

Multiple orbital contribution in multiphoton ionization of H₂O in intense ultrafast laser fields

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Synopsis We present all-electron time-dependent density-functional theory (TDDFT) investigation of multiphoton ionization (MPI) of H₂O in intense ultrafast linearly-polarized laser pulses with arbitrary molecular orientation. A new time-dependent Voronoi-cell finite difference method featuring highly adaptive molecular grids and an efficient time propagator is applied for accurate TDDFT solutions, taking into account the detailed electronic structure and responses in multiple orbital dynamics. Our results demonstrate that the inner orbital dominantly contributes to the overall orientation dependence of H₂O MPI.

The study of MPI of molecules in intense ultrafast laser fields is a subject of much current interest in strong-field molecular physics. Most theoretical studies of MPI today are based on approximate models that usually consider the highest occupied molecular orbital (HOMO) only and neglect multi-electron effects from multiple orbitals. Recently, it has been reported that significant discrepancy exists between experiments and approximate models for the orientation dependence of CO₂ MPI [1]. Furthermore, contribution of lower-lying orbitals below HOMO in high harmonic generation of N₂ has been observed [2]. Thus, it is a timely and important task to develop more detailed and accurate theoretical description of strong-field electronic dynamics.

We recently develop a new grid-based time-dependent Voronoi-cell finite difference method [3] to accurately solve TDDFT calculations for polyatomic molecules. In contrast to the ordinary finite difference method with regular uniform grids, the new method can achieve highly adaptive molecular grids with the help of geometrical flexibility of the Voronoi diagram, and can provide an efficient time-propagation method of the electronic density. With this new method, we first investigate strong-field electronic dynamics of polyatomic molecules including multi-electron effects such as electron correlation effects and multiple orbital contribution.

We present all-electron TDDFT study of the orientation dependence of H₂O MPI in intense ultrafast laser fields. Our results reveal that the orientation dependence is reflected by individual orbital symmetry. In particular, contribution from the inner orbital below HOMO (HOMO-1)

becomes dominant in the overall pattern of the orientation dependence, when the orientation angle is varying in a specific direction with respect to H₂O [Fig. 1]. This interesting prediction emphasizes importance of multiple orbital contribution in molecular imaging and tomography.

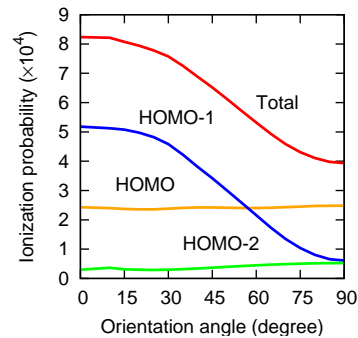


Fig. 1. Orientation dependence of individual ionization probabilities of H₂O with the peak intensity 5×10^{13} W/cm² and frequency 800 nm.

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References

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