The interaction of an intense radiation field with the electronic cloud of atoms and molecules may result in the simultaneous absorption of two or more photons apart from the usual single photon processes. These non-linear processes are widely studied in experiments using intense infrared laser sources. Due to the small photon energy of these sources, only the outermost electrons are ionized and multiple ionization processes leads to the successive stripping of the outer sub-shell. In contrast, the intense XUV radiation from FLASH can uniquely couple so strong with inner shell electrons that an atom can strip off its electrons from the inside out. It can do so not just in single inner shell photoionization interactions, but also in two- and multi-photon processes, which will give rise to novel phenomena observable only with the intense FEL sources, thus open new possibilities to study electron correlations and the dynamics of electronic relaxation. In particular the ejection of two (or more) core electrons will leave the atoms and molecules in a highly excited state with unique, not yet explored relaxation dynamics.

A particularly interesting situation is given when the intensity of the XUV pulse is high enough to induce the ejection of two core electrons, simultaneously or sequentially on a time scale shorter than the core hole lifetime. The feasibility of such experiments has been recently shown for different samples [1–3]. Besides the study of a new class of Auger processes, which are only observable under the action of intense XUV radiation, the process of the double core hole formation provides additional insights into the electronic correlations. Double core hole formation provides precise chemical information, i.e., it is a very sensitive parameter to the local (electronic) environment of the target atom.

Figure 1: Covariance maps of CH$_2$I$_2$ for low (4µJ) and high (14µJ) intense FLASH pulses. For orientation some charge states of iodine are marked on the TOF mass spectra. The TOF mass spectra are a sum, average over all FLASH pulse intensities.

In the case of a sequential double core hole excitation or ionization process the second photoelectron emission will probe the electronic singly core-ionized state of the atom or molecule. Hence, it
will be feasible to study the dynamics of the core hole decay. A further interesting aspect of double core hole excitations can be found in molecular systems. The possibility to create two core holes on the same or on different atoms of a small molecule will give rise to interferences in the photoemission, which should strongly depend on the location of the hole, i.e. on the different screening by the surrounding electrons. The process is expected to be very sensitive to the relative phases of the exciting photons, and thereby to the ultra-fast dynamics of the electronic interactions.

To study such processes, we have measured the fragmentation of diiodomethan (CH$_2$I$_2$) and iodomethan (CH$_3$I) molecules above the I 4d giant resonance with FLASH pulses of 105 eV photon energy (11.8 nm). Iodomethan has been chosen as a reference, as here a core hole can be excited only on one side of the molecule. The experiments have been performed in the multibunch mode using up to 100 pulses per bunch and a bunch spacing of 250 µs. Several million fragmentation spectra have been recorded by an ion time of flight spectrometer and all individual spectra have been stored in the FLASH DAQ system. To study the correlation of the different charge states, all spectra have been analyzed by the covariance method [4].

In Fig.1 the covariance maps of CH$_2$I$_2$ are depicted for two different pulse energies of FLASH. For low pulse intensities ($\approx 4 \mu$J) in particular mid charged states (a) are correlated to each other, e.g. I$^6+$ with I$^5+$ and I$^7+$. For higher intensities this correlation is shifted towards higher charged states (b), showing that for the fragmentation an equally charge distribution is favored. Nevertheless, for the I$_2^+$ fragment in the covariance map a strong shift of the kinetic energy of the fragment with increase charge of the second iodine fragment is found (c), which can be attributed to the Coulomb repulsion of both iodine ions.

**References**


