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Ionization Dynamics of the Small-Sized Water Clusters: A Direct Ab Initio Trajectory Study†

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The ionization dynamics of the water clusters $(H_2O)_n$ ($n = 3-6$) have been investigated by means of the full-dimensional direct ab initio trajectory method. The static ab initio and DFT calculations were carried out at the HF/6-311G(d,p) and B3LYP/6-311G(d,p) levels, whereas the direct ab initio trajectory calculations were performed at the HF/6-31G(d) and 6-311G(d,p) levels of theory. The static ab initio and DFT calculations showed that the most stable structure is the cyclic form for all cases ($n = 3-6$). In the ionization of the water trimer, the complex $(H_3O^+OH)H_2O$ was obtained as a product (complex formation channel). In the larger clusters ($n = 4-6$), the OH dissociation was only found after the ionization of $(H_2O)_n$ (OH dissociation channel). The OH dissociation occurs via two-step processes: the first step is a proton-transfer process from H_2O^+ to H_2O along the hydrogen bond in the cluster, and then the (H_3O^+OH) complex is formed as a core in the cluster, expressed by $(H_2O^+){-}H_2O{-}H_2O \rightarrow (OH)(H_3O^+){-}H_2O$. The next step is the second proton-transfer process from H_3O^+OH to the neighboring water molecule, which is expressed by $(OH){-}H_3O^+{-}H_2O \rightarrow (OH){-}H_2O{-}H_3O^+$. It was found that the OH dissociation takes place immediately after the second proton transfer. The lifetimes of the intermediate complexes are distributed in the range 50−200 fs for $n = 4-6$. The reaction mechanism was discussed on the basis of theoretical results.

1. Introduction

The ionization of water and water clusters plays an important role in neutron irradiation to the cooling water in a nuclear atomic plant and in the photoreaction of water in atmospheric science.[1,2] By irradiation of photo- and high-energy beams to the water, several reactions occur as the decay process of the irradiated water. First, H_2O^+ is formed as a core ion in bulk water following the irradiation to the water. After that, H_2O^+ reacts immediately with the surrounding neutral water molecules. The proton transfer has been considered as a main process in bulk water. In addition to the reaction of H_2O^+, an electron, generated by the ionization of H_2O, starts various events. The electron is trapped by the surrounding water molecules after the relaxation of its translational energy. The hydrated electron is formed in the bulk water. Although overall reactions of H_2O^+ are thus known from several phenomena, a detailed mechanism of the initial reactions is scarcely known because the H_2O^+ ion has a high activity, and also, the reaction of H_2O^+ is a very fast process. Hence, studying of the reaction of water clusters gives important information on the microscopic feature in the initial reactions of the ionized water and water ice.

The information about the structures and energetics for small-sized water clusters has been accumulated mainly from the theoretical point of view.[3−6] The smallest water cluster is a water dimer. The neutral water dimer has a linear form in its equilibrium point. On the other hand, the structure of the cationic state of the water dimer is largely distorted from the neutral one: the structure of $(H_2O)_2^+$ is composed of the H_3O^+ ion and the OH radical, expressed by (H_3O^+OH), where the proton is spontaneously transferred from H_2O^+ to H_2O after the ionization of $(H_2O)_2$.[7] Recently, we have investigated the ionization dynamics of the water dimer by means of the direct ab initio trajectory method.[8,9] The water dimer cation has two low-lying electronic states: the ground state ($^2A''$ state) and the first excited state ($^2A'$ state). From the direct ab initio trajectory calculations, it is found that the ionization of the $^2A''$ state leads to the complex formation, whereas that of the $^2A'$ state gives two reaction channels: complex formation and OH dissociation.

Landman et al. investigated the structure of the water cluster cation $(H_2O)_n^+$ ($n = 3-5$) using ab initio calculations.[10] Their calculations showed that the complex (H_3O^+OH) exists as a core cation in the clusters for all cation clusters. The similar feature has been reported by several groups.[3,6] However, the dynamics of the ionization of the water cluster is scarcely known.

From experimental points of view, photoionization of the small-sized water clusters has been investigated by means of several experimental techniques.[11−14] It is found that the reaction occurs as the following schemes

$$(H_2O)_n + IP \rightarrow [(H_2O)_n{}^+]_{VIP} + e^- \text{ (ionization)}$$

$$\begin{aligned}
&[(H_2O)_n{}^+]_{VIP} \\
&\quad \rightarrow (H_3O^+)(OH)(H_2O)_{n-1} \text{ (complex formation)} \\
&\quad \rightarrow H^+(H_2O)_{n-1} + OH \text{ (OH dissociation)} \\
&\quad \rightarrow H^+(H_2O)_{n-k} + (k-1)H_2O + OH \\
&\qquad\qquad \text{(OH dissociation + } H_2O \text{ evaporation)}
\end{aligned}$$

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where IP and VIP mean ionization potential and vertical ionization point from the neutral cluster, respectively. Three reaction channels are observed as decay processes of the ionized water clusters. The first channel is a complex formation in which the proton is transferred from H_2O^+ to H_2O, and then the long-lived complex composed of the $(H_3O^+)(OH)$ core is formed in the cluster. The second and third channels are the OH dissociation from the cluster and three-body dissociation, respectively. The experiments show that the parent ion $(H_2O)_n{}^+$ is only observed for the water dimer and trimer, whereas the protonated water $H^+(H_2O)_m$ ($m < n$) is observed in the larger clusters. Thus, the OH formation is only observed in larger clusters.

The absence of the parent ion is consistently explained in terms of poor Franck−Condon overlaps between the neutral and the ionic states whose potential minima are largely displaced from each other. Thus, the reaction channels are strongly dependent on the cluster size. However, the detailed dynamics of water clusters is hardly known. In particular, the reason cluster size dependency exists in the ionization of water cluster is not clearly understood.

In the present study, the direct ab initio trajectory calculation has been applied to the ionization dynamics of small-sized water clusters $(H_2O)_n$ ($n = 3-6$) in order to shed light on the effect of the irradiation to water ice. The purposes of this study are to elucidate the initial reaction after the ionization of $(H_2O)_n$ from a theoretical point of view, to estimate the reaction time (lifetime of the intermediate complexes), and also to elucidate the mechanism of the OH dissociation from the ionized clusters. We focus our attention mainly on the cluster size dependency on the reaction channels and the lifetime of the complexes formed by the ionization.

2. Method of Calculation

The present reaction system $(H_2O)_n$ has a large number of degrees of freedom ($3N - 6 = 48$ for $n = 6$, where N is numbers of atoms in the system) so that it is quite difficult to fit an ab initio surface to analytical functions of interatomic potential. Hence, a direct ab initio trajectory calculation[15−17] is the best way to treat the reaction dynamics for the present reaction system. In this work, we used a direct ab initio dynamics calculation using the full-dimensional potential-energy surface. The calculations were carried out at the HF/6-31G(d) and 6-311G(d,p) levels of theory, but we discussed the dynamics using the results obtained by the HF/6-311G(d,p) level.

In the dynamics calculation, first, the geometries of $(H_2O)_n$ ($n = 3-6$) were fully optimized. The trajectory on the ionic state PESs of $(H_2O)_n{}^+$ were run on the assumption of vertical ionization from neutral water clusters. The trajectory calculations of $(H_2O)_n{}^+$ were performed under constant total energy conditions. The velocities of atoms at the starting point were assumed to be zero (i.e., the momentum vector of each atom is zero). The equations of motion for N atoms in a molecule are given by

$$\frac{dQ_j}{dt} = \frac{\partial H}{\partial P_j}$$

$$\frac{\partial P_j}{\partial t} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j}$$

where $j = 1 - 3N$, H is classical Hamiltonian, Q_j is the Cartesian coordinate of the jth mode, and P_j is the conjugated momentum. These equations were numerically solved by the Runge−Kutta method. No symmetry restriction was applied to the calculation of the gradients in the Runge−Kutta method. The time step size was chosen to be 0.10 fs, and a total of 10 000 steps were calculated for each dynamics calculation. The drift of the total energy is confirmed to be less than 1×10^{-3} % throughout all steps in the trajectory. The momentum of the center of mass and the angular momentum are assumed to zero. Static ab initio MO and density functional theory (DFT) calculations were carried out using the Gaussian 98 program package using 6-311G(d,p) basis sets[18] in order to obtain more accurate energetics.

3. Results

A. Structures of the Cyclic $(H_2O)_n$ Clusters. The fully optimized structures of cyclic water clusters $(H_2O)_n$ ($n = 2-6$) are illustrated in Figure 1. For all cases, the most stable form is the cyclic structure. One of the hydrogen atoms of each water molecule orients to the oxygen atom of the neighboring water molecule, and other hydrogen exists as a dangling atom. This tendency is common in all cyclic water clusters ($n = 3-6$). The HF/6-311G(d,p) calculation gives the similar structures for the neutral and cationic clusters obtained by B3LYP/6-311G-(d,p) level of theory.

B. Ionization of Water Trimer ($n = 3$). Snapshots of geometrical configurations during the ionization processes of the water trimer are illustrated in Figure 2. After the ionization, the hole is first localized on one of the water molecules of the water trimer, which is denoted by $H_2O(I)$. The ionized water molecule $H_2O^+(I)$ is given in Figure 2 by a circle. Following the ionization, the proton of $H_2O^+(I)$ is immediately transferred to $H_2O(II)$, and then the oxonium ion $H_3O^+(II)$ is formed at time = 25 fs. The oxonium ion (H_3O^+) forms an ion−radical pair with the OH radical, which is expressed by H_3O^+OH. As we reported in a previous paper,[8] the complex is more stable in energy than the dissociation limit ($H_3O^+ + OH$). After that, the OH radical vibrates periodically near $H_3O^+(II)$, but the structure of the ion−radical pair is maintained. The second proton transfer from $H_3O^+(II)$ to $H_2O(III)$ does not occur in the present trajectory calculation. The water molecule $H_2O(III)$ interacts with H_3O^+ as a solvent molecule.

As a result of the trajectory calculation, the reaction following the ionization of the water trimer is summarized as follows

$$(H_2O)_3 + IP \rightarrow [(H_2O)_3{}^+]_{VIP} + e^- \qquad (1)$$

$$[(H_2O)_3{}^+]_{VIP} \rightarrow (H_3O^+OH)-(H_2O) \qquad (2)$$

First, the ionization takes place in one of the water molecules in $(H_2O)_3$. Immediately, the proton is transferred from H_2O^+ to H_2O. As the final product, the ion−radical pair H_3O^+OH solvated by a water molecule is formed. The complex is expressed schematically by $(H_3O^+OH)-(H_2O)$.

Time evolution of the potential energy of the system, the interatomic distances, following the ionization of water trimer, are plotted in Figure 3. The zero level of the energy corresponds to that of $[(H_2O)_3{}^+]_{VIP}$ at a VIP from the neutral trimer. After the ionization, the energy decreases immediately to −4.0 kcal/mol at 5.0 fs. This energy lowering is caused by a structural deformation of $H_2O^+(I)$, namely, the bending angles of H_2O^+ are suddenly expanded after the ionization because the angle of H_2O^+ is about 5° wider than that of H_2O. This deformation is originated from the electron removal from the nonbonding orbital of $H_2O^+(I)$. The bending mode of $H_2O(I)$ is slightly excited by the ionization.

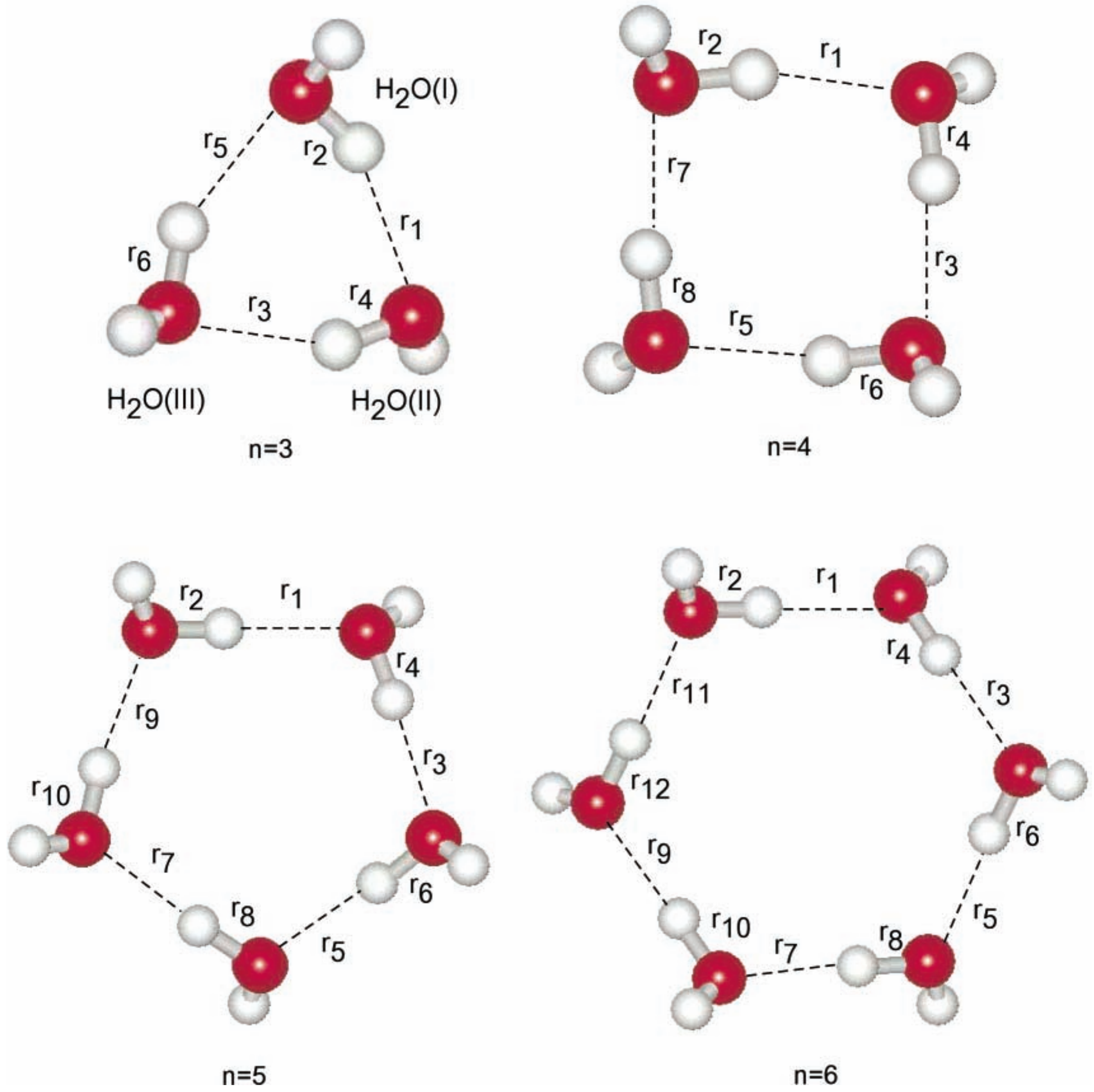

Figure 1. Structures and geometry parameters of cyclic water clusters $(H_2O)_n$ ($n = 3-6$).

The energy decreases further to -36 kcal/mol at time = 25 fs, which corresponds to the energy of the ion−radical pair H_3O^+OH. Figure 3B shows that the distance of H(I) from the oxygen atom of H_2O(II), r_1, decreases gradually and it takes minimum at time = 25 fs. This means that the first proton H^+(I) is directly and spontaneously transferred from H_2O^+(I) to H_2O(II) after the ionization. The oxonium ion H_3O^+(II) is formed at 25 fs. After the first proton transfer, it is seen that r_1 vibrates periodically as a function of time (time = 60−300 fs), indicating that the new O−H bond is formed as H_3O^+ by the first proton transfer.

The intermolecular distances (R_1 and R_2) are plotted in Figure 3c, where the distances are defined by R_1 = O(I) − O(II) and R_2 = O(II) − O(III), respectively. The oxygen−oxygen distances (R_1 and R_2) are 2.88 Å at time zero. After the ionization, R_1 decreases monotonically and is minimized at time = 40 fs (R_1 = 2.25 Å). The energy at this point is calculated to be -9.0 kcal/mol, which is 27.0 kcal/mol higher than the bottom of energy at time = 25 fs (energy = -36 kcal/mol). The rise of the energy is caused by the collision of the OH radical with H_3O^+(II) at time = 40 fs. After the collision, R_1 increases gradually as a function of time, indicating that the OH radical is rebounded from H_3O^+.

At time = 60 fs, the proton H^+(I) binds completely to H_2O(II), and then the energy vibrates strongly in the range (-45) − (-15) kcal/mol. This means that the intermolecular vibration between OH and $H_3O^+(H_2O)$ is excited. However, the OH radical is not dissociated from $H_3O^+(H_2O)$ because the attractive interaction is significantly strong in the ion−radical pair H_3O^+-OH. Time evolution of the distance r_2 also indicates the complex formation.

Before the ionization, the water trimer has a triangle structure as shown in Figure 3. After the ionization, this triangle structure is deformed and is close to a linear structure. The water molecule H_2O(III) leaves gradually from H_2O(I). This is due to the fact that the hydrogen bond between H_2O(I) and H_2O(III) is disappeared after the ionization. Hence, the distance between H_2O^+(I) and H_2O(III) is gradually expanded as time passes.

C. Ionization Dynamics of the Water Tetramer (*n* = 4). Snapshots of the structural configurations of $(H_2O)_4{}^+$, following the ionization of water tetramer, are illustrated in Figure 4. The hole is localized on H_2O^+(I) at time zero. Immediately, the proton of H_2O^+(I) moves toward the oxygen atom of H_2O(II). At time = 15 fs, the proton of H_2O^+(I) collides to H_2O(II), and the ion−radical pair expressed by OH(I)−H_3O^+(II) is formed. The OH radical still binds to H_3O^+, and the dissociation of OH does not occur up to time = 180 fs. At time = 200 fs, the proton of H_3O^+(II) begins to move to H_2O(III). This is “the second proton transfer”. Once the second proton is transferred from H_3O^+(II) to H_2O(III), the OH radical is immediately dissociated

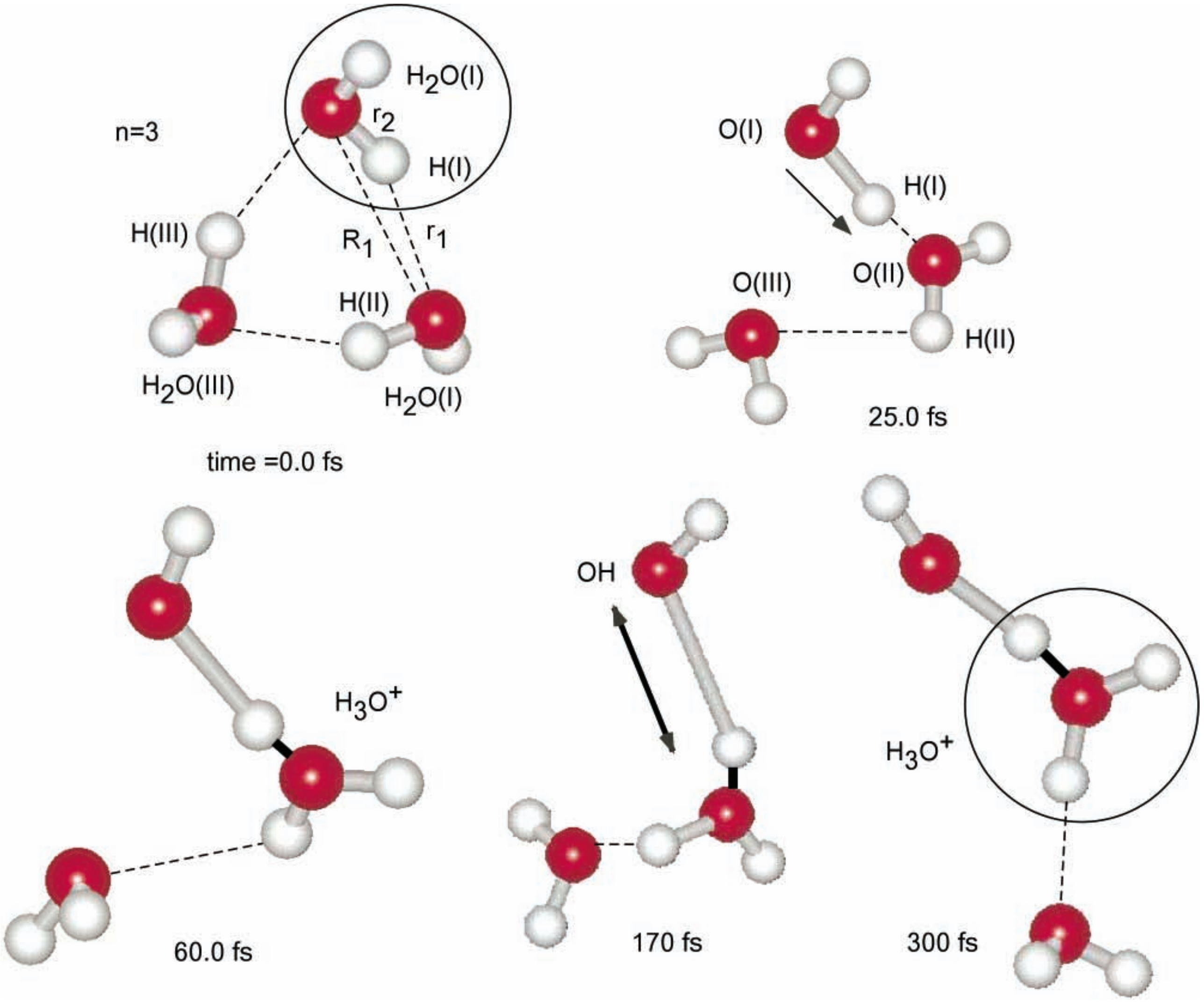

Figure 2. Snapshots for the geometrical configurations of $(H_2O)_3^+$ after vertical ionization of the neutral water trimer, calculated as a function of time.

from the system. This is due to the fact that the attractive interaction between the OH radical and H_3O^+ is disappeared after the second proton transfer; H_2O(II) is located in the middle of OH(I) and H_3O^+(III). The final product is OH(I) + H_2O(II)−H_3O^+(III)−H_2O(IV). The H_3O^+ ion is solvated by two water molecules. Thus, the OH dissociation is completed.

The hydrogen bond between H_2O(I) and H_2O(IV) disappears after the ionization because the charge of the water molecule H_2O(I) is suddenly changed to positive. When the reaction proceeds, the distance between the OH radical and H_2O(IV) is gradually expanded due to no interaction between OH(I) and H_2O(IV). The cyclic structure of $(H_2O)_4^+$ becomes a linear form at 300 fs, as shown in Figure 4.

The potential energy of the system is plotted in Figure 5A. After the ionization of $(H_2O)_4$, the energy is first down to −5.8 kcal/mol within 3 fs, and it decreases further to −44.5 kcal/mol at 13 fs. The former energy shift is caused by the deformation of H_2O^+(I) after the ionization as well as $(H_2O)_3^+$. The latter energy change is caused by the first proton transfer from H_2O^+(I) to H_2O(II). The energy of the system is minimized at this point (time = 13 fs and energy = −44.5 kcal/mol).

The origin of the energy profile is clearly seen in the time evolution of the geometrical parameters of the reaction system. The position of H^+(I) relative to the oxygen atom of H_2O(II) (denoted by r_1) is plotted in Figure 5B as a function of time. The distance r_1 is 1.904 Å at time zero. After the ionization, r_1 decreases gradually and it takes 0.954 Å at the energy minimum (time = 13 fs, and energy = −44.5 kcal/mol). H^+(I) approaches the further H_2O(II) (r_1 = 0.781 Å at time = 14.5 fs). The collision of the proton H^+(I) with H_2O(II) takes place at this region. Hence the energy increases again to −13.5 kcal/mol at time = 14.5 fs. After the collision, the proton binds completely to H_2O(II) and then the ion−radical pair H_3O^+OH is formed.

The distance between H(I) and O(I) in H_2O(I) (denoted by r_2) is plotted in Figure 5B as a function of time. First, the distance r_2 is rapidly elongated from 0.930 to 1.901 Å at time 0−13 fs, meaning that the O−H bond of H_2O(I) is elongated rapidly along the hydrogen bond after the ionization. After that, the distance r_2 increases gradually to 2.5 Å at 150 fs and then it decreases 1.50 Å at 170 fs, indicating that the OH radical leaves once from H_3O^+, but it returns again to the near H_3O^+(II). The dissociation of the OH radical from H_3O^+ does not occur in the time range 0−200 fs. At time = 230 fs, distance r_2 is suddenly expanded, indicating that the dissociation of the OH radical takes place suddenly at 230 fs.

The distance r_3 is minimized at time = 60, 140, and 200 fs, where r_3 means the intermolecular distance between H atom of H_2O(II) and O atom of H_2O(III). Then, it becomes almost a constant value ($r_3 \approx 1.0$ Å) at time = 220 fs, indicating that

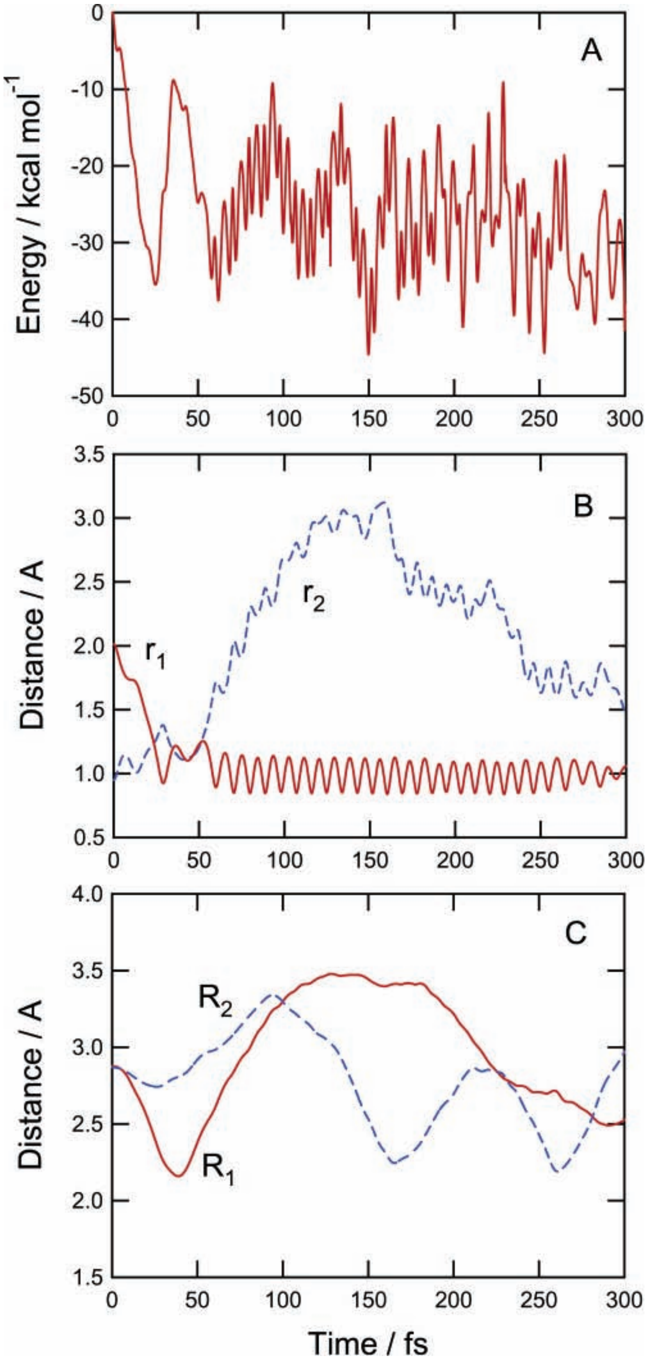

Figure 3. Results of the trajectory for $(H_2O)_3^+$ following the vertical ionization of the water trimer. (A) The energy of the system, (B) bond distances (r_1 and r_2), and (C) intermolecular distances (R_1 and R_2) plotted as a function of reaction time.

the second proton transfers from H_2O(II) to H_2O(III) take place and the O−H bond is newly formed at time = 220 fs.

The intermolecular distances (R_1 and R_2) are plotted in Figure 5C. The oxygen−oxygen distances for H_2O(I) and H_2O(II) (defined by R_1) are 2.836 Å at time zero, which is a normal distance for the hydrogen bond in water system. After the ionization, R_1 decreases gradually, and it takes the minimum at time = 42.2 fs (R_1 = 2.384 Å), indicating that OH(I) collides with H_3O^+(II). At this point, the first proton transfer from H_2O^+(I) to H_2O(II) is already finished (it is completed at time = 13 fs), suggesting that the proton is immediately transferred from H_2O^+(I) to H_2O(II) after the ionization, and then the OH radical approaches gradually to H_3O^+(II). After the collision with the H_3O^+ ion, the OH radical leaves once from near H_3O^+(II) and reaches the distance R_1 = 3.20 Å at time = 120−130 fs. The OH radical approaches H_3O^+(II) again and collides with H_3O^+(II) at time 200 fs. The second proton transfer takes place from H_3O^+(II) to H_2O(III) at time = 200−220 fs. After that, the distance R_1 increases monotonically, meaning that the OH radical is dissociated from the system.

The reaction dynamics for $n = 4$ is clearly explained in terms of the following scheme. When the first proton is transferred from H_2O^+(I) to H_2O(II), the ion−radical pair OH(I)−H_3O^+(II) is formed. The ion−radical pair has a lifetime. If the second proton transfer occurs

$$\mathrm{OH(I)\cdots H_3O^+(II)\cdots H_2O(III)\cdots H_2O(IV) \rightarrow OH(I)\cdots H_2O(II)\cdots H_3O^+(III)\cdots H_2O(IV)} \quad \text{(second proton transfer)}$$

the water molecule H_2O(II) is located in the middle of OH(I) and H_3O^+(III). This change causes the disappearance of the attractive interaction between OH and H_3O^+. Also, the OH radical is weakly bound to $H_3O^+(H_2O)_2$. Hence, the OH radical is spontaneously dissociated from the system. Thus, the OH dissociation is induced strongly by the second proton transfer.

D. Ionization Dynamics of the Water Pentamer and Hexamer (n = 5 and 6). Snapshots of the structural configurations in the ionization of water pentamer (n = 5) are illustrated in Figure 6. The similar dynamics features as n = 4 are obtained in n = 5. The positive charge is localized on H_2O^+(I) at time zero. Immediately, the proton of H_2O^+(I) is transferred to the oxygen atom of H_2O(II), and it collides to H_2O(II) at time = 13 fs. After that, the ion−radical pair, OH(I)−H_3O^+(II)−$(H_2O)_3$, is formed. This process is "the first proton transfer". After 50 fs, the second proton moves against the oxygen atom of H_2O(III) and the ion−radical pair is separated by H_2O(II), as expressed by OH(I)−H_2O(II)−H_3O^+(III)−$(H_2O)_2$. Immediately, the OH radical is dissociated from the system. Thus, the ionization of $(H_2O)_5$ leads to the OH dissociation channel.

The potential energy of the system is plotted in Figure 7. After the ionization of $(H_2O)_5$, the energy is first down to −6.0 kcal/mol within 3 fs due to the internal deformation of H_2O^+, and it decreases further to −46.7 kcal/mol at 12 fs by the first proton transfer from H_2O^+(I) to H_2O(II). The OH dissociation takes place at time = 50 fs. Time profiles of r_2 and R_2 show clearly the OH dissociation from the water cluster. The energy of the system is minimized at this point (time = 13 fs and energy = −44.5 kcal/mol).

For n = 6, the dynamics calculations are preliminarily carried out with the same manner. The results are very similar to those of n = 5. The OH dissociation takes place after the second proton transfer as well as the dynamics of n = 4 and 5.

E. Lifetimes of the Intermediate Complexes. To elucidate the lifetimes of the intermediate complexes, the position of the OH radical is plotted as a function of time, and the results are given in Figure 7. At time zero, the distance of the OH radical (R_1) from H_2O(II) is 2.83 Å. In the ionization of the water tetramer (n = 4), the distance decreases gradually and is bound at time = 45 fs. After two collisions of OH with the $H_3O^+(H_2O)_2$ cluster, the dissociation of the OH radical takes place suddenly at time = 210 fs. This is due to the fact that the second proton transfer is completed at time = 210 fs. Hence, the lifetime of the intermediate is relatively longer. On the other hand, for n = 5 and 6, the OH dissociation occurs at time = 50 fs because the second proton is transferred more immediately than n = 4. In the case of n = 3 and 2, the OH dissociation is not found at the HF/6-311G(d,p) level. Therefore, the long-lived intermediate is alive for n = 2 and 3.

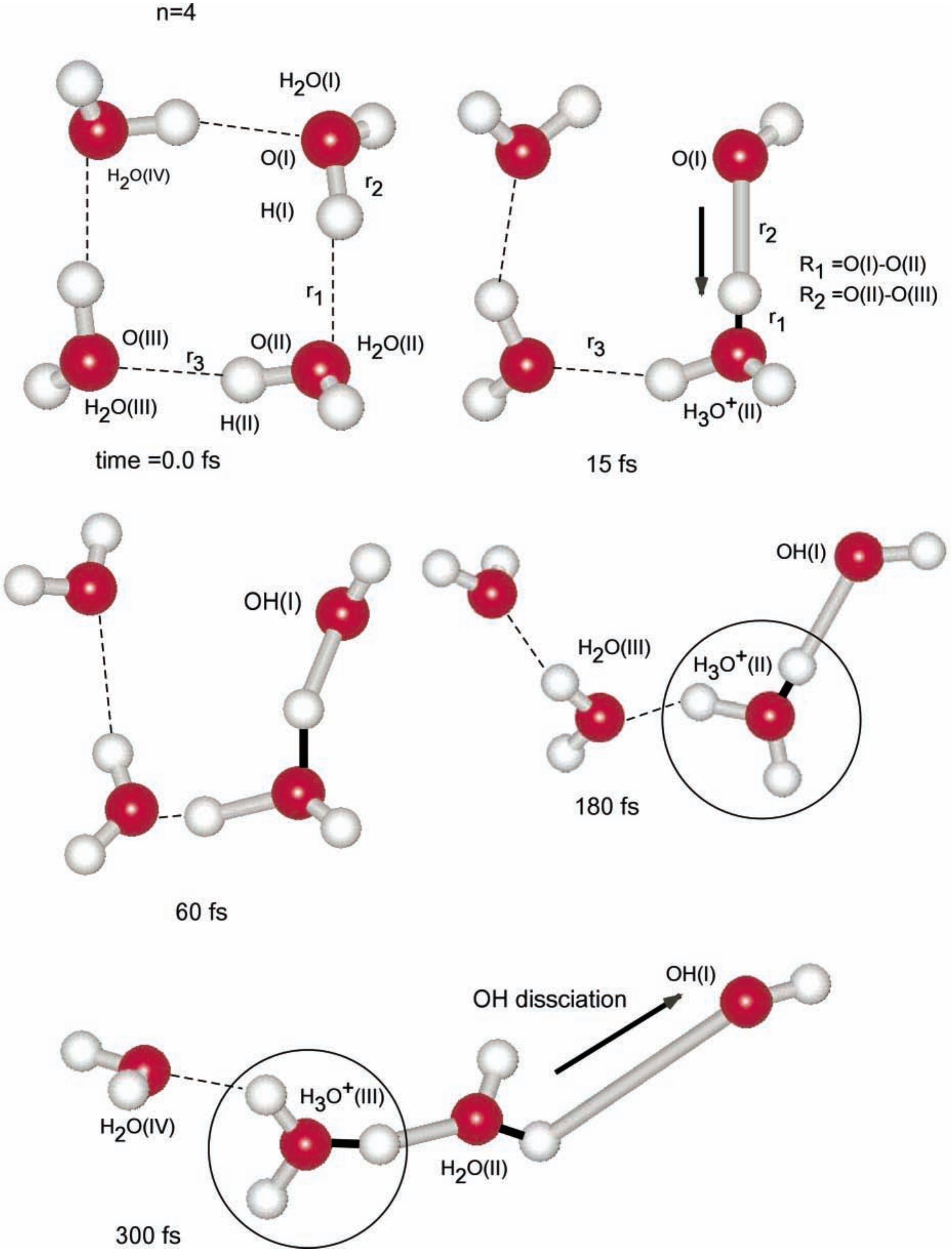

Figure 4. Snapshots for the geometrical configurations of $(H_2O)_4^+$ after vertical ionization of the neutral water tetramer, calculated as a function of time.

4. Discussion

A. Summary. In the present study, the ionization dynamics of water clusters, $(H_2O)_n$ ($n = 3-6$) have been investigated by means of the full-dimensional direct ab initio trajectory method. After the vertical ionization of the neutral water clusters, two reaction channels, complex formation and OH dissociation channels, were found as product channels. In the complex channel, the product is the ion−radical pair expressed by $(H_3O^+)(OH)(H_2O)_{n-2}$, whose the core complex (H_3O^+OH) is solvated by the water molecules. The proton of H_2O^+, formed by the ionization of $(H_2O)_n$, is spontaneously transferred to the neighboring water molecule, and then the ion−radical pair (the H_3O^+−OH complex) is formed as a core complex. After that, the complex is solvated by the other water molecules. The product in OH dissociation channel is expressed by $H_3O^+(H_2O)_{n-2}$

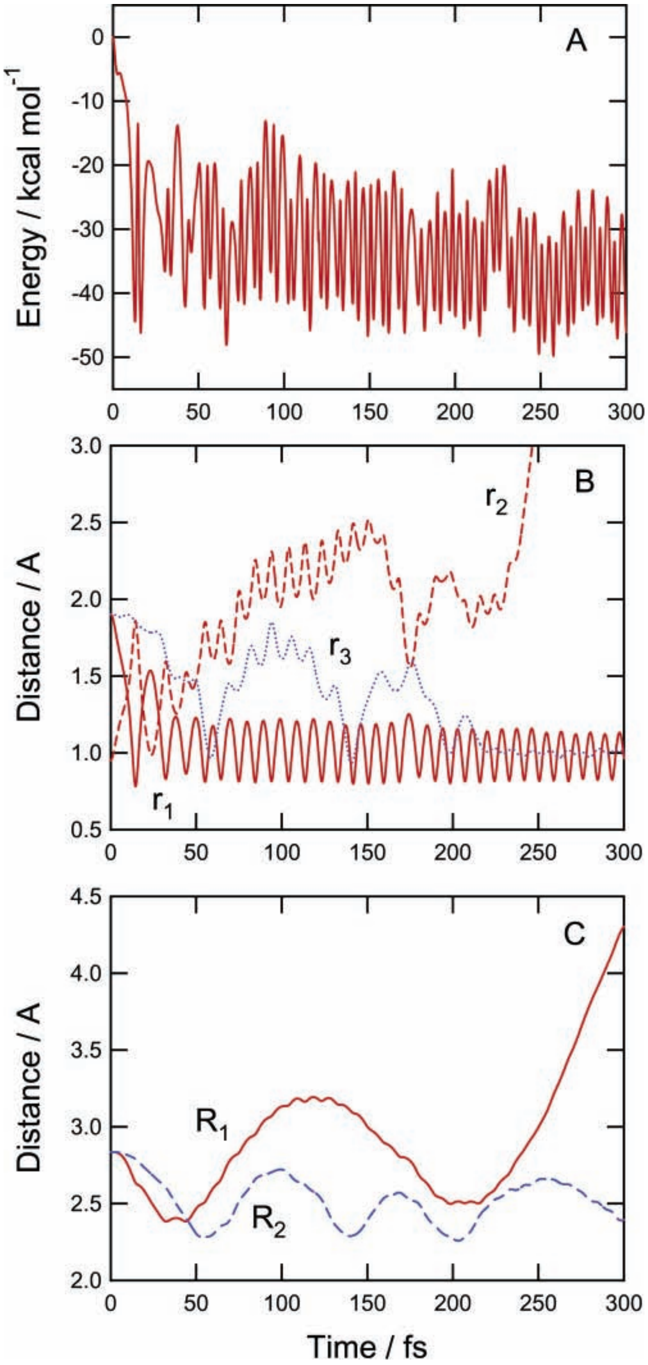

Figure 5. Results of the trajectory for $(H_2O)_4^+$ following the vertical ionization of the water tetramer. (A) The energy of the system, (B) bond distances (r_1, r_2, and r_3), and (C) intermolecular distances (R_1 and R_2) plotted as a function of reaction time.

$+$ OH. The OH radical is dissociated from the system and then hydrated H_3O^+ ion is remained in the water cluster.

As a summary of the present study, the all-product channels, predicted by the present direct ab initio trajectory calculations, are summarized in Table 1. In the case of the water dimer, the product is complex, whereas OH dissociation channel is dominant in larger clusters ($n = 4-6$). For $n = 3$, both complex formation and OH dissociation channels are found, namely, the product is dependent on the level of theory used. This result may imply that $n = 3$ is a boundary region that determines the reaction channels. It should be noted that more detailed calculations would be required to elucidate the reaction dynamics of water trimer.

Next, let us consider the reason the dissociation channel is dominant in the clusters larger than $n > 3$. In the ionization of the water dimer to the ground cationic state ($^2A''$ state), the complex (H_3O^+OH) is only formed and it is not dissociated into $H_3O^+ + OH$. This is due to the fact that the complex is about 1.0 eV more stable in energy than the dissociation limit ($H_3O^+ + OH$), which is large enough to stabilize the complex. Hence, the complex remains as H_3O^+OH. This is due to an attractive interaction between OH and H_3O^+. In the ionization of the tetramer ($n = 4$), the ion−radical pair H_3O^+OH is first formed as well as in the dimer and in the trimer. After several intermolecular vibrations between H_3O^+ and OH, the proton of H_3O^+ is transferred to the neighboring water molecule (the second proton transfer). The water molecule is located in the middle of OH and H_3O^+, meaning that the OH radical is separated by H_2O from H_3O^+ after the second proton transfer. This separation causes the disappearance of affinity between OH and H_3O^+. Hence, the OH radical is easily dissociated from the cluster after the energy transfer from the system to the OH radical. This is the origin of the dissociation channel. From these considerations, it can be concluded that the OH dissociation becomes a bigger favorite in larger water clusters.

B. Reaction Model. On the basis of the present calculations, we propose a reaction model for the ionization of the water clusters. A schematic illustration of this model is given in Figure 9. Ionization occurs within 10^{-15} s, and then a proton of the ionized water molecule H_2O^+ is spontaneously transferred to the neighboring water molecule along the hydrogen bond (first proton transfer). The ion−radical pair H_3O^+OH is formed (time $= 10-20$ fs). After several vibrations of the proton between H_3O^+ and OH, the second proton transfer takes place from H_3O^+ to the next nearest neighboring water molecule along the hydrogen bond. The time scale of the second proton transfer is estimated to be 50−200 fs. After the second proton transfer, one water molecule is located in the middle of OH and H_3O^+, while the OH radical is separated from H_3O^+. Once the second proton transfer takes place, the OH radical accepted to a translational energy is rapidly dissociated from the system. If the second proton transfer does not occur, the complex is remained in the clusters.

C. Comparison with Previous Studies. Ionization processes of small-sized water clusters have been investigated as photoionization efficiency and synchrotron radiation studies.[11−14] From these experiments, it is found that the protonated water molecule $H^+(H_2O)_{n-k}$ is formed by the following reaction

$$[(H_2O)_n{}^+]_{VIP} \rightarrow H^+(H_2O)_{n-k} + (k-1)H_2O + OH$$

where $(k - 1)H_2O$ means water molecules evaporate from the cluster. The unprotonated water cluster $(H_2O^+)_m$ is observed only in the water dimer. This specific feature is considered because Franck−Condon overlaps are probably too small to produce an unprotonated cluster ion $[(H_2O)_m]^+$ ($m > 2$). However, the details of the potential-energy surface (PES) is not clearly understood because the water cluster has multidimensions too large to calculate PES.

The present full-dimensional direct ab initio dynamics calculation strongly indicates that the VIP from the neutral state is largely shifted from the equilibrium point of $[(H_2O)_n]^+$ and the intermediate complex region. Hence, the trajectory passes through the intermediate complex domain quickly, and the reaction leads to the OH dissociation channel. If bath molecules (or atom) coexist around the water cluster, the excess energy

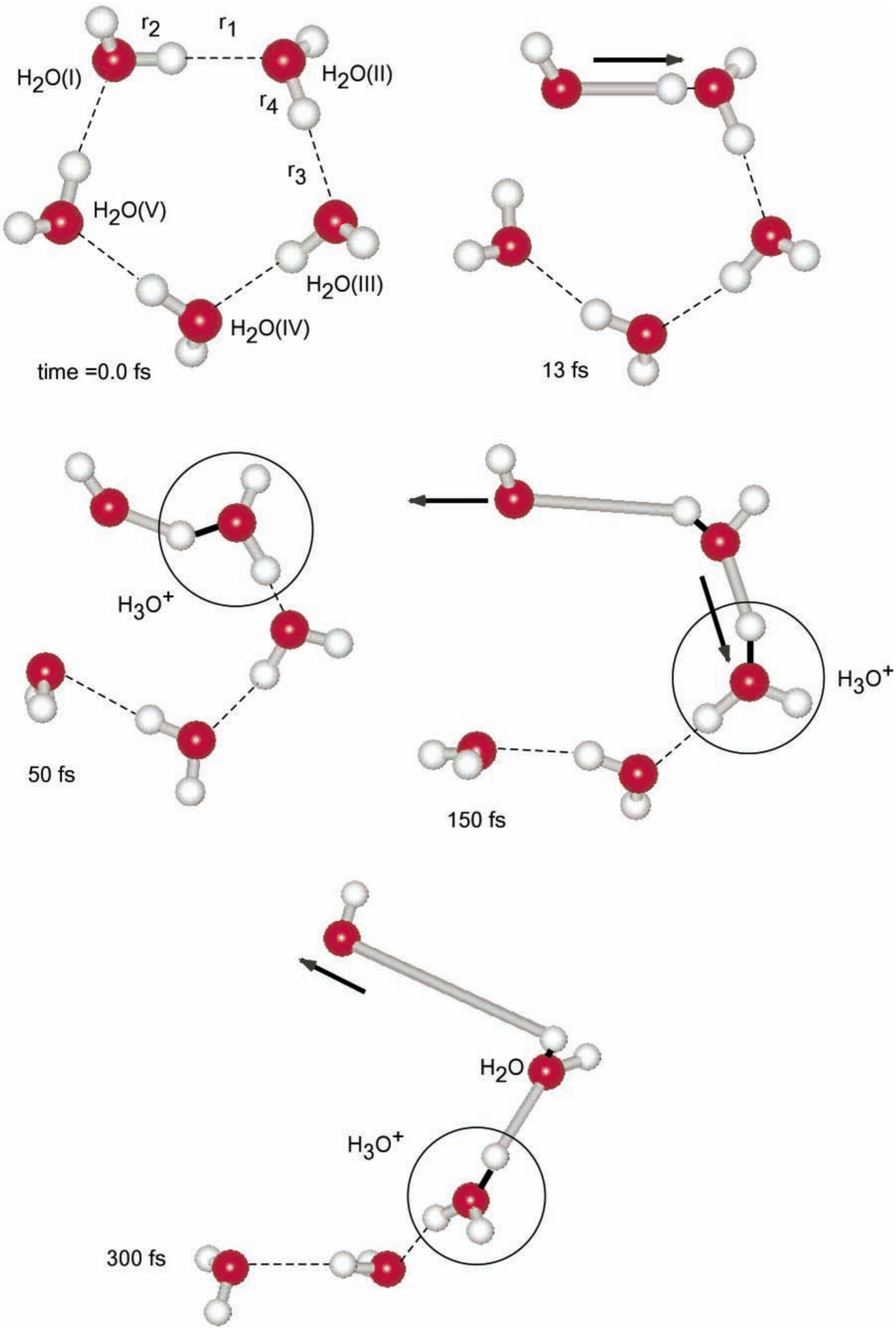

Figure 6. Snapshots for the geometrical configurations of $(H_2O)_5{}^+$ after vertical ionization of the neutral water pentamer, calculated as a function of time.

of $(H_2O)_n{}^+$ formed by the reaction would be absorbed and relaxed. In such a case, the unprotonated water cluster ion would be observed as the product ion.

Shinohara and Nishi[14] and Shiromaru et al.[11−13] found from synchrotron radiation study that unprotonated water cluster ions $[(H_2O)_m]^+$ ($m > 2$) exist if small binary molecular clusters, such

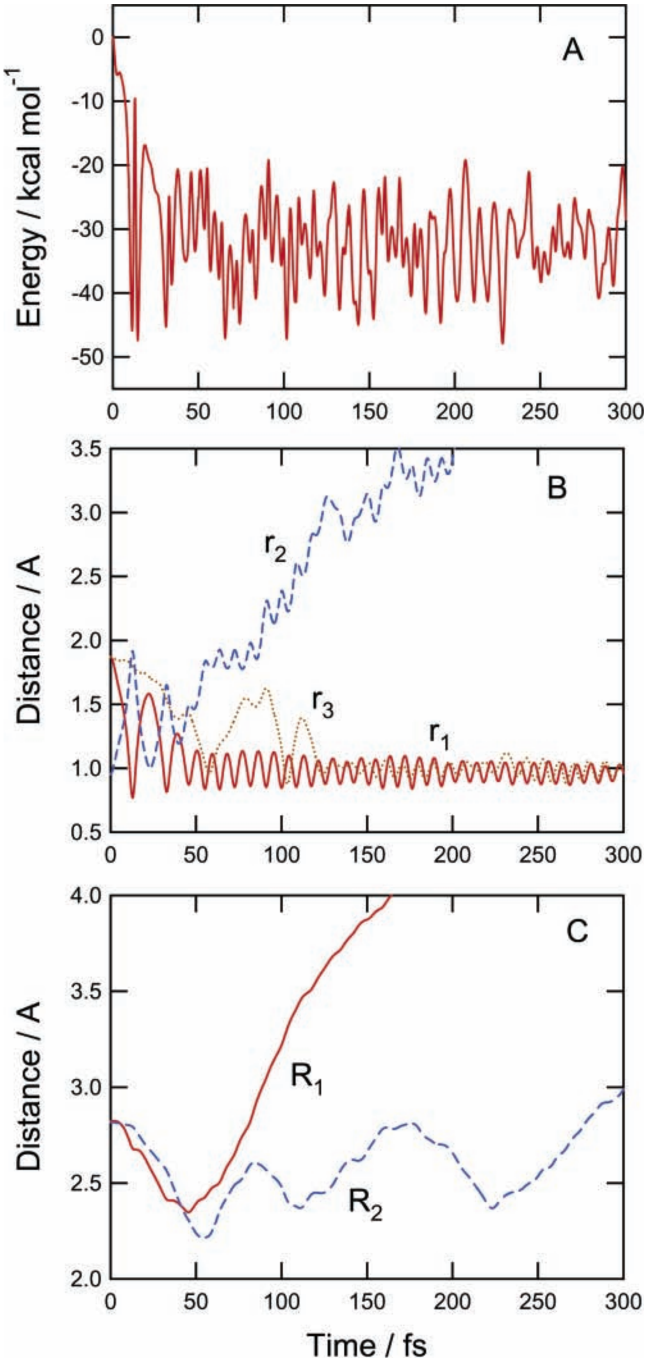

Figure 7. Results of the trajectory for $(H_2O)_5^+$ following the vertical ionization of the water pentamer. (A) The energy of the system, (B) bond distances (r_1, r_2, and r_3), and (C) intermolecular distances (R_1 and R_2) plotted as a function of reaction time.

as H_2O/Ar and H_2O/CO_2 mixtures, are used as the source of the water cluster cation. The second molecules (CO_2 and Ar) in the binary cluster may play as a role of the bath relaxation of the excess energy of $[(H_2O)_m]^+$. These features are in excellent agreement with the present calculations.

As a structure of the water dimer cation, a hydrazinelike structure is proposed on the basis of ab initio calculations.[19] This structure is composed of $(H_2O-OH_2)^+$, where the oxygen atoms bind each other in the cluster and the positive charge is fully delocalized on the complex. In the present dynamics calculations, however, the hydrazinelike structure is not detected. The intermediate in all trajectories has a structure composed of the H_3O^+ ion and the OH radical. The hydrazine-type cation may be formed accidentally by the bimolecular reaction of H_2O^+ with H_2O.

TABLE 1: Summary of the Direct Ab Initio Trajectory Calculations[a]

n	HF/6-31G(d)	HF/6-311G(d,p)
2^b	complex	complex
3	dissociation	complex
4	dissociation	dissociation
5	dissociation	dissociation
6	dissociation	dissociation

[a] Cluster size dependence of the product channels in the ionization of water clusters $(H_2O)_n$ ($n = 2-6$) is shown. [b] From ref 8. If the electronic state of the dimer cation is $^2A''$, all products lead to complex formation. On the other hand, the ionization to the first excited state of dimer cation ($^2A'$ state) gives both complex and OH dissociations.

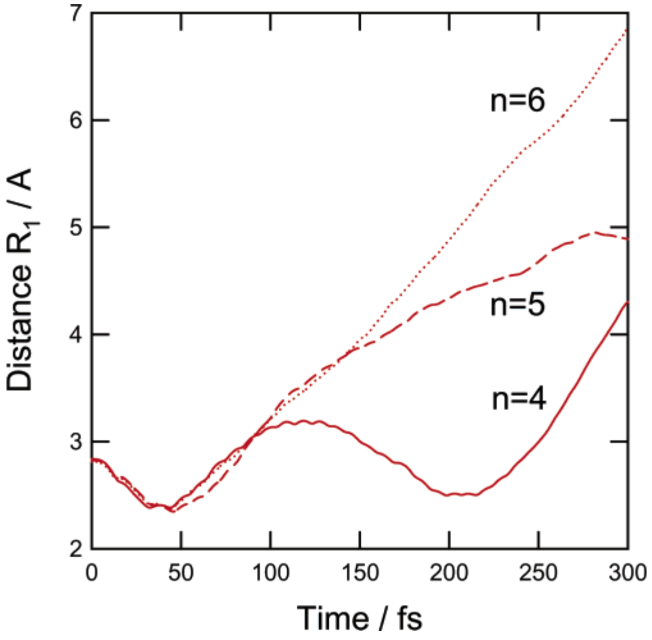

Figure 8. Lifetimes of the intermediate complexes. Time evolutions of intermolecular distances (R_1) for $(H_2O)_n^+$ ($n = 4-6$).

D. Additional Comments. We have introduced several approximations to calculate the PES and to treat the reaction dynamics. First, we assumed that $[(H_2O)_n^+]_{VIP}$ has no excess energy at the initial step of the trajectory calculation (time = 0.0 ps). This may cause a change of lifetime and energy distribution of the products. In the case of higher excess energy, the $[(H_2O)_n^+]_{VIP}$ complexes dissociate more easily into the OH radical and $H_3O^+(H_2O)_{n-2}$. However, this effect was not considered in the present calculations. It should be noted therefore that the present model is limited in the case of no excess energy. Also, we assumed that initial momentum vectors of atoms are zero at time zero. However, this approximation would be adequate to treat the dynamics, because the energy gradients of atoms on the PES of the dimer cation are larger than the momentum vectors of atoms.

Second, we assumed that the electronic state of $(H_2O)_n^+$ keeps itself during the reaction. This means that the electronic transition probability between ground and excited states is assumed to be zero. Therefore, we monitored carefully whether the electronic state is held in the running of the trajectory or not. In the results given in the present paper, all trajectories kept their own electronic state. Therefore, there is no problem for instability of the electronic state during the trajectory.

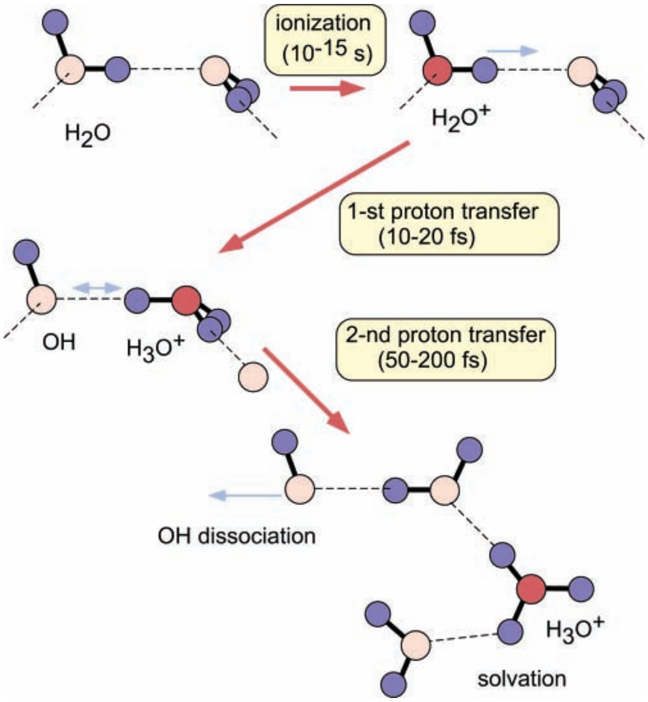

Figure 9. Model of ionization of water clusters constructed on the basis of the present dynamics calculations.

However, complete active space self-consistent field-contracted configuration interaction dynamics may be required in order to obtain more detailed information. The surface hopping, which is completely neglected in the present study, may be important to gain the whole ionization processes of the water cluster. However, these calculations were future work so that we do not make reference any more.

Third, the zero-point vibrational energies (ZPEs) of the clusters are completely neglected in the present dynamics calculations. To estimate this effect on the ionization dynamics, the ZPEs are calculated for $(H_2O)_3$ and $(H_2O)_3{}^+$. The energy difference is calculated to be 1.92 kcal/mol, indicating that the effect of the ZPE would be a secondary matter. However, to obtain detailed feature of the dynamics, the calculation including the ZPE would be required in future work.

Last, we assumed a HF/6-311G(d,p) multidimensional PES in the trajectory calculations throughout. As shown in our previous paper,[8] this level of theory represents reasonably a PES obtained by the MP4SDQ calculation. Also, it is in good agreement with the QCISD calculations.[8] Therefore, the level of theory used in the present calculation would be adequate to discuss qualitatively the ionization dynamics of the water clusters. For example, the binding energies of the complex (H_3O^+OH) relative to the dissociation limit ($H_3O^+ + OH$) are calculated at the HF/6-311G(d,p) level to be -19.0 kcal/mol ($^2A''$ state) and -18.3 kcal/mol ($^2A'$ state). The QCISD/6-311G-(d,p) calculations gave -21.6 ($^2A''$ state) and -19.0 kcal/mol ($^2A'$ state), indicating that the HF calculation would give a shallow trapping energy. This may cause a slight change of a lifetime of the complex. More accurate wave functions may provide deeper insight in the dynamics. Such a calculation will be possible after development of high-speed CPU computer in near future. Despite the many assumptions introduced here, the results enable us to obtain valuable information on the mechanism of the ionization of the small-sized water clusters.

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Supporting Information Available: Selected optimized geometrical parameters of $(H_2O)n$ ($n = 3-6$) at the HF/6-311G-(d,p) and B3LYP/6-311G(d,p) levels of theory, total energies of $(H_2O)n$ ($n = 3-6$) calculated at the HF/6-311G(d,p) and B3LYP/6-311G(d,p) levels of theory, and total energies of $(H_2O)n^+$ ($n = 3-6$) calculated at the HF/6-311G(d,p) and B3LYP/6-311G(d,p) levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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