Systematics of the gradient on the resonant core-hole state

Osamu Takahashi, * Takayuki Matsui, Akio Kawano,
Kiyohiko Tabayashi, Katsuyoshi Yamasaki

Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

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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.

Key words: chemical reaction following core-excitation, soft X-ray, density functional theory, core-hole excited state dynamics, site-specific chemical reaction, molecular size effect

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* Corresponding author. FAX: +81-82-424-0727
Email address: `shu@hiroshima-u.ac.jp` (Osamu Takahashi,).

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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.

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 1*s* 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].

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) $\longrightarrow \pi^*$(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) $\longrightarrow \pi^*$(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) $\longrightarrow \pi^*$(CN) excitation. Actually, fast bond scission has been observed at the N(1s) $\longrightarrow \pi^*$(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) $\longrightarrow \pi^*$(CN) excitation. Neutral and ionized states by the Z+1 approximation correspond to the first resonant and ionized state by core-excitation, respectively. Although the same trends with the gradients for the core-hole states can be reproduced by those for the Z+1 approximation at the N(1s) and C^1(1s) excitations, the magnitude of the gradient by the core-hole states is more negative than that by the Z+1 approximation, suggesting that the nuclear-nuclear repulsion between a core-hole atom and a bonded atom also contributes to the negative gradient.

Core-hole excited state molecular dynamics simulation [6,15,25] was performed for the first resonant excited state to examine the bond elongation of a C-N triple bond of acetonitrile during the dynamics on the core-hole state. The starting geometry was the equilibrium geometry in the ground state. We found that a C-N triple bond of acetonitrile elongates only 0.092 $\mathring{A}$ during the core-hole lifetime of N(1s) atom, ca. 5.0 fs, because of the heavy masses of the fragments, indicating that the most parts of dissociation depend on the potential of the Auger final state. The dynamics of the core-hole state are important to determine the initial acceleration of the dissociation motion.

Similarly, gradients of the potential curves for two bonded atoms were examined for many compounds listed in Table 1; the most negative one among the five low-lying core-excited states was chosen because the selected state can be expected as the most efficient state for bond scission of the target bond. The low-lying resonant excited state remains valence type in character. The gradient for the target bond will become more negative by the anti-bonding character of the excited state. For higher excited states, because of mixing with Rydberg resonances, it is expected that the anti-bonding character will be decreased. Although we do not show the state of character explicitly, we confirmed that the excited state of the same character was chosen in the same functional groups automatically. The results are summarized in Fig. 2. Note that functional groups connected by several groups such as the ester functional group and conjugated double bonds are excluded to avoid confusing the discussion. Analogously to Stöhr [26], we grouped the target bonds according to Z, the sum of atomic numbers of the bonded atomic pair, such that a C-C bond is characterized by $Z = 12$, etc. An asterisk indicates a core-excited atom. Depending on the chemical environment around the target bonds, gradients have some distribution in the same Z. With few exceptions, the gradient apparently becomes more negative with increasing Z. Furthermore, even if the Z is the same, the gradient is more negative when a heavier atom is core-excited, e.g., the gradient of N*-C bond is more negative than that of N-C* bond, etc., i.e., the core-hole state with larger Z causes more repulsive potential because of the large nuclear charge.

Correlations of the gradient with the bond length for the target bond are shown in Fig. 3. As typical examples, X*-H, C*-X, and C-N* cases are illustrated, where X means C, N, O, and F atoms. As shown in Fig. 2, gradients have some distribution depending on the chemical environment around the target bond in the molecule. Gradients become more negative with shortening bond length of the target bond. Especially in Fig. 3(c), the correlation between the gradient and the bond order is readily apparent. The repulsion induced by the core-hole becomes strong with decreasing bond length. Therefore, the degree of steepness can be understood as the following effects; the repulsion from occupying the anti-bonding orbital by the excited electron and the nuclear-nuclear repulsion between the core-hole and another atom associated by the target bond. These contributions are enhanced by a shorter bond length.

Similar figures to Figs. 2 and 3 can be found in a monograph written by Stöhr [26]. That monograph described the systematics of π^* and σ^* positions and 1s ionization potentials. The trends of bond scission or bond elongation seem to have similar systematics because of the perturbation of the core-hole atom to the chemical bond and because of the anti-bonding character of the excited orbital.

Previous studies have examined the molecular size effect of the chemical reaction following core-excitation both experimentally [23,24] and theoretically [27,28]. Those studies showed that the site-specificity of chemical reaction following the core-excitation in the molecule is decreased by some CH_2 functional groups, to which the target functional groups are connected by a single bond. In the theoretical papers, the effect has been explained as the difference in bond order between the ground and Auger final states. Our results suggest that this effect was confirmed implicitly by the relationship between the gradients on the core-hole state and the excited atom's position.

A molecule that includes conjugated double bonds cannot be expected to exhibit the effect discussed in the previous paragraphs. To explain that point theoretically, we examined the gradient of the first resonant excited states for butadiene, hexatriene, acrolein (CH_2=CH-CHO), and acrylonitrile (CH_2=CH-CN). Note that we limited the investigation to the first resonant excited state to illustrate the effect of the conjugation explicitly. Gradients for each C-X bond, where X is C, N, and O atoms, are shown in Fig. 4. Alternating negative and positive gradients are obtained for each case because of the short bond length of the double bond. It is noteworthy that gradients of a double bond that is not connected to the core-hole atom also become negative. For the conjugated double bonded system, it might be expected that distinct site-selective bond scission is observed.

Many investigations of ultrafast dissociation following core-excitation have been reported subsequent to the pioneering work by Morin [29], most of which are systems including 16 and 17 group elements, i.e., the core-excited atom lies on the right side in the periodic table of the elements. We expect to find a strong repulsive potential on the core-excited state in the low-lying core-excited states attributable to the anti-bonding valence character and a strong repulsive force induced by the core-hole state. Therefore, the bond dissociation or elongation of the target bond will be accelerated within the core-hole state.

Site-specific chemical reactions following core-excitation have been observed for some thin films such as PMMA [3,5], and have been examined theoretically very recently [6]. In those systems including an ester functional group, investigators have found site-specific bond scission around O-C bonds. These experimental results can be interpreted by the relationship we discussed in the present paper.

4 Summary

Conclusions of this study can be summarized as follows:

(1) The core-excitation of the atom associated with the target bond is the most efficient for the site-specific bond scission.
(2) The gradient of the resonant core-hole state in the FC region becomes more negative with the increasing sum of atomic numbers of bonding pair atoms.
(3) The gradient becomes more negative by core-excitation of an atom with a larger atomic number.
(4) The gradient becomes more negative with increased bond order.

Fast dissociation in the resonant core-hole state should correlate with the site-specific chemical reaction following core-excitation. The above rules will be helpful to elucidate the dynamics of the resonant core-hole state and to explore new chemical reactions following core-excitation.

In this study, we specifically examined bond elongations on the core-hole state by the most primitive approximation, i.e., elongation of the target bond only. Excitations of bending motion are also important for the geometry change in the molecule to discuss dynamics of the core-hole state. Actually, highly excited vibrational structure of O(1s) $\longrightarrow$ $2b_2$ core-excitation of H_2O were observed [30]. Furthermore, the fragment mass effect should be also important to consider the chemical reactivity, i.e., when the fragment ions are massive, the bond scission might not be accelerated within the lifetime on the core-hole state due to the slow dynamics. However, bond scission will be assisted by the dynamics of the core-hole state as we have discussed in the previous section. Fully relaxed dynamic calculations are necessary to understand the whole mechanism of the chemical reaction through core-excitation.

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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)

Table 2

Gradients of potential curves (in eV Å^{-1}) for five resonant excited and core-ionized states of acetonitrile by core-excitation. Gradients by the equivalent core approximation, which correspond to the first resonant and core-ionized states, are also shown.

core-excited state	N(1s)	C^1(1s)	C^2(1s)
first	-7.17	-6.87	1.18
second	-7.19	-6.88	-1.96
third	-0.04	1.78	-1.97
fourth	1.33	2.62	-3.50
fifth	1.38	2.46	-3.49
core ion$^{(a)}$	1.05	2.07	1.37
Z+1$^{(b)}$	-6.72	-5.65	-0.50
ion$^{(c)}$	1.50	3.63	0.84

(a) Gradients on the core-ionized state.

(b) Gradients for the first resonant state by the equivalent core approximation.

(c) Gradients for the core-ionized state by the equivalent core approximation.

Figure captions.

Fig. 1. Potential energy curves for C-N bond of acetonitrile. Dotted vertical lines indicate the equilibrium bond distance of C-N bond at the ground state.

Fig. 2. Most negative gradient for the five low-lying core-excited states as a function of Z, the sum of atomic numbers of bonded atomic pairs. (a) Single bond. (b) Double bond. (c) Triple bond. (d) X-H bond, where X means C, N, O, and F atoms.

Fig. 3. Most negative gradient for the five low-lying core-excited states as a function of bond length. (a) X^*-H bond, (b) C^*-X bond, (c) X^*-C bond, and (d) C-N bond, where X means C, N, O, and F atoms.

Fig. 4. Gradient for the first resonant core-excited states of molecules including the conjugated double bond as a position of the chemical bond.

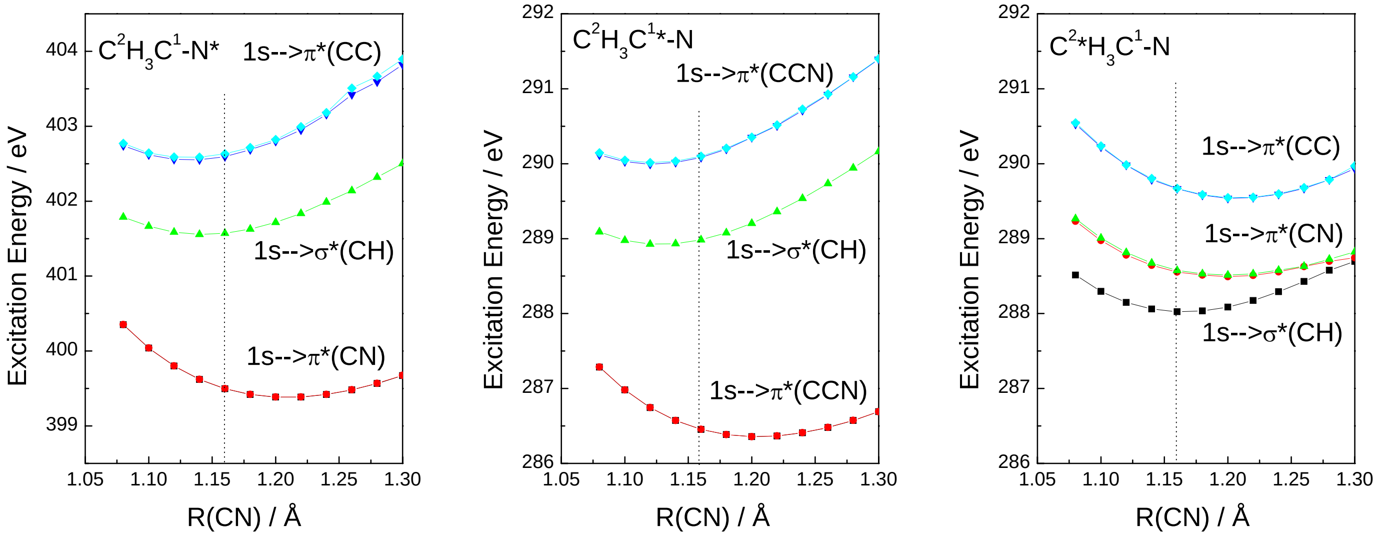

Fig.1 Takahashi et al.

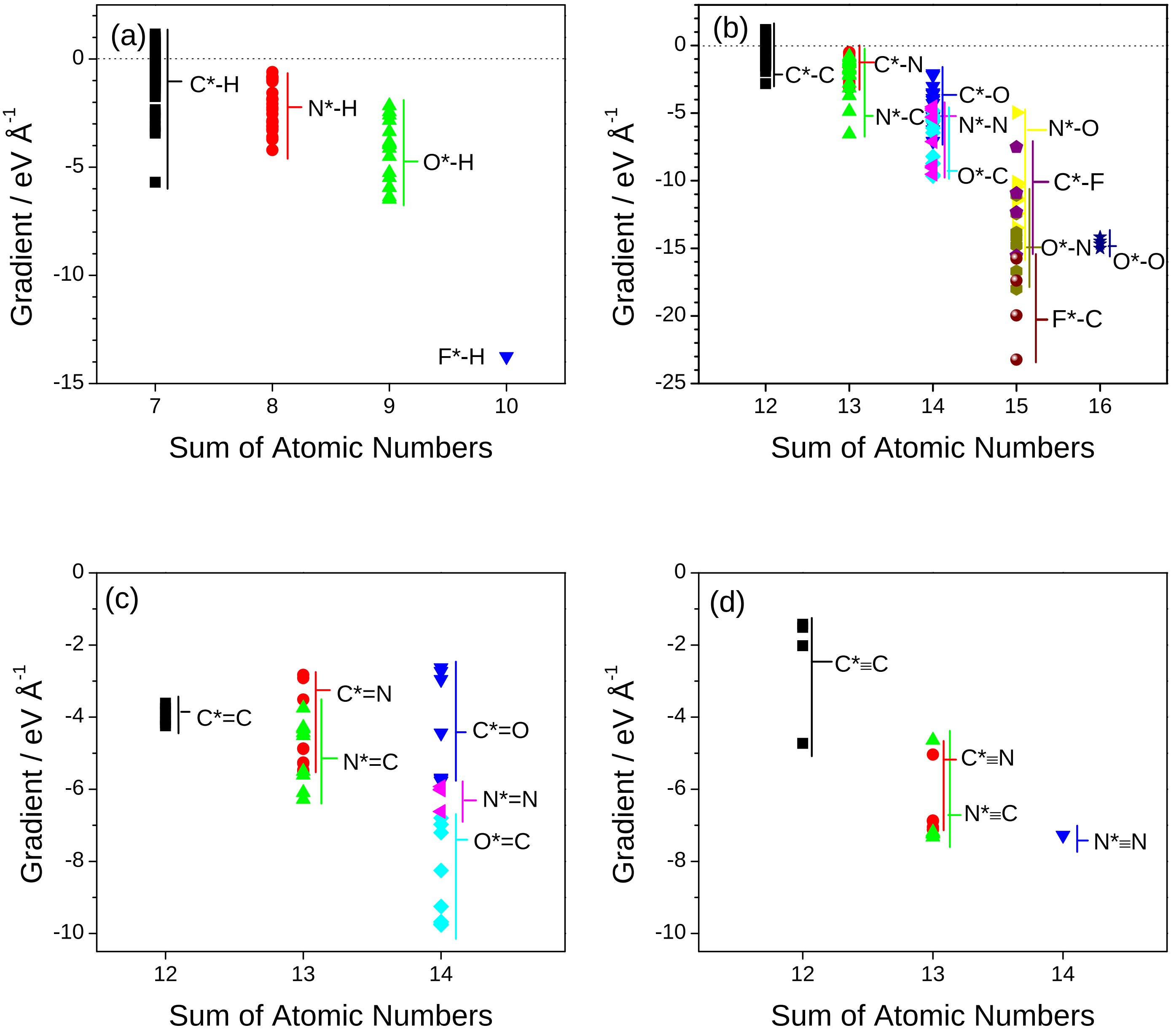

Fig.2 Takahashi et al.

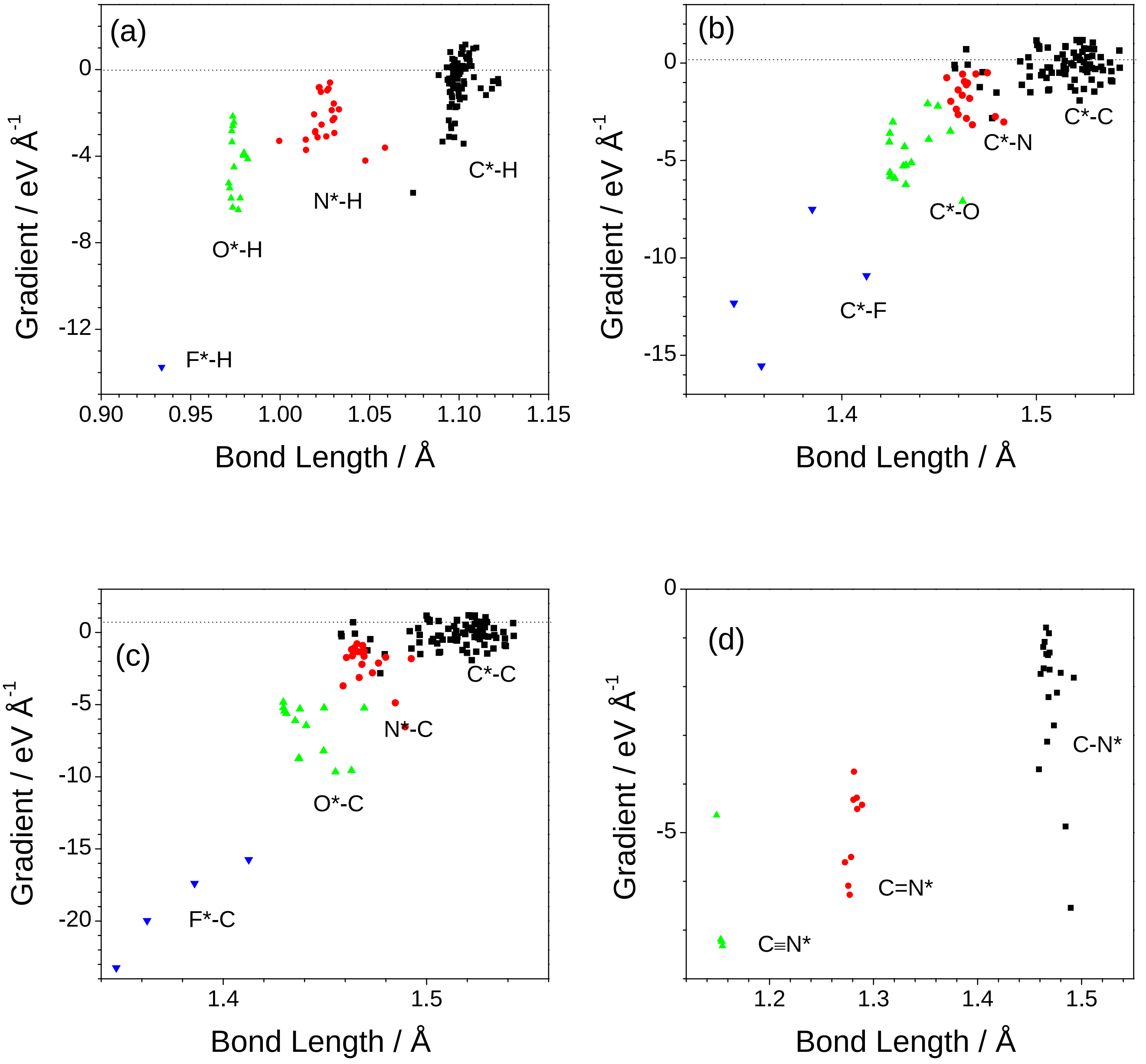

Fig.3 Takahashi et al.

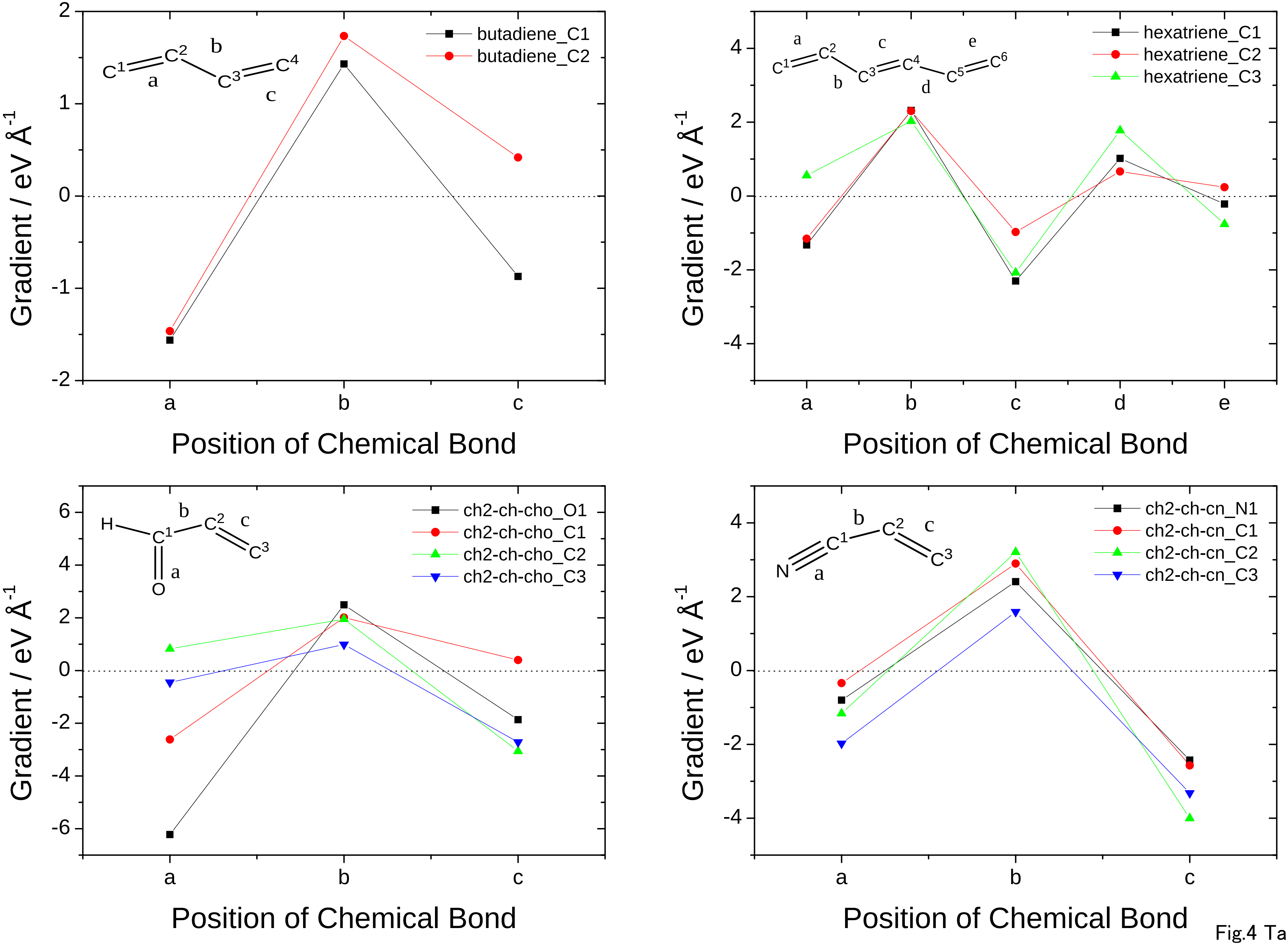

Fig.4 Takahashi et al