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Watching the electronic motions driven by a conical intersection

DAVID JONAS, University of Colorado at Boulder

In chemistry, the fastest electronic rearrangements proceed through “conical intersections” between electronic potential energy surfaces. With sufficiently short pulses, the electronic motion can be isolated by polarized excitation of aligned electronic wavepackets at a conical intersection. Polarized femtosecond probing reveals signatures of electronic wavepacket motion (due to the energy gaps) and of electron transfer between orbitals (due to the couplings) driven by the conical intersection. After exciting a D_{4h} symmetry silicon naphthalocyanine molecule onto a Jahn-Teller conical intersection in the first excited state, electronic motions cause a ~ 100 fs drop in the pump-probe polarization anisotropy. The polarized vibrational modulations of the signal can be used to deduce the symmetry and stabilization energies for each vibration. The initial decay of the polarization anisotropy can be quantitatively predicted from these vibrational parameters. Both coupling and energy gap variations are important on the ~ 100 fs timescale. A 1 meV stabilization drives electrons from orbital to orbital in 100 fs, and the theory indicates that a chemically reactive conical intersection with 1000x greater stabilization energy could cause electronic equilibration within 2 fs. We have recently carried out experiments on a nominally D_{2h} symmetry free-base naphthalocyanine for which the splitting between x and y polarized transitions is not resolved in the linear spectrum. For this molecule, the anisotropy also decays on a similar timescale and exhibits damped modulations whose origin (vibrational or electronic) has not yet been determined. The role of the central protons and nominal D_{2h} symmetry in the electronic dynamics will be discussed.