WATCHING ELECTRONS AT CONICAL INTERSECTIONS AND FUNNELS

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The electronic motion at conical intersections and funnels is probed after polarized excitation of aligned electronic wavepackets. The pulses have bandwidth sufficient to observe vibrations mainly through their effect on the electrons. Vibrational symmetry can be identified by the polarization anisotropy of vibrational quantum beats. The polarized transients show 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. For a conical intersection in a four-fold symmetric symmetry silicon naphthalocyanine molecule, electronic motions on a 100 fs timescale are driven by couplings of 1 meV. In the lower symmetry free-base naphthalocyanine, the conical intersection may be missed or missing (conical funnel), and the motions are nearly as rapid, but electronic equilibration is incomplete for red-edge excitation. These experiments probe non-adiabatic electronic dynamics with near-zero nuclear momentum - the electronic motions are determined by the principal slopes of the conical intersection and the width of the vibrational wavepacket.