

# Charge migration dynamics after xuv photo excitation of small iodine containing molecules

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**Synopsis** We investigated the charge migration pathways of CH<sub>3</sub>I and CH<sub>2</sub>I<sub>2</sub> with a xuv-pump xuv-probe setup at the free electron laser FLASH in Hamburg, Germany. The observed fragmentation dynamics show a significantly different efficiency for both molecules. Theoretical calculations can relate this to a molecule specific charge redistribution process following directly the photoionization. Additionally, simulated ion time-of-flight spectra link the experimental and theoretical calculations [1].

The evolution of electron charge distribution after a site specific excitation can be perfectly studied with x-ray pump-probe setups. The x-rays thereby excite the target, e.g. small iodine containing molecules site specifically by tuning to the correct photon energy. To study charge migration processes, the photon pulse length must be comparable to intrinsic molecular time-scales.

The free electron laser FLASH at DESY in Hamburg, Germany, provides short photon pulses with an average duration of  $\sim 100$  fs, at a photon energy of 83 eV. The photon energy is tuned to the iodine giant resonance to create an inner-shell iodine-*4d* vacancy. By using the pump-probe technique, the pump pulse triggers the start of the dissociation, whereas the second pulse probes the status of the fragmentation. By creating an inner-shell core hole, the subsequent relaxation pathways are mainly dominated by the following Auger decay resulting in a double core hole at the iodine site. This difference in charge distribution will be equalized by charge migration over the whole molecule which is only limited by atomic separation caused by nuclear motion. The time evolution of this relaxation pathway depends on the geometrical and electronic structure of the investigated molecule.

The final molecular fragments can be detected by using an ion time-of-flight spectrometer (ToF). To study the time evolution, the initial photon beam is guided through a split-and-delay-unit (SDU) [2], that allows changing the delay between the two parts of the splitted photon beam.

We compare the two iodine containing molecules CH<sub>3</sub>I and CH<sub>2</sub>I<sub>2</sub>. After the creation of a double core hole at the iodine site with the pump pulse the charges are redistributed along the molecules. In the case of CH<sub>2</sub>I<sub>2</sub> a charge mi-

gration between both iodine atoms leads to an equalized charge at the two iodine atoms. For CH<sub>3</sub>I, charges can only migrate between the iodine and the methyl group. By varying the time delay between pump- and probe-pulse, the nuclear motion of the nuclear separation can be followed. Its spatial range is well estimated by the classical over-the-barrier model [3,4].

Within the ion- ToF spectra it is found, that the abundance of I<sup>3+</sup> ions shows a characteristic delay dependency on the timescale of the photon pulse length. It can be shown, that the envelope of the delay dependent effect can be described by a single Gaussian envelope. For CH<sub>3</sub>I the FWHM of 85 fs is much shorter than for CH<sub>2</sub>I<sub>2</sub>: 235 fs.

The experimental results are backed by ab-initio electronic structure calculations including correlations. The fragmentation dynamics are reviewed by the fact, that the induced positive charge is redistributed with a significantly different efficiency for CH<sub>3</sub>I and CH<sub>2</sub>I<sub>2</sub>. This can be related to a strongly molecule specific, purely electronic charge redistribution process directly following the photoionization. Furthermore, the exact flight paths of ionized species through the interaction zone and into the ToF are additionally simulated according to the results of the attosecond calculations. The application of this combined approach gives insight into the electronic and nuclear dynamic of photo excited molecular fragmentation pathways.

## References

- [1] M. Hollstein *et al.* 2016 arXiv:1605.09317
- [2] F. Sorgenfrei *et al.* 2010 *Rev. Sci. Inst.* **81** 043107
- [3] H. Ryufuku *et al.* 1980 *Phys. Rev. A.* **21** 745
- [4] A. Niehaus *et al.* 1986 *J. Phys. B.* **19** 2925

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