

Fragmentation Dynamics of Small Molecules upon Multiple Ionization by X-Ray Free-Electron Laser Pulses

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The microscopic response of a polyatomic molecular system to inner-shell photoabsorption, i.e., the electronic relaxation dynamics and motion of atomic nuclei after creation of one or several core-shell vacancies, plays a crucial role for our understanding of X-ray interactions with matter, and is essential for most applications of novel ultraintense, ultrafast X-ray FELs. In this work we address this issue by studying multiphoton X-ray ionization of several small molecular systems containing a single heavy atom (Se or I). In these systems, the X-ray absorption cross section of this high-Z constituent is much higher than for the rest of the atoms in the molecule, resulting in a well-localized photoabsorption.

By measuring charge state distributions, kinetic energies, and emission angles of coincident ionic fragments we trace the electronic and nuclear dynamics subsequent to multiple inner-shell photoionization. Comparing the ionization of such a molecular system to the case of an isolated high-Z rare gas atom of similar electronic configuration (Se \leftrightarrow Kr, I \leftrightarrow Xe) [1,2], we find that while the total charge induced on the system is similar in both cases, the highest final charge state of the high-Z atom in the molecules is considerably lower, pointing towards efficient charge redistribution within the molecule.

The measured kinetic energies of the ionic fragments indicate considerable motion of nuclei on the time scale of multiple ionization. We also observe signatures of charge rearrangement involving protons that happens on a fs time scale before substantial nuclear motion.

In order to shed more light on the mechanisms of the charge redistribution and on the role of inter- and intra-atomic effects within the molecular fragmentation process, we performed similar measurements on CH₃I molecules pre-dissociated by short 800 nm laser pulses. Varying the delay between the IR and X-ray pulses, we studied X-ray ionization of molecules as a function of internuclear separation R. We observe significant changes in the charge distribution within the molecular fragments for different R, indicating a transition to isolated atoms where no charge exchange with the molecular environment can occur any more.

References:

- [1] B. Erk et al, Phys. Rev. Lett. **110**, 053003 (2013).
- [2] B. Rudek et al, Nature Photonics **6**, 858 (2012).