Abstract Submitted
for the MAR06 Meeting of
The American Physical Society

Non-adiabatic Electronic Excitation of Linear Polyenes in the Strong Field Regime STANLEY SMITH, Wayne State University, Detroit, MI, XIAOSONG LI, University of Washington, Seattle, WA, ALEXEI MARKOVICH, DMITRI ROMANOV, ROBERT J. LEVIS, Temple University. Philadelphia, PA, 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 8.75×10^{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.

Dmitri Romanov
Temple University

Date submitted: 19 Dec 2005 Electronic form version 1.4