

Controlling charge migration in molecules

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Synopsis Due to electronic many-body effects, the ionization of a molecule can trigger ultrafast electron dynamics appearing as a migration of the created hole charge throughout the system. Here we propose a scheme for control of the charge migration dynamics with a single ultrashort laser pulse. We demonstrate by fully *ab initio* calculations on a molecule containing a chromophore and an amine moieties that simple pulses can be used for stopping the charge-migration oscillations and localizing the charge on the desired site of the system. We argue that this control may be used to predetermine the follow-up nuclear rearrangement and thus the molecular reactivity.

In recent years, the rapid development of the attosecond pulse techniques opened the door for studying and eventually controlling the electronic motion. Due to the coupling between the electronic and the nuclear motion, the control over the pure electronic step offers the extremely interesting possibility to steer the succeeding chemical reactivity by predetermining the reaction outcome at a very early stage.

One example of physical phenomena, where an electronic dynamics significantly affect on reactivity is the process of an ultrafast *charge migration* [1]. The positive charge created upon ionization of a molecule can migrate throughout the system on a few-femtosecond time scale solely driven by the electron correlation and electron relaxation. Charge migration triggered by ionization appeared to be a general phenomenon taking place both after inner- [2] and outer-valence [3] ionization of molecules.

We present a scheme for controlling the many-body electron dynamics of the charge migration process by a single ultrashort laser pulse. We show that by appropriately tailored [4] infrared pulses one can stop the pure electronic, few-femtosecond oscillation of the charge, localizing it on the desired site of the molecule 3-methylen-4-penten-*N,N*-dimethylamine (MePeNNA) [5]. To describe the correlated motion of 69 electrons (the number of electrons in MePeNNA cation) in the presence of a laser field we use *ab initio* methods only.

We would like to emphasize that the scheme presented in this work is general and not restricted to only stopping the charge migration oscillations. Through the appropriately chosen laser pulses it is possible to drive the system to any combination of the two electronic states, and thus bring the ion to the optimum initial condition for the desired follow-up nuclear motion.

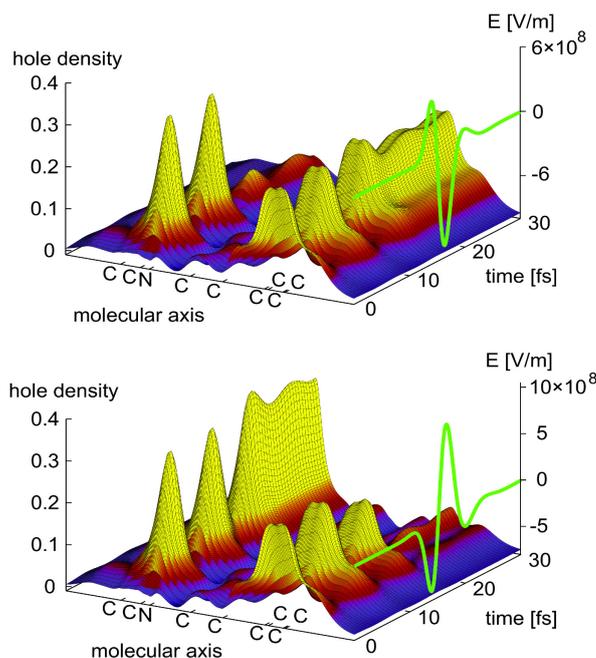


Figure 1. Time evolution of the hole density along the molecular axis of the molecule MePeNNA, after an initial localized ionization of the chromophore, controlled with a laser pulse (shown on the right) centered at 15 fs. Upper panel: the laser pulse is designed to achieve localization of the charge on the chromophore. Lower panel: the laser pulse is designed to achieve localization of the charge on the amine site.

References

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