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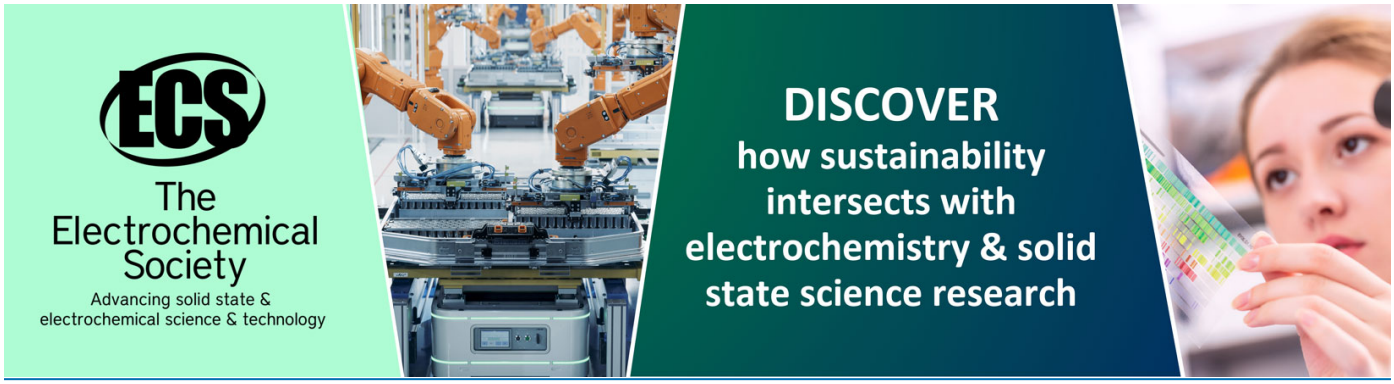

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Photo-induced ultrafast dissociation following deep-core-electron excitation

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Synopsis Creation of deep core holes leads to extensive nuclear dynamics on a few femtosecond timescale despite the very short ($\tau \leq$1 fs) lifetime of such states. This is because the 1^{st} steps of the relaxation processes (*i.e.* both radiative and non-radiative decays) generate intermediate states with one and multiple holes in core orbitals. As an example, ultrafast dissociation is observed in three well-distinguishable LVV Auger decay channels for HCl following Cl1$s\rightarrow\sigma^*$ excitation.

Absorption of an X-ray photon by a molecule may lead to the excitation of a localised core electron to a specific unoccupied valence orbital if the energy of the photon matches exactly the difference between the involved core and valence electronic levels. The created core-hole states are highly unstable and eventually decay on a very short timescale emitting a photon (radiative decay) or a so-called *A*uger electron (non-radiative or *A*uger decay).

Hard X-ray photons (>1keV) may reach deeper-lying core electrons. The lifetime (τ) of deep-core-hole states is very short – of the order of 1 fs or below. Nevertheless, the signature of nuclear dynamics was observed for Cl1$s\rightarrow\sigma^*$ ($\tau \approx$1 fs) core-excited states of HCl [1] and even on a sub-femtosecond timescale ($\tau \approx$200 attoseconds) in the case of I2$p\rightarrow$15a_1^2 core electron transitions in CH_3I [2].

The electronic relaxation dynamics of deep-core-hole states is very rich. At variance with that, the very short lifetimes of these states do not allow for extensive nuclear dynamics to take place before electronic relaxation occurs. However, the dominant channels of the 1^{st} step relaxation processes (both radiative and *Auger* decays) lead to intermediate states which bear 1 or *2* holes in *c*ore-electron shells. In the HCl molecule, the leading relaxation decays of the Cl$1s^{-1}\sigma^*$ state are Auger KLL and radiative Kα channels, which create Cl$2p^{-\mathbf{2}}\sigma^*$ and Cl$2p^{-1}\sigma^*$ intermediate states, respectively. The latter one can be created by direct soft X-ray absorption and has been well characterised [3]. It is known to undergo ultrafast dissociation (UFD) within the Cl$2p^{-1}$ lifetime of ∼8 fs [3, 4]. The former double core-hole Cl$2p^{-\mathbf{2}}\sigma^*$ states are yet exotic and can be also created as so-called *"super"*-satellites [5] of direct $2p^{-\mathbf{2}}$ double core-hole ionisation. Very recent theoretical studies [5] show that the energy gradients of the *core*$^{-\mathbf{2}}$V states can be very large (3 times larger compared to the *core*$^{-1}$V state in the case of H_2O [5]). Therefore, nuclear dynamics is correspondingly faster in *core*$^{-\mathbf{2}}$V *"super"*-satellites.

Our experimental measurements reveal UFD phenomena in Cl$2p^{-\mathbf{2}}\sigma^*$ state of HCl with τ only about 3 fs. The measured LVV *Auger* decay spectrum of HCl clearly shows 3 possible decay channels following Cl1$s\rightarrow\sigma^*$ excitation. In fact, ultrafast dissociation is observed in *every* step of these LVV decay channels before the next electronic relaxation takes place. The observed results are supported by *ab initio* theoretical calculations.

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