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Photoinduced Ultrafast Electronic Dynamics in Polyatomic Molecules: A time-dependent computational study

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Synopsis We report on the dynamics of photoexcitation and photoionization induced by ultrashort strong optical pulses in two medium sized polyatomic molecules, 1-azabicyclo[2,2,2]octane and caffeine. The time-dependent Schrödinger equation is solved for an electronic Hamiltonian that includes the interaction with the strong pulse. The partitioning technique is applied to include both the neutral and the ionized subspaces.

The interaction between middle sized polyatomic molecules and ultrashort optical pulses with XUV or IR carrier frequencies can lead to photoexcitation or photoionization. To describe the dynamics of these processes, we solve the time-dependent Schrödinger equation for an electronic Hamiltonian that includes the interaction with the strong pulse within the partitioning approach, so that both the neutral and the ionized subspaces are taken into account. As a basis set, we use the field free stationary states of the neutral and the cation at frozen nuclei geometry, which can be gotten by methods like averaged CASSCF or TD-DFT. When the pulse is over one gets a coherent superposition of electronic states [1].

We report on electronic photoexcitation and photoionization dynamics in two medium sized molecules: 1-azabicyclo[2,2,2]octane and caffeine. While both molecules are of comparable size they have different symmetries, which influences their interaction and their response to the strong optical pulse. We are especially interested in the charge beating of the coherent superposition of states after the pulse. The charge transfer between different molecular moieties is reflected in the oscillations of the time dependent dipole moment, an observable that can be probed experimentally.

Not only the spatial distribution of the density of the bound electrons is of interest but also the one of the unbound electron after the ionization. Figure 1 shows preliminary results on the electronic dynamics in both the photoelectron spectrum and the angular distribution computed at two values of the kinetic energy for the caffeine molecule. The dynamics is computed for a EUV pulse with a carrier frequency of 7.6 eV, a width of 2fs and a strength of 0.005 a.u., polarized in the z direction of the molecular frame. At

the end of the pulse, mainly the GS and the 8th excited state of the cation are populated, as can be seen in the inset of Figure 1a). In Figure 1b) one sees that the spatial distribution for the first peak in the photoelectron spectrum is dominated by the angular distribution of the ground state of the cation, while that of the second peak is dominated by that of the 8th state.

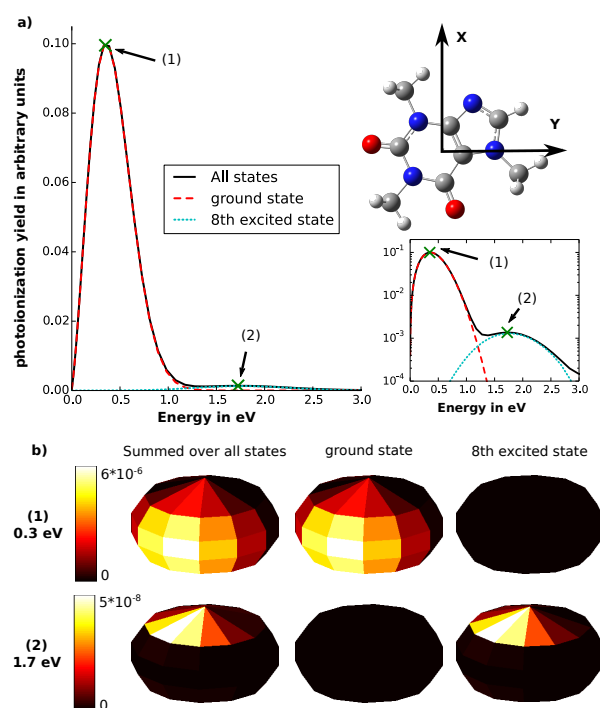


Figure 1. (a) Photoelectron spectrum. Shown are also the photoelectron spectra for selected states of the cation. (b) Angular distribution at different energies for some cationic states.

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References

- [1] B. Mignolet *et al* 2014 *J. Phys. B* **47** 124011

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