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Probing chemical environment with molecular double core-hole electron spectroscopy

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ABSTRACT

With the advent of X-ray free electron lasers and the development of elaborate multi-coincidence methods combined with conventional synchrotron radiation, the interest in double core-hole spectroscopy revived. To describe the measured data and provide the guideline for yet coming experiments, theoretical studies are required. In this paper we review previous theoretical works on double core-hole states and discuss new theoretical results for the XH_m–YH_n (X, Y = C, N, O, or F; m,n = 0–3) molecules and their fluorine substituted compounds. We compute the single and double core-hole binding energies of these systems using different methods and show that the DFT results agree well with the results of other *ab initio* methods. In agreement with previous theoretical works, our study demonstrates that the changes in the ionization potential resulting from fluorine substitutions mainly arise due to changes in the ground state and not due to electron relaxation. Special emphasis is given to interatomic relaxation originating from creation of two core holes on different atomic sites. We demonstrate that there exists clear correlation between this quantity, the number of hydrogen atoms and the order of the bond between the heavy atoms in the systems studied.

1. Extended introduction: Recent history of DCH spectroscopy

It is well known that the core electron binding energy is influenced by chemical environment around the core-ionized atom. X-ray photoelectron spectroscopy (XPS) can probe this chemical shift and thus is widely used for chemical analysis [1]. A change in the core-electron binding energy is caused by two different effects [2]. The first effect is often called the initial-state energy shift and originates from the change in the bonding interaction of the given molecule in the ground state. This effect is reflected in the Hartree–Fock (HF) core orbital energy. The second effect is caused by the change of the polarizability of external ligands that leads to different screening contributions to the core hole. This effect is related to the change of electronic relaxation energy.

Almost three decades ago, Cederbaum et al. [3–5] demonstrated that the energy shifts of double core-hole (DCH) states are much more sensitive to the chemical environment than the energy shifts of single core-hole (SCH) states. These theoretical works on DCH states were followed by that of Ågren et al. [6]. Experimental measurements of DCH states were, however, very difficult because of small cross sections and thus only a few experimental observations of such states were reported until very recently [7–10].

Interest in DCH spectroscopy revived with the recent advent of intense free electron lasers (FEL) in the soft X-ray spectral range as, for example, Linac Coherent Light Source (LCLS) [11] in USA. Santra et al. [12] proposed X-ray two-photon photoelectron spectroscopy (XTPPS) as a promising tool for measuring DCH states with LCLS. In the first term of the LCLS user operations, Young et al. [13] created DCH states in the atomic neon while Cryan et al. [14] and Fang et al. [15] created DCH states in the nitrogen molecule. At nearly the same time, Eland et al. [16] and Lablanquie et al. [17] measured DCH states in a number of other molecules using multi-coincidence methods with conventional synchrotron radiation sources.

There are two classes of DCH states: with two holes at one atomic site and with two holes at two different atomic sites. The first experimental DCH studies dealt mainly with single-site DCH (ssDCH) states as these states can be created easier. In particular, two core holes in an L-shell can be produced in systems with heavy elements *via KLL* Auger decay as reported in Refs. [18,19]. Note that one of the advantages of the ssDCH spectroscopy is the ability to separate the contributions to the chemical shift originating from the initial-state

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effect and from the relaxation energy as noted in Refs. [18–20] in connection with core–core–core Auger spectroscopy. This aspect of ssDCH spectroscopy was recently re-addressed by creating ssDCH states using single photon absorption [21].

As demonstrated by Cederbaum et al. [3–5], two-site DCH (tsDCH) states, which are hardly accessible *via* Auger decay, is the heart of DCH spectroscopy since these states are most sensitive to the chemical environment. Because of the revival experimental interest in DCH spectroscopy, Tashiro et al. [22,23] investigated double core-hole states of small molecules (mostly diatomic and triatomic) using the complete active space self-consistent field (CASSCF) method and found that interatomic relaxation energies are different for diatomic and triatomic molecules. In triatomic molecules, these energies were shown to strongly depend on the location of the two core holes.

The theoretical work of Tashiro et al. [22,23] was followed by experimental studies on tsDCH states. Berrah et al. [24] created the tsDCH states in CO using XTPPS, while Lablanquie et al. [25] measured the tsDCH states in C_2H_2 with multi-coincidence methods and synchrotron radiation. Salén et al. [26] investigated the tsDCH states in N_2, CO, N_2O and CO_2 applying XTPPS and elucidated the role of interatomic relaxation energy in the chemical sensitivity of DCH spectroscopy following the recipe of Tashiro et al. [22]. Nakano et al. [27], on the other hand, investigated the tsDCH states in C_2H_2, C_2H_4 and C_2H_6 using multi-coincidence methods and discussed the chemical sensitivity of tsDCH spectroscopy, following the discussion given in the pioneering paper of Cederbaum et al. [3].

Stimulated by the experimental progress described above, Tashiro et al. [28] investigated Auger decay of ssDCH and tsDCH states. The Auger spectra calculated using CASSCF were compared with experimental ones [16,24,26,27,29–31] Tashiro et al. [32] also computed satellites in DCH spectra which agree well with those seen in the experimental spectra reported in Ref. [17]. Niskanen et al. [33] studied theoretically the relativistic contributions to DCH states in noble gases. Localization properties of multiple core hole states were explored by Carravetta et al. [34] using restricted active space (RAS) SCF method.

Large molecules were in focus of DCH studies as well. Kryzhevoi et al. [35] investigated the DCH states of *para*-, *meta*- and *ortho*-aminophenol molecules using Green's functions methods and demonstrated that these isomers are distinguishable by DCH spectroscopy. Takahashi et al. [36,37] were the first who applied the density functional theory (DFT) for computing energies of DCH states. In the beginning, the DFT computations were carried out for relatively small molecules (*e.g.*, formamide) where the DFT results can be directly compared with the CASSCF results [36]. This study demonstrated the feasibility of DFT for computing DCH states. Then, larger molecules were considered (*e.g.*, SiH_4 and nucleobases) where the application of CASSCF is practically impossible [37].

The above-mentioned theoretical works on large molecules stimulated experimental investigations of these molecules at LCLS. For these molecules, a straightforward XTPPS did not work well. Instead, the international team developed a novel approach, a partial covariance mapping combined with a magnetic bottle spectrometer and succeeded to demonstrate proof-in-principle experiment using the atomic neon [38,39]. The data analysis for the DCH states and subsequent Auger decay in C_2H_2 and C_2H_6 has been just completed [40]. The data analysis of other more complex molecules are still in progress.

The DFT study of Takahashi et al. [37] stimulated further theoretical studies on DCH states. Thomas [41] calculated DCH states for a number of molecules and explained the results using graphical representations, called Wagner plots. These are known for a long time in the field of core–core–core Auger spectroscopy [18–20]. Wagner plots allow one to separate the contributions from the initial-state effect and the relaxation energy to core level ionization potentials. Thomas extended the concept of Wagner plots to tsDCH states and called the new plots the *generalized* Wagner plots. Stimulated by this work, Ueda and Takahashi [42] performed DFT calculations of DCH states for a series of molecules XH_m–YH_n (X, Y = C, N, O, F; m,n = 0–3), NX_2CXO (X = H or F) and C_{60} and explained the general trends of initial-state energy shifts and relaxation using Wagner plots for the ssDCH states and the interatomic relaxation of tsDCH states using generalized Wagner plots.

Most of the molecules described above contain only the second-row atoms C, N, O and F. As for molecules with third-row elements, Ohrendorf et al. [43] investigated the K^{-2}, $K^{-1}L^{-1}$ and L^{-2} DCH states of SiH_4 and SiF_4 using the Green's functions method, whereas Takahashi et al. [36] extended the study of Ohrendorf et al. by considering in addition two other molecules SiX_4 (X = Cl, and CH_3) and a series of bridged trihalosilyl–trimethylsilyl molecules $Si(CH_3)_3$–$(CH_m)_n$–SiX_3 (X = F, Cl; m = 0,1,2; n = 0–4) using DFT methods [44]. The work on SiX_4 [36] invoked renewed interest in core–core–core Auger spectroscopy.

The work on the $Si(CH_3)_3$–$(CH_m)_n$–SiX_3 chain molecules [44] is important also because it shed light on the dependence of the interatomic relaxation energy on the distance between the two holes in tsDCH states, as well as on polarization. Tashiro et al. [45] investigated systematically how the interatomic relaxation energy of the tsDCH states changes with polarization and location of the polarizable unit in molecules, while Kryzhevoi et al. [46] investigated the distance-dependence of the interatomic relaxation energy in molecules with two terminal nitrogen atoms bridged by different carbon chains. In both these cases, the ΔSCF approach at the HF level was applied to extract the interatomic relaxation energy.

The work of Kryzhevoi et al. [46] on the bridged dicyano molecules illustrated that the interatomic relaxation energy is negative everywhere and increases monotonically toward zero with increasing distance between the two core holes. This trend was in sharp contrast to that found in the bridged disilyl molecules $Si(CH_3)_3$–$(CH_m)_n$–SiX_3 [44] where positive interatomic relaxation energies were obtained for systems with short carbon chains. Due to these apparent differences, Kryzhevoi et al. pointed out that DFT may fail to properly estimate the energies of tsDCH states. Later on, Takahashi and Ueda [47] reinvestigated the dicyano molecules, disilyl molecules and C_{60} using both the HF method according to the recipe of Kryzhevoi et al. [46] and DFT. It was confirmed that the interatomic relaxation energy in the disilyl molecules indeed decreases from positive to negative values and then approaches zero with increasing hole–hole distance, and that the apparent difference between dicyano and disilyl molecules is due to different polarization effects.

In the present work, we revisit the series of molecules XH_m–YH_n (X, Y = C, N, O, F; m,n = 0–3). In the previous study [42] we employed DFT. Here, we use the CASSCF and ΔSCF methods. Furthermore, we extend the calculations to fluorine substituted systems using DFT. Section 4 describes the details of these calculations while Section 5 is the summary of the results obtained.

The present paper pursues several goals. The first goal is to provide the readers with the current understanding of DCH spectroscopy and to show how to extract the chemical information using this spectroscopy. For this purpose, following the above extended introduction and recent history of DCH spectroscopy, we will briefly describe the theoretical background of DCH spectroscopy in Section 2 and the recipe of how-to-make Wagner plots in Section 3. In Sections 6.1 and 6.2, we will illustrate how to extract the chemical information based on the Wagner plots by using target sample molecules given above.

The second aim of this article is to get deeper insight into interatomic relaxation energy and its relation to charge transfer. For that, in Sections 6.3 and 6.4, we focus on the interatomic