

Imaging the temporal evolution of molecular orbitals during ultrafast dissociation

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Synopsis We investigate the temporal evolution of molecular frame angular distributions of Auger electrons emitted during ultrafast dissociation of HCl following a resonant single-photon excitation. The electron emission pattern changes its shape from that of a molecular σ orbital to that of an atomic p state as the system evolves from a molecule into two separated atoms.

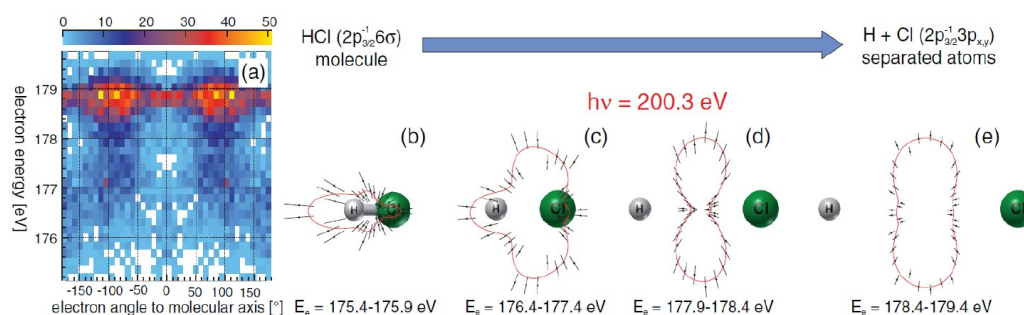


Figure 1. (a) Electron angular emission distribution with respect to the molecular axis as a function of the electron energy. (b-e) Subsets of the data shown in (a) for different regions of electron energy. (b) Corresponds to decay of the still intact molecule, (c,d) show emission patterns during bond breakage, (e) shows emission from the Cl^* fragment.

In the present work [1], we revisit the problem of probing the charge cloud upon the transition from a molecule into separated atoms on an even shorter time scale of a few femtoseconds. We excite an electron from an inner shell of a HCl molecule to the lowest antibonding orbital. This establishes the pump step of our experiment. The potential energy surface of the excited HCl^* is steeply repulsive. Thus, after the pump step, the molecule rapidly dissociates into two separated atoms. The time scale for this ultrafast dissociation is a few femtoseconds only. In order to access this time scale in our experiment, we employ the dissociation process as an ultrafast intrinsic molecular clock, which is started by the excitation. During the dissociation, the inner shell excited state decays and an Auger electron is emitted. The Auger lifetime is of the order of the dissociation time, so that the decay can take place either within the molecular Franck-Condon region, during the dissociation when the system is in a transition state between a molecule and two separated atoms, or at larger

distances when the molecule is already fragmented into two atoms. In traditional pump-probe experiments the probe step is initiated by the experimentalist after a certain time delay which is then scanned. In our approach, for each molecule the individual delay between the excitation and the probe (i.e. the emission of the Auger electron) is given by the quantum nature of the Auger decay, but the delay is encoded in measured quantities. By measuring the energies of the reaction fragments, the internuclear distance and hence (indirectly) the time at which the decay occurred are inferred for each individual decay event.

The talk will briefly introduce the topic of ultrafast dissociation, the measurement technique [2] and present the results obtained.

References

- [1] H. Sann *et al.* 2016 *Phys. Rev. Lett.* **117** 243002
- [2] R. Dörner *et al.* 2000 *Phys. Rep.* **330** 95

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