

Steering Nuclear Motion by Ultrafast Multistate Non Equilibrium Electronic Quantum Dynamics in Atto Excited Molecules

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Few-cycle short pulses allow excitation of coherently coupled electronic states towards steering nuclear motions in neutral molecules and cations. The progress of the non stationary vibronic density towards the products can be monitored using a second pulse, by transient absorption spectroscopy or photoionization. The Hamiltonian used to simulate the quantum dynamics includes the pump and probe pulses which provides a quantum mechanical description of both excitation and ionization.

We first report on **bond formation** induced by an ultrashort UV pulse.[1] We investigate quantum mechanically the coherent electronic and nuclear motions during the ring closure of norbornadiene to quadricyclane induced by a short UV pulse. Norbornadiene consists of two ethylene moieties connected by a rigid C₃H₄ bridge. The short femtosecond UV pulse yields a non-equilibrium electronic density in the open norbornadiene form that evolves towards the closed four-atom ring quadricyclane form. Norbornadiene exhibits a high density of electronic states of Rydberg and valence character just above the first excited state. As the coherent electronic-nuclear coupled dynamics unfold, the excited states change character through non-adiabatic interactions and become valence states for the two new C-C bonds of quadricyclane. Our quantum dynamical simulations show that short UV pulses of different polarization allow tailoring markedly different initial non-equilibrium electronic densities that follow different dynamical paths (Figure 1A), thereby opening the way to controlling bond-making by selective pumping of electronic states with attopulses.

In our second example, we report on the electronic coherence driven isotope effect in the ultrafast Jahn-Teller structural rearrangement that follows the sudden ionization of methane by a short XUV pulse.[2] The Jahn-Teller effect makes the methane cation unstable in the T_d geometry of the neutral. The sudden ionization of the neutral leads to a coherent superposition of the three lowest electronic states of the cation that are strongly coupled by non adiabatic interactions (Figure 1B). This non equilibrium electronic density is driving the ultrafast nuclear rearrangement occurring in the first few fs, through population transfers between the three electronic states in regions of different geometrical configurations. Our quantum dynamical simulation on an ensemble of suddenly ionized randomly oriented molecules show that on the ground state of the cation, the less distorted D_{2d} configurations are populated before the C_{2v} minimum is reached. The isotope effect on the coherent dynamics leads to a value of three for the ratio of the CD₄⁺/CH₄⁺ autocorrelation functions in the first 2 fs of the dynamics, in agreement with the ratio of the yields in high harmonics that has been experimentally measured.[3] Such a strong isotopic effect on the non adiabatic population transfers between electronic states in a coherent superposition has already been reported by us for N₂[4, 5] and LiH[6].

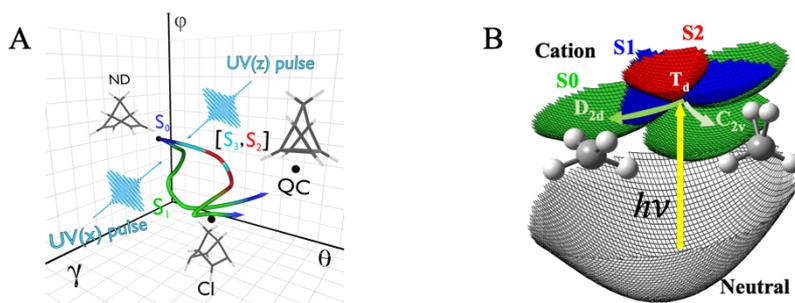


Figure 1 A. Norbornadiene (ND) photoisomerization to quadricyclane (QC). Paths followed by the non equilibrium vibronic density for two different linear polarizations of a fs short UV exciting pulse. B. Schematic view of the PES of the neutral ground state of methane and of the three lowest excited states of the cation involved in the Jahn-Teller effect.

References

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