

Charge transfer in dissociating molecules upon multi-photon X-ray ionization

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When isolated molecules absorb an intense, femtosecond X-ray pulse from a free-electron laser, a complex interplay of inner-shell photo absorptions, Auger decays, and nuclear motion takes place. All processes happen on timescales similar to the pulse duration. Their final outcome can be experimentally determined by means of ion time-of-flight spectroscopy, 3d ion momentum imaging or velocity map imaging. Of particular interest are polyatomic molecules containing a single heavy atom that acts as a localized absorber due to the strongly increased X-ray photo absorption cross section. This element-specificity or site-selectivity of X-ray absorption gets stronger for higher photon energies. Different probe wavelengths can thus yield complementary results due to the different degree of site-selectivity.

A possibility to disentangle the nuclear motion from purely electronic processes in the experiment is by controlling the internuclear distance between the heavy absorber and the rest of the molecule with the help of a preceding laser pump pulse that triggers a bond cleavage. Such internuclear-distance-resolved (pump-probe) studies in the XUV and soft X-ray regime have revealed that the critical distances up to which electron transfer from the molecular environment to the heavy atom is allowed can be well reproduced by calculations following a classical over-the-barrier model [1, 2]. Such electron rearrangement is evident in different halogen-containing molecules, and for internuclear distances of 15 Å and beyond [1-3].

We have seen experimental indications that in halogenated aromatic systems, a fast re-localization of charge towards the carbon atom with the largest distance to the halogen may take place [3]. Similar observations were also made in a recent theoretical investigation [4]. Our time-resolved studies are complemented by single-pulse Coulomb explosion imaging studies, where detailed information about the fragmentation dynamics can be extracted from the mass spectra, kinetic energies, and relative angles between multiple ions detected in coincidence [5-8]. The X-ray fluence was determined to be the most important parameter for the charging up of the molecule [7], but also the pulse duration plays a crucial role [8]. An upcoming experiment at the European XFEL will investigate the charge rearrangement and the fragmentation dynamics upon absorption of very intense soft X-ray pulses in more detail.

References

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