

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.

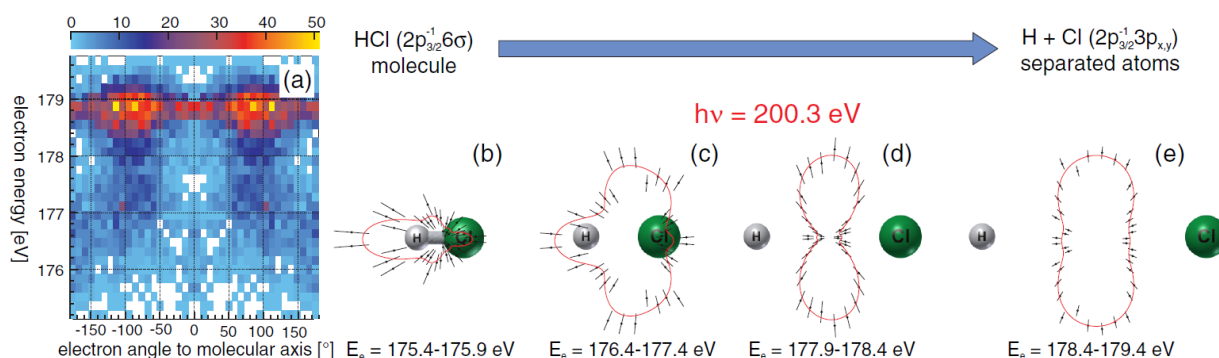


Figure 1. (a) Electron angular emission distribution with respect to the molecular axis as a function of electron energy. (b-e) Subsets of data shown in (a) for different regions of electron energy. (b) Corresponds to decay of the still intact molecule, (c,d) show emission patterns during bond breakage,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

We investigate the breaking of chemical bonds and thus the transition of a molecular orbital to an atomic orbital. To realize this, we coincidentally measure the fragment momenta of the molecular decay of HCl through Ultrafast Dissociation with a COLTRIMS system.

Ultrafast Dissociation proceeds as follows: Using narrow-bandwidth synchrotron radiation, an inner shell electron is resonantly excited to an antibonding molecular $6\sigma^*$ -orbital in the pump step. The molecule now rapidly dissociates in the timescale of a few femtoseconds along the steeply repulsive potential energy surface. Competing with the molecular dissociation, Auger decay takes place. The Auger electron can be emitted either within the molecular Franck-Condon region, during bond breakage or when the molecule is already fragmented into two atoms. The Auger decay can thereby be used as a probe of the state of the decaying system. By coincidentally measuring the ionic fragment and the emitted electron, we gain information about internuclear distance and hence

the timespan from excitation to the point when each decay took place. The internuclear distance is encoded in the kinetic energy of the fragments as well as in the energy of the emitted Auger electron. For different time steps we can now investigate the Auger electron angular distribution in the molecular frame. These distributions are a fingerprint of the systems orbital structure.

In reality, the situation is considerably more complicated because many initial and final states are involved. In the analysis, these states as well as the two possible fragment channels could be separated by restricting to the channels of interest via coincident energy maps.

Figure 1 finally shows the transition of the molecular σ -type orbital (b) via bond breakage (c, d) to the atomic p -orbital (e) mapped in the Auger electron emission pattern.

Reference

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