Coupled electronic and protonic motion in H_2O in intense laser fields by extended multi-configuration time-dependent Hartree-Fock method

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When hydrocarbon molecules are exposed to an intense laser field, ultrafast hydrogen migration proceeds associated with the tunnel ionization. In order to describe the ultrafast hydrogen migration, we developed the extended multi-configuration time-dependent Hartree-Fock (Ex-MCTDHF) method[1-2], in which protons are expressed in terms of protonic orbital functions in a similar manner as electrons, so that the coupled motion of the electrons and protons within a molecule can be treated beyond the Born-Oppenheimer approximation. By performing the Ex-MCTDHF calculation for methanol, we confirmed that the resultant protonic wave functions describe appropriately the distribution of the protons within methanol and showed that the Ex-MCTDHF method can treat electrons and protons on an equal footing.

In the present study, we apply the Ex-MCTDHF method to the calculation of the temporal evolution of the electronic and protonic wave functions of H_2O being exposed to an intense three-cycle ultraviolet (λ = 400 nm) laser field. In the calculation, we describe the positions of the 10 electrons and the two protons by adopting a cylindrical coordinate (ρ, z) system whose origin is located at the position of the oxygen atom of H_2O.

The results of the Ex-MCTDHF calculation shown in Fig. 1 reveal that the electronic dipole moment follows the temporal variation of the laser field with high fidelity while the protonic dipole moment exhibit a phase shift corresponding to the delay of about 1 fs, which can be ascribed to the correlation among the electrons and protons, both of which are driven by the external field of light, as well as to the much heavier mass of a proton than an electron.

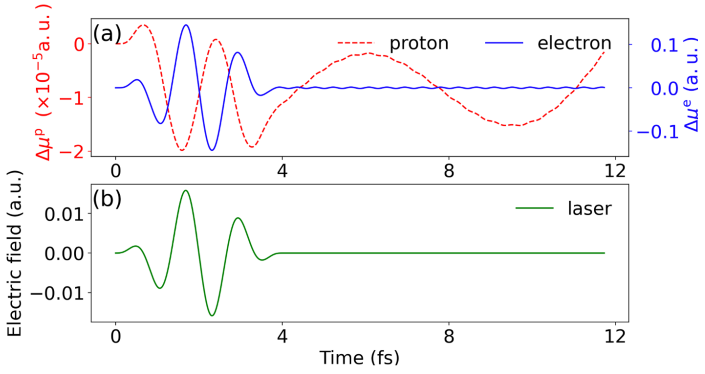

Fig. 1 (a) The temporal evolution of the variation of the electronic dipole moment ($\Delta\mu^e$) and the variation of the protonic dipole moment ($\Delta\mu^p$) of H_2O driven by a three-cycle ultraviolet (λ = 400 nm) laser field with the peak field intensity of 10^{13} W/cm^2 in the cylindrical coordinate system along the z directions. (b) The temporal shape of the laser electric field whose polarization is along the z axis.

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2) T. Kato, K. Yamanouchi, *Phys. Rev.* A **85**, 034504 -1-5 (2012).