Multistep ultrafast dissociation and its control by hard x-ray photons

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Synopsis Hard X-rays create deep electron vacancies, which have very rich relaxation decay dynamics. We describe a mechanism of multi-step ultrafast dissociation, using the example of HCl following Cl $1s \rightarrow \sigma^*$ excitation. Furthermore, we demonstrate that by tuning the photon energy multi-step ultrafast dissociation can be controlled on a subfemtosecond timescale.

Absorption of hard x-ray photons leads to creation of deep electron vacancies, which have a very short lifetime ($\tau \leq 1fs$). The decay of a deep core hole is very complex, and occurs via a series of subsequent relaxation steps. We studied in detail [1, 2] the dominant *KLL*-decay path following Cl $1s \rightarrow \sigma^*$ excitation in HCl as an example, in the course of which 3 *Auger* electrons are ejected sequentially:

$$
\begin{aligned}
h\nu + \mathrm{HCl} &\xrightarrow{\sim 2.8keV} \mathrm{HCl}^*_{(1s^{-1}\sigma^*)} \xrightarrow{KLL} \\
&\xrightarrow{KLL\ (\tau_{eff} \lesssim 1fs)} \mathrm{HCl}^{+}_{(2p^{-2}\sigma^*)} + e^-_{Auger} \xrightarrow{LMM1} \\
&\xrightarrow{LMM1\ (\tau_1 \sim 3fs)} \mathrm{HCl}^{2+}_{(2p^{-1}(V\sigma^*)^{-2})} + e^-_{Auger} \xrightarrow{LMM2} \\
&\xrightarrow{LMM2\ (\tau_2 \sim 8fs)} \mathrm{HCl}^{3+}_{((V\sigma^*)^{-4})} + e^-_{Auger}
\end{aligned}
$$

In general, intermediate states with one or multiple holes in the shallower core electron shells are generated in the course of such cascades. The longer lifetime and steep potential energy surfaces of these intermediates may enable ultrafast nuclear dynamics and even bond breakages if the reduced mass is sufficiently low. This phenomenon was called multistep ultrafast dissociation (MUST UFD) [1] to distinguish it from the single-step ultrafast dissociation (UFD) induced by soft X-rays. UFD was extensively investigated in a number of molecular systems since its discovery in 1986 [3] (see e.g. [4, 5]).

Following Cl $1s \rightarrow \sigma^*$ excitation in HCl, a part of the wave packet in the intermediate Cl $2p^{-2}\sigma^*$ double-core-hole states with the lifetime of $\tau \sim 3$ fs has already enough time to propagate towards the region of the dissociation to create the atomic peak [1, 2]. The H–Cl bond continues to elongate in the next intermediate doubly charged Cl $2p^{-1}(V\sigma^*)^{-2}$ core-hole states leading to even more abundant fragmentation before the system relaxes by emitting another Auger electron in the last *LMM*2 *Auger*-decay step. As a result, the total fragmentation rate is predicted to be $\sim$50% in the *KLL* cascade following Cl $1s \rightarrow \sigma^*$ excitation in HCl, compared to $\sim$37% predicted for direct Cl $2p \rightarrow \sigma^*$ excitation by soft X-rays.

Furthermore, MUST UFD can be controlled by tuning the photon energy. This is the heart of the well-known *core-hole clock* method, which has been successfully applied to the studies of UFD in soft-x-ray energy regime [6]. In the present case (a multistep process), we control the dynamics of the overall Auger cascade by *manipulating* the effective duration time of the very first step corresponding to the decay of the Cl $1s^{-1}\sigma^*$ state, which is the shortest part ($\sim$1 fs) of the overall MUST UFD process (6–20 fs). Remarkably, this leads to drastic changes in nuclear dynamics, which are observed on the hundreds of attoseconds timescale [2]. Energy dependent molecular fragmentation is observed and explained by a strong interplay between the *core-hole-clock* and the topology of the potential energy curves, involved in the Auger-cascades. As a result of detuning, a coherent nuclear wave packet is created in the primary core-excited state with different initial conditions, which determine its group velocity and, therefore, its evolution in the following relaxation steps.

References

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