論文の内容の要旨

Ionization and dissociation dynamics of H₂O in ultrashort intense near-IR laser fields by the time-dependent adiabatic state method and the time-dependent configuration interaction method

(時間依存断熱状態法と時間依存配置間相互作用法による H₂O の超短高強度近赤外レーザー場におけるイオン化と解離のダイナミクス)

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1. Introduction

When molecules are exposed to an intense laser field, they are strongly coupled with the light field and their structural deformation and bond breaking processes are governed by the light-dressed potential energy surfaces [1-3]. It was reported 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 as shown in Figs. 1(a) and 1(b) [4]. In the present study, in order to interpret the experimental findings, I performed theoretical calculations and established the assignment of the observed peak profiles. I performed first *ab initio* molecular dynamics (MD) calculations using the time-dependent adiabatic state (TDAS) approach [5] to examine the effect of the laser field on the momentum distribution of protons ejected from H_2O^{2+}, and then, time-dependent configuration interaction calculations with complete active space expansion (TD-CASCI) to examine the charge resonance enhanced ionization process of H_2O^{2+}.

2. Computation methods

2.1. Calculation of the momentum distribution of H⁺ ejected from H₂O²⁺ using *ab initio* MD

A TDAS, $|n(\boldsymbol{R}, t)\rangle$ characterized by the nuclear coordinate $\boldsymbol{R}$ and time t, is an eigenfunction of the instantaneous electronic Hamiltonian $\boldsymbol{H}_{el}(\boldsymbol{R}, t)$,

$$\boldsymbol{H}_{el}(\boldsymbol{R}, t)|n(\boldsymbol{R}, t)\rangle = E_n(\boldsymbol{R}, t)|n(\boldsymbol{R}, t)\rangle. \tag{1}$$

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, $-\mu\varepsilon(t)$, as

$$H_{el}(R, t) = H_{el}(R, \varepsilon(t) = 0) - \mu\varepsilon(t), \tag{2}$$

where μ and $\varepsilon(t)$ denote the dipole moment and the laser electric field, respectively.

I calculated classical trajectories on the lowest-energy TDAS surfaces of H_2O, H_2O^+ and H_2O^{2+} for the two different sets of 800 nm light-field conditions, $(\Delta t, I) = (8\ fs, 1.6\ PW/cm^2)$ and $(20\ fs, 0.64\ PW/cm^2)$, corresponding to the experimental conditions [4], where Δt denotes the light pulse duration and I denotes the peak light-field intensity. I assume that H_2O 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. I started the calculation on the TDAS of neutral H_2O and switched the TDAS to that of H_2O^+ when the laser intensity exceeds $10^{13}\ W/cm^2$. The timing of the generation of H_2O^{2+} from H_2O^+ was varied within the light pulse. For each timing, 100 trajectories were calculated.

2.2. Estimation of the ionization probability of H_2O^{2+} using TD-CASCI

I estimated the charge resonance enhanced ionization probability from H_2O^{2+} to H_2O^{3+} using TD-CASCI method. The time-dependent electronic Schrödinger equation within the dipole approximation for fixed molecular structure can be written as

$$i\hbar\frac{\partial}{\partial t}\Psi(R, t) = [H_{el}(R) - \mu \cdot \varepsilon(t)]\Psi(R, t), \tag{3}$$

where $H_{el}(R)$ denotes the field-free electronic Hamiltonian and the dipole coupling term $-\mu \cdot \varepsilon(t)$ is the scaler product of the transition dipole moment μ and electric field $\varepsilon(t)$. The time-dependent wavefunction $\Psi(R, t)$ is a linear combination of the eigenstate functions $\phi_n(R)$ of $H_{el}(R)$,

$$\Psi(R, t) = \sum_n C_n(t)\phi_n(R). \tag{4}$$

I performed TD-CASCI calculations at 369 different geometrical structures of H_2O^{2+} in order to estimate the dependence of the ionization probability on the geometrical structure. I used two models for the deformation of the geometrical structure of H_2O^{2+} as shown Fig. 3, i.e., (a) the asymmetric stretching model corresponding to the two-body dissociation channel, $H_2O^{2+} \rightarrow H^+ + OH^+$, and (b) the symmetric stretching model corresponding to the three-body dissociation channel, $H_2O^{2+} \rightarrow H^+ + O + H^+$. In the asymmetric stretching model, one of the two OH bond was fixed at 1.0 Å and the other OH bond and the H-O-H angle were varied. In the symmetric stretching model, two OH bonds were varied equally. I adopted a laser pulse with the Gaussian envelope whose pulse duration is 3 fs in order to obtain the ionization probability at a given geometrical structure defined as

$$P = 1 - \sum_{E_n < E_{IP}} |C_n(t_{end})|^2, \tag{5}$$

representing the total population in the states whose energies are above the ionization threshold E_{IP} at the end of the laser pulse, t_{end}.

3. Results and discussion

From the results of the MD calculations, I found that H_2O^{2+} decomposes on the lowest-energy TDAS surface through the following two dissociation channels;

(i) $H_2O^{2+} \rightarrow H^+ + OH^+$

(ii) $H_2O^{2+} \rightarrow H^+ + O + H^+$.

In the case of the two-body dissociation (i), the peak positions of the momentum distribution of H^+ observed experimentally at 32×10^3 ums^{-1} as Peak 4 at the two different laser-field conditions are reproduced well by the present calculations as shown Fig. 1. The peak position of momentum distribution of H^+ does not vary when the timing of the preparation of H_2O^{2+} is changed as shown in Fig. 2. This is because the geometrical structure of H_2O^+, prepared in the equilibrium structure on the lowest-energy TDAS surface, does not change so much before H_2O^{2+} is created, leading to the two-body Coulomb explosion of H_2O^{2+}. For the three-body dissociation (ii), I found that the momentum distribution of protons varies sensitively to the timing of the preparation of H_2O^{2+} 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.
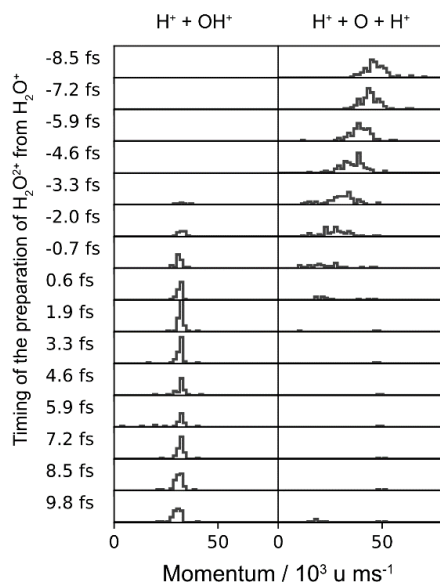

Fig. 1. The momentum distributions of H^+ ejected from H_2O by the irradiation of (a) an 8-fs laser pulse whose peak intensity is 1.6 PW/cm² and (b) a 20-fs laser pulse whose peak intensity is 0.64 PW/cm² [4]. The sloid curve and dashed curve show the results obtained when the laser polarization direction is set to be parallel and perpendicular to the TOF axis, respectively. The total momentum distributions of H^+ along the direction parallel to the laser polarization ejected through the two-body dissociation when the laser pulse durations are (d) 8 fs and (d) 20 fs, obtained as the sums of the momentum distributions calculated at all the timings of the preparation of H_2O^{2+} from H_2O^+.

Fig. 2. The momentum distribution of H^+ obtained by the *ab inito* MD calculation at different timings of the preparation of H_2O^{2+} within a 8-fs pulse for the two-body dissociation (left column) and the three-body dissociation (right column).
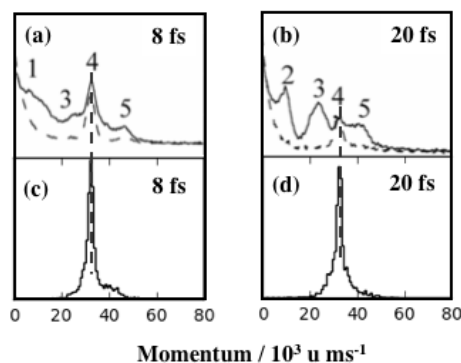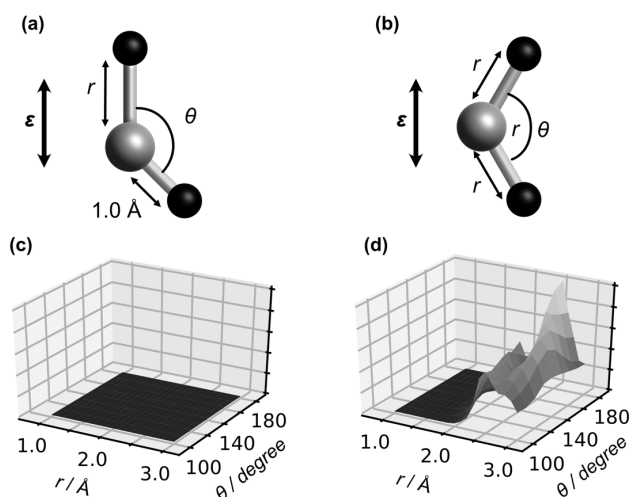

Fig. 3. (a) The asymmetric stretching model and (b) the symmetric stretching model. In (a) and (b), ε denotes the direction of the laser polarization. (c) The ionization probability calculated using the model (a). (d) The ionization probability calculated using the model (b).

The results of the TD-CASCI calculations showed that the ionization probability is strongly enhanced when the two O-H bonds stretch equally in the linearly polarized light field whose polarization direction is parallel to the line connecting the two H atoms (Fig. 3(d)). This finding suggests that the charge resonance enhanced ionization process of H_2O^{2+} plays a key role in generating H_2O^{3+}, from which H^+ is ejected in the direction parallel to the laser polarization, resulting in Peak 5 in Figs. 1(a) and 1(b). The difference in the position of Peak 5 at the two different laser-field conditions can be explained by the fact that the geometrical structure of H_2O^{2+} prior to Coulomb explosion of H_2O^{3+} stretches more when the laser pulse duration is longer.

4. Conclusion

I performed *ab initio* MD calculations combined with the TDAS approach and showed that the peak positions of the momentum distribution of H^+ ejected through the two-body dissociation of H_2O^{2+} are in good agreement with the observed peak positions. I also performed TD-CASCI calculations to estimate the ionization probability of H_2O^{2+} and showed that H_2O^{3+} is created by the charge resonance enhanced ionization of H_2O^{2+}.

References
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