

Time-resolved Imaging of Purely Valence Electron Dynamics during a Chemical Reaction

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Chemical reactions are manifestations of the dynamics of molecular valence electrons and their couplings to atomic motions. Emerging methods in attosecond science can probe purely electronic dynamics in atomic and molecular systems. By contrast, time-resolved structural-dynamics methods such as electron or X-ray diffraction and X-ray absorption yield complementary information about the atomic motions. Time-resolved methods that are directly sensitive to both valence-electron dynamics and atomic motions include photoelectron spectroscopy and high-harmonic generation: in both cases, this sensitivity derives from the ionization-matrix element. Here we demonstrate a time-resolved molecular-frame photoelectron-angular-distribution (TRMFPAD) method for imaging the purely valence-electron dynamics during a chemical reaction. Specifically, the TRMFPADs measured during the non-adiabatic photodissociation of carbon disulphide demonstrate how the purely electronic rearrangements of the valence electrons can be projected from inherently coupled electronic–vibrational dynamics. Combined with ongoing efforts in molecular frame alignment and orientation, TRMFPADs offer the promise of directly imaging valence-electron dynamics during molecular processes without involving the use of strong, highly perturbing laser fields.