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Systematics of the gradient on the resonant core-hole state

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Abstract

Systematics of the gradient on the resonant core-hole state in the Franck-Condon region were investigated theoretically. The steepest gradient for a target bond in the resonant core-excited states becomes more negative with increasing sum of atomic numbers of the atom in the bonded pair and increasing bond order for the associated chemical bond. Gradients for molecules that include conjugated double bonds such as butadiene and hexatriene were also examined at the lowest core-hole state. The gradients for the double bond become negative while that those for the single bond become positive with few exceptions, suggesting that a fragment from a target molecule gains its initial momentum at the multiple bond.

Keywords: Chemical reaction following core-excitation; Soft X-ray; Density functional theory; Core-hole excited state dynamics; Site-specific chemical reaction; Molecular size effect

1. Introduction

Reaction dynamics following core-excitation by soft X-ray radiation constitute an active field in physical chemistry and chemical physics [1–4]. In deexcitation via the core-hole state, specific chemical reactions inaccessible by valence excitation are expected. The core-hole state is unstable, whether it might be dissociative or predissociative, and Auger decay takes place within a few femtoseconds. Site-specific and state-specific bond scissions or bond elongations have been observed for polymer thin films such as poly-(methyl methacrylate) (PMMA) [5,6], and ice surfaces [7]. It is important to examine the dynamics of the core-hole state to elucidate these phenomena. Although many experimental and theoretical studies have been reported, general trends of the dynamics on the core-hole state have not been described explicitly. As a key point to understand these phenomena, we theoretically investigated the general trends of the gradient on the resonant core-hole state at the equilibrium geometry for many kinds of molecules, within the framework of density functional theory (DFT).

Recent developments of theoretical procedures to describe the core-excited state are remarkable. Especially, DFT can describe the core-excited state within chemical accuracy despite its simple formulation. This procedure has been widely applied to systems ranging from small molecules in the gas phase [8–10] to large systems such as surface adsorbed molecules using cluster models [11] and to models of liquid water and ice [12,13]. Furthermore, this procedure has been recently extended to decay processes such as Auger electron spectroscopy [14] and X-ray emission spectroscopy [15] with dynamics of the core-hole state.

In the present study, we report the relationship between the gradient of the potential energy surface at the resonant core-excited state and the associated chemical bond. This is of importance for elucidating not only the dynamics in the resonant core-hole state, but also the chemical reaction after Auger decay.

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2. Calculation procedure

The molecules investigated in the present study are listed in Table 1. Equilibrium geometries for each molecule on the ground state are first optimized at the MP2/cc-pVDZ level. Then the obtained structures are reoptimized at the DFT level with the same basis sets and functionals used by the following calculations for the core-excited state. Gradients are so sensitive for the computational level, optimized geometries should be estimated by the same level of approximation that we used for the core-hole state.

Details of the computational procedure to obtain the core-hole state have been described elsewhere [9,10]. The resonant core-excited states were determined variationally with maintained orthogonality between the excited states through the following procedure: the first excited state was obtained by fixing the occupation of the core spin orbital to zero and placing the excited electron in the first unoccupied orbital. A full relaxation with this constraint engenders a state that is near-orthogonal to the ground state because of the $1s^{-1}$ configuration. The subsequent state was then obtained by removing the variationally determined excited orbital from the variational space and occupying the next level. This procedure gives a variational upper bound to the energy and guarantees orthogonality between the excited states because all remaining orbitals now must be orthogonal to the successively defined and eliminated levels [9]. The non-core-excited atoms were described by effective core potentials (ECP) [16], which simplifies the definition of the core-hole state because the use of an ECP description eliminates the 1s level of the atom to which it is applied. This approximation is very helpful in core-hole calculations for an atom. Calculations of the core-hole states with ECPs have already been applied to the study of the resonant Auger spectroscopy and X-ray emission spectroscopy of water, including core-hole excited state dynamics simulations [14,15].

Table 1
Calculated molecules in the present study

Compounds	Molecules
Carboxylic acid	R—COOH (R = H, CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9)
Alcohol	R—OH (R = H, CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9)
Aldehyde	R—CHO (R = H, CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9)
Alkane	R—CH_3 (R = H, CH_3, C_2H_5, *i*-C_3H_7,*t*-C_4H_9)
Alkene	R—CH=CH—R′ (R,R′ = H, CH_3)
Alkyne	R—C≡C—R′ (R,R′ = H, CH_3)
Amine	R—NH_2 (R = H, CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9), $(CH_3)_2NH$, $(CH_3)_3N$
Azo	R—N=N—R′ (R,R′ = H, CH_3)
Azomethine	RR′—CN—R″ (R,R′,R″ = H, CH_3)
Ether	R—O—CH_3 (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9)
Fluoromethane	CH_3F, CH_2F_2, CHF_3, CF_4
Hydrazine	NRR′—NR″R‴ (R,R′,R″ = H, CH_3)
Hydroxyamine	NRR′—OR″ (R,R′,R″ = H, CH_3)
Ketone	CH_3COCH_3, CH_3CONH_2, NH_2CHO, NH_2CONH_2
Nitrile	R—C≡N (R = H, CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9)
Nitro	R—NO_2 (R = H, CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9)
Oxime	RR′—C=N—OH (R,R′ = H, CH_3)

To obtain an improved representation of relaxation effects in the inner orbitals, the ionized center was described using the IGLO-III basis of Kutzelnigg et al. [17], whereas a (311/1) basis set was used for the hydrogen atom. Gradient-corrected exchange and correlation functionals attributable to Perdew and Wang were applied in the present study [18,19]. The first geometry optimizations were performed using the Gaussian 03 program [20]; other calculations were performed using the StoBe-DeMon program [21].

3. Results and discussion

The gradients on the core-excited state are examined over the Franck-Condon (FC) region for specifically targeted chemical bonds of interest for measurement of bond scission. As a typical example, potential energy curves for a C—N triple bond of acetonitrile in the N(1s) and C(1s) core-excitations by fixing other geometrical parameters are shown in Fig. 1; the gradients at the equilibrium geometry of the ground state are listed in Table 2. A fast scission of the C—N triple bond of acetonitrile with $N(1s) \rightarrow \pi^*(CN)$ excitation has been reported [22], and specific chemical reactions following core-excitation such as sudden C—N bond scission have been observed for other molecules that include a C—N triple bond [23,24]. We see that the first resonant state has the most negative gradient in the FC region at the N K-edge, which is assigned to $N(1s) \rightarrow \pi^*(CN)$ excitation. Moreover, the magnitude of the most negative gradient of the resonant excited state for each core atom decreases in the order of N(1s), C^1(1s), and C^2(1s), i.e., the gradient of the resonant core-excited states is more negative when the core atom is connected directly to the target bond. Also, that of the resonant core-excited states from the atom with a larger nuclear charge is more negative. To elongate a target bond on the core-excited state (the C—N triple bond in this case), it is most efficient to excite either of the two atoms directly involved in the bond. Moreover, it is more efficient to excite the atom with the larger nuclear charge. The results described above show that the C—N triple bond scission, or elongation, is accelerated by the dynamics induced by $N(1s) \rightarrow \pi^*(CN)$ excitation. Actually, fast bond scission has been observed at the $N(1s) \rightarrow \pi^*(CN)$ excitation in the molecule including a C—N triple bond. On the other hand, a specific bond scission has not been observed at the C K-edge.

To discuss the origin of the repulsion of the resonant core-excited state, the gradients of the core-ionized state and those by the equivalent core approximation, i.e., the $Z+1$ approximation, are also listed in Table 2. The positive gradient of the core-ionized state by N(1s) and C(1s) excitations suggests that the anti-bonding character of the excited orbital contributes to the negative gradients by N(1s) and $C(1s) \rightarrow \pi^*(CN)$ excitation. Neutral and ionized