

Ultrafast non-adiabatic relaxation of the naphthalene molecule after iner-valence ionization by a short XUV pulse

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XUV induced dynamics in molecules are nowadays accessible in experiment thanks to the development of attosecond laser pulses.^[1] The simulation of such dynamics is, however, very challenging. With such photon energies, iner-valence electrons can be removed, which, due to the strong multi-electronic effects, populate a large multitude of electronic states.^[2] Furthermore, a strong non-adiabatic coupling between the electronic and the nuclear degrees of freedom is expected.^[3] To overcome these difficulties we developed a model that permits to treat the ultrafast non-adiabatic relaxation that occurs in the naphthalene molecule (C₁₀H₈) after the population of cationic eigenstates lying close to the double ionization threshold. The model is based on a vibronic-coupling Hamiltonian derived from the electronic potential energy surfaces obtain with the Algebraic Diagrammatic Construction scheme. It includes 23 cationic states and 25 normal vibrational modes. The model Hamiltonian was used to propagate nuclear wave packets on the coupled manifold of cationic states with the Multi Configuration Time Dependent Hartree method. Our results have permitted to interpret a recent experiment performed by the group of F. Lépine (Institute of Light and Matter, Lyon). Using time-resolved electron momentum imaging, the relaxation times of several cationic states of naphthalene have been directly observed. The measured relaxations times fall in the range of few tens of femtoseconds and, counter intuitively, increase with the increase of the energy of the states. Our simulations well reproduce this behavior and show that it is a result of the increasing density of states when approaching the double ionization threshold.

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References:

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