



## Theoretical study on decay of molecular double core-hole state

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### ABSTRACT

Molecular double core-hole (DCH) state, having two core-hole vacancies in its K-shell orbital(s), has attracted attention in recent experiments using X-ray free electron laser and synchrotron radiation with multi-electron coincidence technique. From theoretical point of view, we describe basic properties of ionization energy of molecular DCH state, including dependence of the ionization energies on molecular environments. Decays of molecular DCH state by Auger electron emission and X-ray emission will be discussed, using CH<sub>4</sub> and CO as representative examples.

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### 1. Introduction

Recently, molecular double core-hole (DCH) state, i.e., a state with two core-hole vacancies in its K-shell orbital, has been successfully detected in several experiments using X-ray free electron laser (XFEL) [1–4] and synchrotron radiation (SR) with multi-electron coincidence technique [5–7]. Only the single-site (ss-) DCH state, in which two core-electrons are ionized from the same atomic site, has been found in the earlier experiments [1,2,5,6]. Later, the two-site (ts-) DCH state, whose two core-electrons are ionized from different atomic sites, has also been detected in both XFEL and SR experiments [3,4,7]. Formation mechanism of molecular DCH state is different in XFEL and SR experiments [7]: sequential two-photon two-electron ionization in XFEL experiment and one-photon two-electron ionization, even in ts-DCH formation, in SR experiment. The motivation of these experiments is partly related to the theoretical observation [8,9] that so-called inter-atomic relaxation energy can be extracted from the ionization energy of ts-DCH state, which contains information not easily available by single core-hole ionization energy.

Molecular DCH state decays by Auger electron emission or X-ray emission, as single core-hole state does. Auger electrons emitted by DCH decay have been observed in some experiments. For example, the Auger spectrum of ss-DCH decay was measured for NH<sub>3</sub> in the SR experiment using triple electron coincidence method [5], while two-dimensional Auger spectra of N<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> ss-DCH decays, showing energy correlation between two Auger electrons, were obtained by four-electron coincidence experiments [6,7,10]. In the

XFEL experiments, Auger spectra of N<sub>2</sub> and CO have been obtained by taking difference of focused high-intensity beam and de-focused low-intensity photon beam [2,3]. These Auger electron spectra are expected to contain valuable information on how molecular DCH state decays. So far, X-ray emission by molecular DCH decay has not been reported. In atomic case, there have been several studies on X-ray emission from DCH (hypersatellite) decay. For example, X-ray emission from decay of the atomic neon DCH state was experimentally observed [11] and has been theoretically analyzed [12,13].

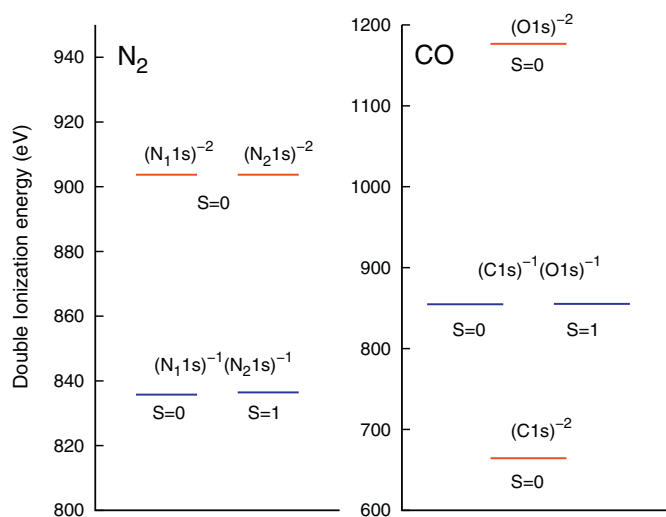
For the past few years, we have performed theoretical studies [9,14–18] on molecular DCH state in order to understand its basic properties. In this presentation, we first describe the properties of ionization energy of molecular DCH state, based on our recent theoretical works as well as newly calculated data. Then, we discuss Auger decay of molecular DCH state [16] using CH<sub>4</sub> as an example. In addition, possible X-ray emission from DCH decay of CO molecule is also discussed.

### 2. Ionization energy of double core-hole state

In Fig. 1, double ionization energies (DIEs) of DCH states are shown, using N<sub>2</sub> and CO as examples. These energies were taken from our previous paper [9]. In the N<sub>2</sub> case, and also other homonuclear closed-shell molecule, four main lines exist, of which two higher energy main lines correspond to ss-DCH states, and two lower energy main lines correspond to ts-DCH states. The ionization energies of the ss-DCH states are located much higher than those of the ts-DCH states, because of strong Coulomb repulsion between two core-holes. In the CO case, and also other heteronuclear closed-shell molecule in general, we have three groups of main lines. In this case, the ts-DCH main lines are located between the two different ss-DCH main lines. The arrangement of DCH main

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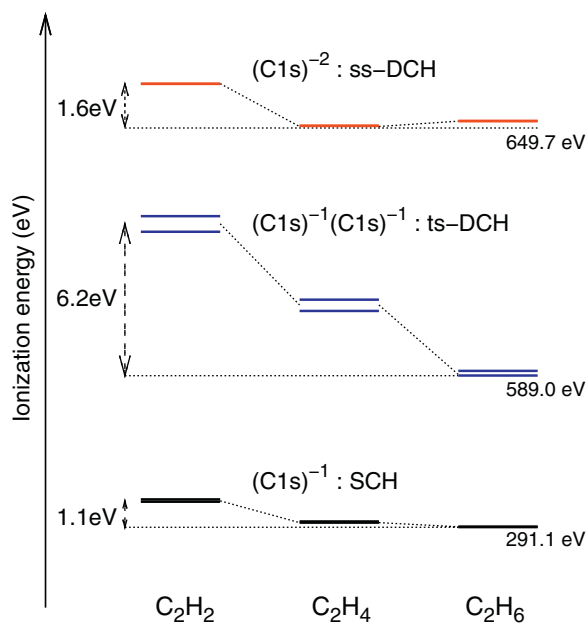
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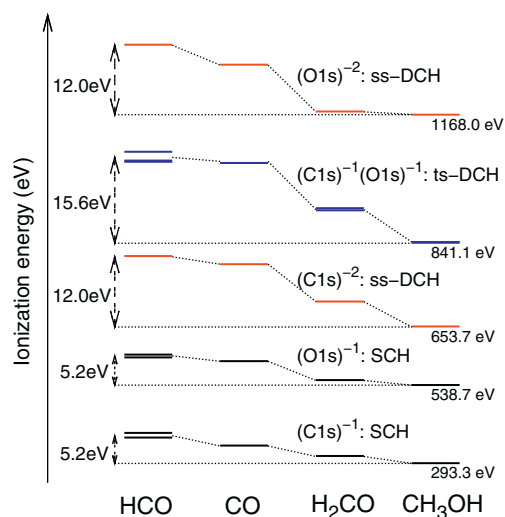
**Fig. 1.** Typical arrangement of double ionization energies for small molecule DCH states.  $S$  represents total spin. Red lines show location of the ss-DCH states, whereas blue lines shows ts-DCH states. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

lines in larger molecules can be understood in similar manner. For open-shell molecule, more complex arrangement of main lines is observed because of spin coupling between valence-shell electrons and core electrons [14].

Fig. 2 compares differences of ionization energies for ts-DCH, ss-DCH and single core-hole (SCH) states in  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ . Although the same comparison was made by Cederbaum and co-workers in 1986 [8], we show Fig. 2 here for explanation purpose. These ionization energies were calculated by full-valence CASSCF method [19,20] with cc-pVTZ basis set [21] as described in our previous paper [9]. Maximum difference of the SCH ionization energies among these three molecules is relatively small, 1.1 eV. The difference of the ss-DCH ionization energies is similarly small, 1.6 eV. In contrast, the variation of the ts-DCH ionization energies, 6.2 eV, is



**Fig. 2.** Comparison of two-site (ts-) DCH, single-site (ss-) DCH, and single core-hole (SCH) ionization energies for  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ . Relative values with respect to the lowest value (indicated at lower right position of black horizontal line) in the same group of core-hole state are shown in the figure.



**Fig. 3.** Comparison of two-site (ts-) DCH, single-site (ss-) DCH, and single core-hole (SCH) ionization energies for HCO, CO,  $H_2CO$  and  $CH_3OH$ . The ionization energies were calculated using the same method as in our previous work [9]. The other details are the same as in Fig. 2.

much larger than those of the other two cases: 3.9 and 5.6 times larger than that of ss-DCH and SCH ionization energy, respectively. In other word, in the case of  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ , the ts-DCH ionization energy is much more sensitive to the change of molecular environment compared to the ss-DCH and SCH ionization energies. Because of this large variation in ionization energies, it has been suggested [8,9] that spectroscopy of ts-DCH state may be used for chemical analysis as in electron spectroscopy for chemical analysis (ESCA) [22]. In case of HCO, CO,  $H_2CO$  and  $CH_3OH$  molecules shown in Fig. 3, variation of ionization energies in ts-DCH states is still the largest, 15.6 eV, however, it is only 1.3 times larger than the variation in ss-DCH ionization energies, and 3 times larger than that of SCH energies. Thus, in this sequence of molecules, ts-DCH and ss-DCH ionization energies have similar sensitivity to the molecular environment. As can be seen from Figs. 2 and 3, putative “superiority” of ts-DCH ionization energy over ss-DCH and SCH energies in chemical analysis may depend on which kind of molecules we will compare. Here the term “superiority” is used just in theoretical consideration, meaning larger energy variation of ts-DCH states as seen in Fig. 2. Needless to say, conventional spectroscopy of SCH ionization energy is practically much more accurate and convenient compared to that of DCH state at present.

### 3. Decay of molecular double core-hole state

#### 3.1. Auger decay

Molecular DCH state decays by Auger electron emission or X-ray emission. In case of low- $Z$  element, Auger electron emission may be the dominant decay pathway, considering the theoretical work on atomic DCH decay [23]. In order to understand basic properties of Auger spectrum originated from molecular DCH decay, we have performed theoretical calculation on small molecules [16]. In our calculation, two-step Auger decay mechanism was assumed: the 1st Auger decay from DCH state to singly core ionized doubly valence ionized (CVV) states, and the 2nd Auger decay from CVV states to quadruply valence ionized (VVVV) states. The relative Auger intensities were evaluated using Wentzel’s formula. The two-electron integrals containing an Auger electron orbital were approximated by valence electron population at core-ionized site [16].

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