Ultrafast Electronic□Structural Dynamics in the Smallest Polyene: 1,3-butadiene

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The ultrafast electronic-nuclear dynamics of the smallest polyene, trans-1,3-butadiene, was studied by (1+1') femtosecond time-resolved PhotoElectron-PhotoIon coincidence (TRPEPICO) spectroscopy. The known predissociative character of the cation excited states helps assign photoelectron bands to specific continua using TRPEPICO spectroscopy. We report the first direct observation of the famously elusive S1(2A 1Ag) dark electronic state during the internal conversion, as well as the overall decay lifetimes of the bright 1B 1Bu and dark 2A 1Ag states. We also observe the re-appearance of the hot ground state molecule. We offer an explanation of the extreme breadth of the absorption spectrum as being principally due to large amplitude torsional motion on the bright 1Bu surface. Ab Initio Multiple Spawning (AIMS) on-the-fly computations of the excited state non-adiabatic wavepacket dynamics and their associated experimental observables allow direct comparisons of experiment with theory.