Dissociation and ionization dynamics of H\textsubscript{2}O in an ultrashort intense laser field by the time-dependent adiabatic-state method and the time-dependent configuration interaction method

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[Abstract] In order to investigate the effect of laser parameters on the dissociation dynamics of H\textsubscript{2}O in intense near-IR fields, we performed \textit{ab initio} molecular dynamics calculations combined with the time dependent adiabatic state approach and showed that the peak positions of the momentum distribution of H\textsuperscript{+} ejected through the two-body dissociation of H\textsubscript{2}O\textsuperscript{2+} are in good agreement with the experimental data. We also performed time dependent configuration interaction calculations to estimate the ionization probability of H\textsubscript{2}O\textsuperscript{2+} and revealed that the charge resonance enhanced ionization of H\textsubscript{2}O\textsuperscript{2+} plays an important role in the formation of H\textsubscript{2}O\textsuperscript{3+}.

[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]. In our previous experiment, we showed that the momentum distribution of protons ejected from H\textsubscript{2}O in an ultrashort intense laser field exhibited multiple peak profiles and that these profiles vary sensitively to the laser pulse duration as shown in Fig. 1 [4]. In the present study, we performed \textit{ab initio} molecular dynamics (MD) calculations using the time dependent adiabatic state (TDAS) approach [5] in order to investigate the effect of the laser field on the momentum distribution of protons ejected from H\textsubscript{2}O\textsuperscript{2+}. We also performed time dependent configuration interaction calculations with a complete active space expansion (TD-CASCI) in order to examine the charge resonance enhanced ionization (CREI) process of H\textsubscript{2}O\textsuperscript{2+}.

[Theoretical calculations] We first calculated classical trajectories on the lowest TDAS surfaces of H\textsubscript{2}O, H\textsubscript{2}O\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{2+} for two different sets of near-IR (800 nm) light-field conditions, (\textit{\Delta}t, \textit{I}) = (8 fs, 1.6 PW/cm\textsuperscript{2}) and (20 fs, 0.64 PW/cm\textsuperscript{2}), corresponding to the experimental conditions [4], where \textit{\Delta}t denotes the light pulse duration and \textit{I} denotes the peak light-field intensity. We assume that H\textsubscript{2}O 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 H\textsubscript{2}O and switched the TDAS to that of H\textsubscript{2}O\textsuperscript{+} when the laser intensity exceeds 10\textsuperscript{13} W/cm\textsuperscript{2}. We varied the timing of the generation of H\textsubscript{2}O\textsuperscript{2+} from H\textsubscript{2}O\textsuperscript{+} within the light pulse.

Next, we performed TD-CASCI calculations at around 400 different geometrical structures.
of H$_2$O$^{2+}$ in order to estimate the dependence of the ionization probability on the geometrical structure. We used two models for the deformation of the geometrical structure of H$_2$O$^{2+}$ as shown in Fig. 2, i.e., (a) the asymmetric stretching model corresponding to the two-body dissociation channel, H$_2$O$^{2+}$ → H$^+$ + OH$^+$, and (e) the symmetric stretching model corresponding to the three-body dissociation channel, H$_2$O$^{2+}$ → H$^+$ + O + H$^+$. In the asymmetric stretching model, one of the two OH bond was fixed and the other OH bond and the H-O-H angle were varied. In the symmetric stretching model, two OH bonds were varied equally. We adopted a laser pulse with the Gaussian envelope whose pulse duration is as short as 3 fs in order to obtain the ionization probability at a fixed geometrical structure. We estimated the ionization probability as the total population in the states whose eigenenergies are above the ionization threshold after the laser-molecule interaction period.

**[Results and Discussion]** From the results of the MD calculations, we found that H$_2$O$^{2+}$ 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 32×10$^3$ u ms$^{-1}$ (peak 4 in Fig. 1) at the two different laser-field conditions are reproduced well by the present calculations.

From the results of the TD-CASCI calculations, we found 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. 2 (h)). This finding suggests that the CREI of H$_2$O$^{2+}$ plays a key role in generating H$_2$O$^{3+}$, from which H$^+$ is ejected in the direction parallel to the laser polarization, resulting in peak 5 in Fig. 1.

![Fig. 2](image-url) Fig. 2. Upper figures: the asymmetric stretching model (a) and the ionization probabilities calculated when the laser polarization is parallel to the X axis (b), the Y axis (c), and the Z axis (d). Lower figures: the symmetric stretching model (e) and the ionization probabilities calculated when the laser polarization is parallel to the X axis (f), the Y axis (g), and the Z axis (h).

**[References]**