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Electronic and nuclear dynamics of doubly core-ionized and excited states: Vibrationally resolved photoelectron and Auger spectra of small molecules

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Synopsis In this work we want to assess the influence of nuclear dynamics on the features of the double core-hole photoelectron and Auger spectra of small isolated molecules by performing wave packet propagation on precomputed ab initio potential energy surfaces.

X-ray photoelectron spectroscopy (XPS), also known as ESCA, is a widely used method for chemical analysis. Since core electrons are highly localized around the nucleus, they encode element specific spectroscopic informations. Accordingly, a detailed analysis of the emitted electrons produced during the photoionization and the decay of the metastable states is a powerful mean to access electronic and structural properties of the ionized molecular states.

In 1986, Cederbaum and coworkers proposed to use double-core hole (DCH) spectroscopy [1], for which two inner-shell electrons are ejected, as an even more sensitive probe of the chemical composition of materials. In the last decade, the study of the spectroscopy of doubly core-ionized molecules received a strong impetus through the development of new generation synchrotron radiation and X-ray free electron lasers (XFELs).

The two vacancies in the K shell can be observed either on a single (K^{-2}) or on different atomic sites ($K^{-1}K^{-1}$), the latter configuration allowing for instance to precisely probe the bond length [2]. The creation of core holes induces a rearrangement of the electronic distribution, which can lead to electronic excitation in valence orbitals and decay via electron emission (Auger process), see Figure 1.

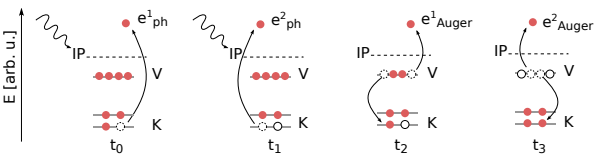

Figure 1. Schematic diagram of DCH state formation by sequential double ionization in the K shell, producing two photoelectrons (e_{ph}) in the continuum, followed by electronic relaxation in the valence (V) shell via Auger electron emission (e_{Auger}).

In previous theoretical studies, spectroscopic observables for DCH states were obtained in the frozen nuclei approximation [3], and molecular dynamics simulations were carried out for the Auger spectrum [4]. We will present our simulations on small isolated molecules interacting with (i) weak electromagnetic field such as synchrotron radiation, for which DCH states are created through single photon absorption; (ii) intense ultrashort pulse such as XFEL which induces sequential multiphoton absorption leading to DCH states. In the latter case, competing pathways complicate the theoretical investigations, as the sequential photoionization and the successive decays by electron emission channels are involved, depending on the lifetime of the core hole states.

Electronic structure simulations are carried out to get highly accurate ab initio potential energy surfaces for the various ionized/excited intermediate states and the final states reached via successive Auger decays. In this work we tackle to the challenging task to develop a method for computing vibrationally resolved photoelectron as well as Auger spectra of singly and doubly ionized small molecules, including the nuclear dynamics explicitly at a quantum level of theory.

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