perform selective excitation from the T_1 without hindrance by S_0-XAS.

3.2. Bond dynamics

Time evolution of bond length and departing kinetic energy of the O—H bond in BzA after the $O_{(O-H)}$ core-excitation and of the O—CH$_3$ bond in BzAMe after the $O_{(O-CH3)}$ core-excitation are shown in Fig. 2. It was observed for the $O_{(O-H)}$ 1s core excitation to the LUMO and LUMO+1 from the S_1 of BzA that the O—H bond exhibits rapid elongation reaching to kinetic energy of 1.0 and 1.6 eV respectively for transitions to LUMO and LUMO+1 at the O 1s core-hole lifetime (4 fs) [9], and finally reaching constant kinetic energy state i.e. dissociation state after $\sim$ 10 fs. This result shows that about 8%, exp (-10/4), of the core excited state that survived Auger decay gives neutral H atom. O—H bond dissociation for core excitation to LUMO and LUMO+1 is originated from that characters of these orbitals are changed to strongly antibonding σ^* by considerable change of attractive potential after core-hole formation.

Rapid elongation is also observed for the O—CH$_3$ bond of BzAMe in the $O_{(O-CH3)}$ 1s to LUMO+2 excitation from the S_0 and T_1. Especially in the core excitation from the T_1, the O—CH$_3$ bond dissociates after $\sim$10 fs and will give neutral CH$_3$ fragment. On the other hand core excitation from the S_0 result in not dissociation but vibrational excitation of O—CH$_3$ bond with fairly large kinetic energy of 0.45 eV reached at 4 fs.

Experimentally, however, CH$_3^+$ ion yield peak has been observed at around 536.5 eV in the O 1s core excitation of thin-layer molecules containing —COOCH$_3$ group [10]. This state selective