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Synopsis Thiophene is a cyclic molecule that becomes unstable as a molecular dication. We followed the multi-step dissociation dynamics triggered by soft x-ray FEL pulses from SACLA, core-ionizing the S 2p orbital and creating parent dications by the Auger decay. The time-evolution was probed by optical laser pulsesthat reveal the survival lifetime of the parent dication and the build-up of fragmentation proceeding by ring opening and rupture, accompanied by hydrogen ejection and secondary dissociation. Experimental results are compared to statistical analysis of molecular dynamics simulations.

In a pump-probe experiment performed at the SACLA free-electron-laser facility in Japan, thiophene (C_4H_4S) molecules were core-ionized from the S 2*p* orbital, using 180 eV photons as a pump. The subsequent Auger decay produced molecular dications with internal energy up to about 50 eV. The molecular dications are, except in the lowest energy states, unstable. Molecular dynamics simulations using density functional tight-binding theory (DFTB) [1] have shown that the ensuing dynamics spans a time range from tens of femtoseconds to tens of picoseconds, depending on the internal energy available. The cyclic parent molecules can occasionally exhibit long survival times even at high energies, before the first step of fragmentation – the ring opening – occurs. The dissociation then proceeds quickly with a rupture of another bond, creating two charged fragments. In addition, hydrogen ejection and secondary dissociation take place over the course this complex dynamics. Near-infrared (NIR) 800 nm Ti-Sapphire laser pulses were used to probe the status of the molecular dynamics with pump-probe delays in the femto- and picosecond scale. The optical laser pulses served to alter the dissociation pathways. In particular, a strong time-dependent enhancement of secondary dissociation channels was seen with characteristic rise- and delay times. These, an other time-dependent effects are used to obtain insight into the kinematics and dynamics of multi-step dissociation processes of cyclic molecules.

We interpret the experimental results with the help of a statistical analysis of trajectories from *ab initio* molecular dynamics simulations, carried out over a broad range of internal temperatures (as atomic velocities).

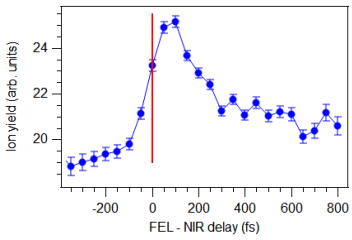

Figure 1. NIR-induced enhancement of the C^+ ion yield from secondary fragmentation.

References

[1] Kukk E *et al* 2015 *Phys. Rev. A* **91** 43417

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