Ultrafast Dynamics in Thiophene Investigated by Femtosecond Pump Probe Photoelectron Spectroscopy and Theory

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Abstract:

A hybrid of a time-of-flight mass spectrometer and a time-of-flight “magnetic-bottle type” photoelectron (PE) spectrometer is used for fs pump-probe investigations of the excited state dynamics of thiophene. A resonant two-photon ionization spectrum (R2PI) of the onset of the excited states has been recorded with a tunable UV laser of 190 fs pulse width. With the pump laser set to the first intense transition we find by UV probe ionization first a small shift of the maxima in the PE spectrum and then a fast decay to a low constant intensity level. The fitted time constants are 80 ± 10 fs, 25 ± 10 fs and >50 ps, respectively. Theoretical calculations show that upon geometry relaxation the electronic state order changes and conical intersections between excited states exist. We use the vertical state order S₁, S₂, S₃ to define the corresponding terms S₁, S₂, and S₃ for the electron configuration of these states. On the basis of the theoretical result we discuss the electronic state order in the UV spectra and identify the origin of the first cation excited state D₁. The observed excited state dynamics agrees best with a vibrational dynamics in the photo-excited S₁ (80 ± 10 fs) and an ultrafast decay via a conical intersection, presumably a ring opening to the S₃ state (25 ± 10 fs). The subsequently observed small long-lasting signal is taken as an indication, that in the gas phase the ring-closure to S₀ is slower than 50 ps.

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