

強光子場中の H_2O^{2+} から放出されたプロトンの運動量分布：
時間依存断熱状態法による評価

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Momentum distribution of protons ejected from H_2O^{2+} in an ultrashort intense laser field obtained by time-dependent adiabatic-state method

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【Abstract】 We performed *ab initio* molecular dynamics calculations combined with a time dependent adiabatic state approach in order to investigate the effect of a laser field on the momentum distribution of protons ejected from H_2O^{2+} and found that H_2O^{2+} decomposes on the lowest time-dependent adiabatic-state surface through the two-body dissociation into $\text{HO}^+ + \text{H}^+$ as well as through the three-body dissociation into $\text{H}^+ + \text{O} + \text{H}^+$. For the two-body dissociation, the peak position of the proton momentum distribution is in good agreement with that observed in the previous experiment. For the three-body dissociation, we found that the momentum distribution of protons varies sensitively to the timing of the preparation of H_2O^{2+} , reflecting the temporal variation of the barrier along the three-body dissociation coordinate on the time-dependent adiabatic-state potential of H_2O^{2+} .

【Introduction】 In an intense laser field, molecules are strongly coupled with the light field, and their structural deformation and bond breaking processes are governed by their light-dressed potential energy surfaces [1,2], and therefore, in these decades, control of chemical bond breaking processes in polyatomic molecules in an intense laser field has been an attractive research topic [3]. In our previous report, we showed experimentally that the momentum distribution of protons ejected from H_2O in an ultrashort intense laser field exhibited multiple peak profiles and that these profiles vary sensitively to the laser pulse duration [4].

In the present study, in order to investigate the laser field effect on the momentum of protons ejected from H_2O^{2+} , we performed *ab initio* molecular dynamics calculation using the time-dependent adiabatic-state (TDAS) approach [5].

【Theoretical calculations】 A TDAS, $\{|n(R, t)\rangle\}$, characterized by the nuclear coordinate R and time t , is an eigenfunction of the instantaneous electronic Hamiltonian $H_{el}(R, t)$, that is,

$$H_{el}(R, t)|n(R, t)\rangle = E_n(R, t)|n(R, t)\rangle.$$

The instantaneous electronic Hamiltonian can be expressed as the sum of the field-free adiabatic electronic Hamiltonian, $H_{el}(R, \varepsilon(t) = 0)$, and the electric dipole interaction $-\mu\varepsilon(t)$, that is,

$$H_{el}(R, t) = H_{el}(R, \varepsilon(t) = 0) - \mu\varepsilon(t),$$

where $\varepsilon(t)$ stands for the laser electric field.

We calculated the classical trajectories on the lowest energy TDAS surfaces of H_2O , H_2O^+ and H_2O^{2+} for the two different sets of near-IR (800 nm) light field conditions, $(\Delta t, I) = (8 \text{ fs}, 1.6 \text{ PW/cm}^2)$ and $(20 \text{ fs}, 0.64 \text{ PW/cm}^2)$, corresponding to the conditions adopted in the previous experiment [4], where Δt denotes the light pulse duration and I denotes the peak light-field intensity. The electronic states were calculated using the complete active space self-consistent

field (CASSCF) method with the basis set of 6-311+G(*d,p*). We assume that H₂O takes initially the equilibrium structure in the electronic ground state, and that the initial velocities of the nuclei take a Wigner distribution at the vibrational and electronic ground state. We started the calculation on the TDAS of neutral H₂O, and switched the TDAS to that of H₂O⁺ when the laser intensity exceeds 10¹³ W/cm². We varied the timing of the generation of H₂O²⁺ from H₂O⁺ within the light pulse.

【Results and discussion】 We found that H₂O²⁺ decomposes on the lowest-energy TDAS surface through the two-body dissociation into HO⁺ + H⁺ as well as through the three-body dissociation into H⁺ + O + H⁺. In the case of the two-body dissociation, the peak positions of the momentum distribution of the protons observed experimentally at 32×10³ u ms⁻¹ (peak 4 in Figures 1 (a) and 1 (b)) [4] for the two different laser-field conditions were reproduced well by the present calculations. Figures 1 (c) and 1 (d) show the total momentum distribution along the direction parallel to the laser polarization of the ejected protons through the two-body dissociation, obtained by the sum of the distributions at all the timings of the preparation of H₂O²⁺ from H₂O⁺. The present theoretical results show that the peak momentum positions are located at 32×10³ u ms⁻¹ in both of the two different laser pulse durations, which is consistent with the experimental results in which the momentum for the peak 4 does not change for the two different laser pulse durations.

For the three-body dissociation, we found that the momentum distribution of protons varies sensitively to the timing of the preparation of H₂O²⁺ because the barrier on the TDAS potential along the three-body dissociation coordinate varies largely in response to the temporal variation of the light field intensity.

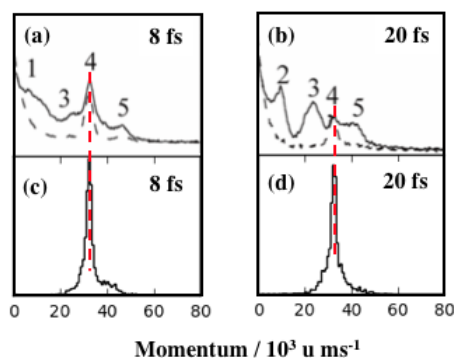


Fig. 1. (a) The momentum distribution of H⁺ ejected from H₂O by the irradiation of an 8-fs laser pulse whose peak intensity is 1.6 PW/cm² and (b) the momentum distribution of H⁺ ejected from H₂O by the irradiation of a 20-fs laser pulse whose peak intensity is 0.64 PW/cm² [4]. The solid curve and dashed curve show the results obtained when the laser polarization direction is set to be parallel and perpendicular to the TOF axis, respectively. (c), (d) The total momentum distributions along the direction parallel to the laser polarization of H⁺ ejected through the two-body dissociation when the pulse durations are (c) 8 fs and of (d) 20 fs obtained as the sums of the momentum distributions for all the timings of the preparation of H₂O²⁺ from H₂O⁺.

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