Non-adiabatic Electronic Excitation of Linear Polyenes in the Strong Field Regime

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H. BERNHARD SCHLEGEL, Wayne State University, Detroit, MI — Using a newly developed unitary transform time-dependent Hartree-Fock (UT-TDHF) algorithm, the electronic response to an ultrashort strong-field laser pulse was studied on a series of molecules – ethylene, butadiene, and hexatriene – in which molecular size and conjugation increase systematically. The evolution of electronic subsystem of molecules exposed to 760 nm $8.75 \times 10^{13}$ W/cm$^2$ of 7 fs duration was calculated using the 6-31G(d,p) basis set. Two scenarios are envisioned: in the first, the molecule interacts with the pulse immediately after ionization; in the second, sufficient time elapses for the molecular geometry to relax. The non-adiabatic behavior of the instantaneous dipole moment and the charge distribution in a molecule is more pronounced for the monocations than for the dications or neutrals. For a given charge state and geometry, the non-adiabatic effects increase with the length of the molecule. As Fourier analysis reveals, the residual (after-pulse) oscillations of the dipole moment are mainly due to non-resonant excitations of the lowest excited states with significant oscillator strength. For each molecule, the non-adiabatic coupling is greater for geometry with the lower excitation energies.