COUPLED ELECTRON-NUCLEAR DYNAMICS FOLLOWING IONIZATION OF SUBSTITUTED BENZENES

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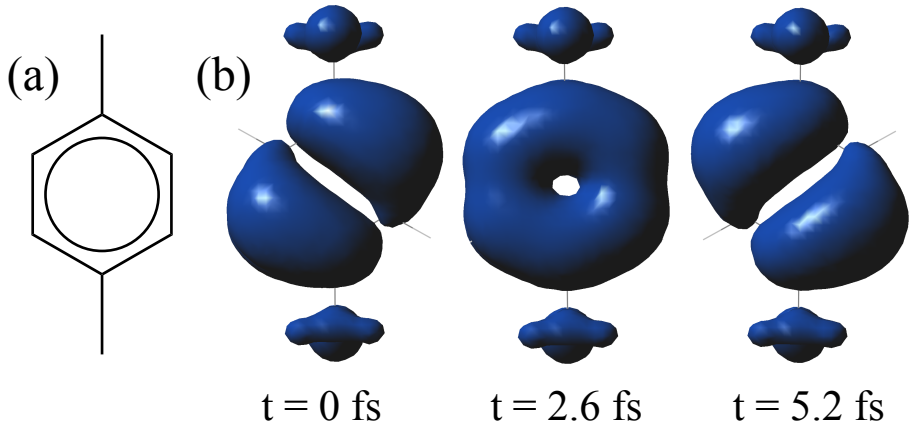
Photoionization can create a coherent superposition of electronic states and therefore initiates electron dynamics in molecules. Observing and controlling this experimentally is a target of attosecond spectroscopy. Theoretical studies of pure electron dynamics at a fixed nuclear geometry have demonstrated oscillatory charge migration.[1] Using a CASSCF implementation of the Ehrenfest method,[2] we can study the evolution of a non-stationary electronic wave function for fixed atomic nuclei, and where the nuclei are allowed to move, to investigate the differences.[3-5]



We show the effect of sampling the initial geometry on both electron and coupled electron-nuclear dynamics in toluene cation, with a Wigner distribution to mimic the zero-point energy of the neutral species.[5] For example, sampling changes the initial energy gap between the electronic eigenstates and therefore the timescale of electron dynamics.

We systematically investigated the effect of changing the relative amplitude and phase in the initial superposition of electronic states. By controlling the initial electronic conditions in this way, we can control the subsequent initial nuclear motion.[5] For example, if vertical ionisation of toluene prepares an equal superposition of the two lowest energy states, the nuclear relaxation takes place in a direction orthogonal to the adiabatic dynamics, following the gradient of the superposition.

KEYWORDS: coupled electron-nuclear dynamics; ionization; Ehrenfest method; conical intersection.

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