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Electron hydration dynamics in water clusters: A direct *ab initio* molecular dynamics approach

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Electron attachment dynamics of excess electron in water cluster $(H_2O)_n$ ($n=2$ and 3) have been investigated by means of full-dimensional direct *ab initio* molecular dynamics (MD) method at the MP2/6-311++G(d,p) level. It was found that the hydrogen bond breaking due to the excess electron is an important process in the first stage of electron capture in water trimer. Time scale of electron localization and hydrogen bond breaking were determined by the direct *ab initio* MD simulation. The initial process of hydration in water cluster is clearly visualized in the present study. In $n=3$, an excess electron is first trapped around the cyclic water trimer with a triangular form, where the excess electron is equivalently distributed on the three water molecules at time zero. After 50 fs, the excess electron is concentrated into two water molecules, while the potential energy of the system decreases by -1.5 kcal/mol from the vertical point. After 100 fs, the excess electron is localized in one of the water molecules and the potential energy decreases by -5.3 kcal/mol, but the triangular form still remained. After that, one of the hydrogen bonds in the triangular form is gradually broken by the excess electron, while the structure becomes linear at $100-300$ fs after electron capture. The time scale of hydrogen bond breaking due to the excess electron is calculated to be about 300 fs. Finally, a dipole bound state is formed by the linear form of three water molecules. In the case of $n=2$, the dipole bound anion is formed directly. The mechanism of electron hydration dynamics was discussed on the basis of theoretical results. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2348870]

I. INTRODUCTION

When an excess electron is injected into water, a hydrated electron is formed. Since first discovered in 1962,[1] this fascinating species is of fundamental importance in radiation chemistry and biochemistry. Therefore, the physical and chemical properties of the hydrated electron have been widely investigated from both experimental and theoretical points of view.[2–7] However, it remains unclear how an excess electron is solvated by the water molecule. In particular, the initial process after the electron attachment to water and also time scales of solvation (solvent reorientation) are still unclear. In this report, electron hydration dynamics in water cluster anions following an electron attachment to water clusters have been investigated by means of direct *ab initio* molecular dynamics (MD) method.

In bulk water, the static solvation structure of the hydrated electron was determined by analyzing electron spin echo (ESE) modulation of γ-irradiated $10M$ NaOH solution.[8] From the experiment, it was proposed that an excess electron is solvated equivalently by six water molecules, and the coordination structure for the oxygen of H_2O around the excess electron has a O_h symmetry.

Recently, experimental techniques in gas-phase cluster chemistry have been greatly developed. In particular, the small sized water cluster anion in gas phase has been extensively studied because it is one of the most importance spe-

cies in chemistry.[9–13] Haberland and co-workers[9–11] showed using ion cyclotron resonance (ICR) and mass spectroscopy that the smallest water cluster anion is a water dimer anion $(H_2O)_2^-$. The strong intensities of mass spectra are measured for $n=2$, 6, 7, and 11, while weak intensities are obtained for $n=3$, 4, 5, and 8. For larger clusters, Bragg *et al.* and Paik *et al.* used pump-probe photoelectron spectroscopy to elucidate the dynamics of photoexcited clusters containing 15–50 water molecules and one excess electron.[14,15] The lifetime of the excited state of the water cluster anion was determined. Hammer *et al.* used vibrational predissociation spectroscopy to obtain the information for structures of smaller clusters with four to six water molecules and one excess electron.[16] The vibrational spectra show that the excess electron binds in the vicinity of water molecules.

The structures and energetics for small sized water cluster anions $(H_2O)_n^-$ ($n=2$, 3, 4, 5, and 6) have been calculated by several groups using *ab initio* and density functional theory (DFT) methods.[17–24] Smith *et al.* investigated the water dimer, trimer, and tetramer anions ($n=2$, 3, and 4) using *ab initio* calculation, and the most stable structures were determined.[17,18] Kim *et al.* investigated the hexamer anion ($n=6$) and showed that the prism structure is most favorable in gas phase.[20–24] Structures of the water dimer anion were also investigated by several workers. More recently, Tsurusawa and Iwata suggested from more accurate *ab initio* calculation that the water dimer anion possesses a positive vertical electron detachment energy.[25]
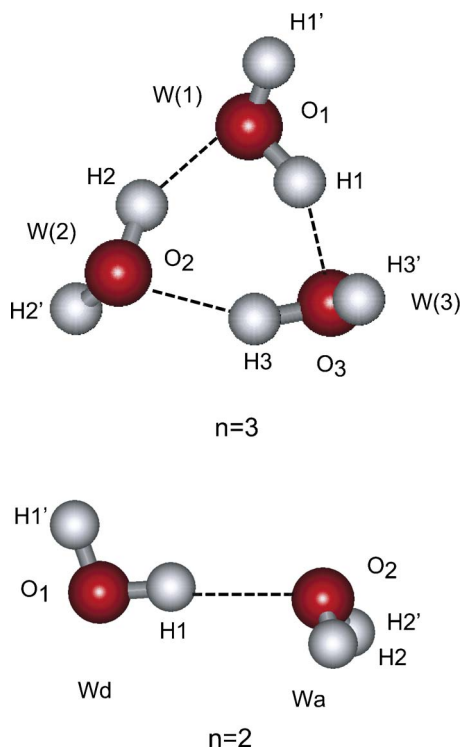
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FIG. 1. (Color online) Structures and geometrical parameters of water trimer ($n=3$) and water dimer ($n=2$).

Although the energetics and structures of the water cluster anions have been, thus, extensively studied from a theoretical point of view, the dynamics of the electron attachment process in water cluster is not clearly understood. In particular, the nature of the electron localization, i.e., time scale of electron localization, and hydrogen bond breaking time are still unclear.

In the present study, direct *ab initio* MD method is applied to the electron attachment processes of water dimer and trimer $(H_2O)_n$ ($n=2$ and 3) in order to elucidate the real time solvation dynamics of excess electron in water clusters. In this paper, we show the results for electron attachment pro-

cesses in a linear form water dimer and in a cyclic water trimer. The main purpose of this study is to elucidate the dynamics of electron localization and solvent reorientation as a function of time, i.e., how the localization of excess electron takes place in the water cluster after electron attachment to the clusters.

II. METHOD OF CALCULATION

Direct *ab initio* MD calculation[26–28] was carried out at the MP2/6-311++G(d,p) level of theory. First, the structures of the neutral water clusters were determined by static *ab initio* calculation. And then, dynamics calculations were carried out on the assumption of vertical electron attachment to the neutral water clusters.

The equations of motion for N atoms in the reaction system are given by

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

$$\frac{\partial P_j}{\partial t} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j}, \tag{1}$$

where $j=1-3N$, H is the classical Hamiltonian, Q_j is the Cartesian coordinate of the jth mode, and P_j is the conjugated momentum. U is the potential energy of the reaction system. These equations were numerically solved by the Runge-Kutta method. No symmetry restriction was applied to the calculation of the energy gradients. The time step size was chosen to be 0.10 fs, and a total of 5000 steps were calculated for each dynamics calculation. The drift of the total energy is confirmed to be less than $1 \times 10^{-3}\%$ throughout at all steps in the trajectory. The trajectory calculations of $(H_2O)_n^-$ were performed under constant total energy condition. The velocities of atoms at the starting point were assumed to be zero (i.e., momentum vector of each atom is zero). We checked that the values of $\langle S^2 \rangle$ and the basis set
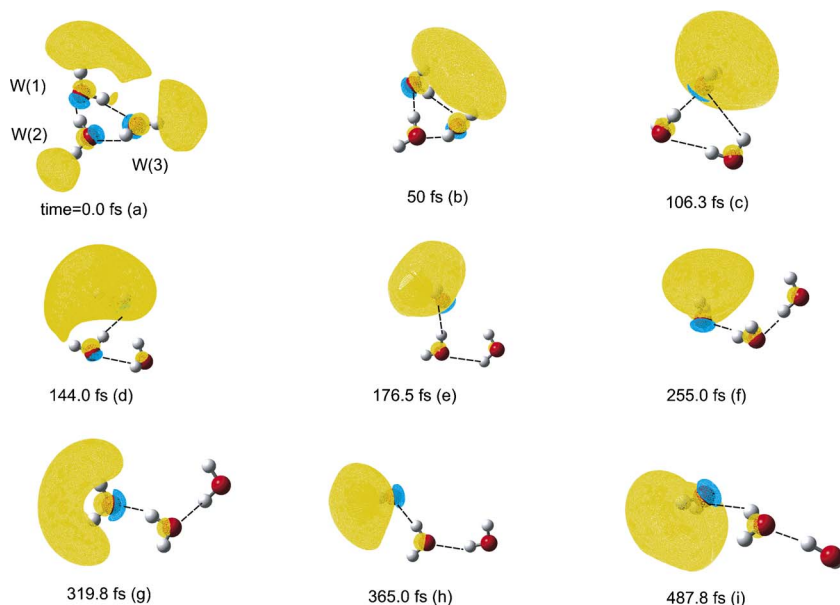

FIG. 2. (Color online) Snapshots of water trimer anion after an electron attachment to neutral water trimer, obtained by direct *ab initio* MD calculation. The trajectory was started from the optimized geometry of neutral water trimer. The calculation was carried out by MP2/6-311++G(d,p) level. Isosurface indicates the spin density around water trimer.

superposition error were less than 0.765 and 0.54 kcal/mol at all points, respectively.

Next, a total of 30 geometrical configurations were randomly generated around the optimized structure. From the 30 geometrical configurations, ten configurations were selected so that the energy differences from the optimized structure are less than 0.12 kcal/mol. And then, ten trajectories on the potential energy surface (PES) of $(H_2O)_n^-$ were run from the vertical points. The excited state of the present system is 2.0 eV higher in energy than that of the ground state, so that we considered only the ground state PES of $(H_2O)_n^-$.

Static *ab initio* calculations were performed using the GAUSSIAN 03 program package[29] using the 6-311++G(d,p) basis set in order to obtain more accurate energetics. For comparison, MP4SDQ and QCISD calculations were also carried out for the molecules at the stationary points. The structures and geometrical parameters of the water trimer and dimer are illustrated in Fig. 1.

III. RESULTS

A. Electron attachment to water trimer

The snapshots of structure and spin densities of the water trimer anion after the electron capture are illustrated in Fig. 2. Isosurface depicts the spin density on the water trimer anion. When an excess electron is injected into the neutral water trimer, the electron is almost equivalently distributed around three water molecules (point *a*). Since the environment of the water molecules differs slightly from each other, the spin densities on the water molecules are somewhat different from each other. The spin densities on the water molecules $W(1)$, $W(2)$, and $W(3)$ are calculated to be 0.373, 0.293, and 0.335, respectively, at time zero. The distances between water molecules are 2.7917, 2.7960, and 2.8037 Å for oxygen-oxygen atoms, and angles are close to 60°. At time=50 fs (point *b*), the structure of the water trimer anion is still a triangle: the angles θ_1, θ_2, and θ_3 are calculated to be 60.6°, 60.8°, and 58.6°, respectively. Only a hydrogen atom of $W(3)$ reorients to $W(1)$ due to an internal rotation of $W(3)$. This reorientation causes an electron localization on $W(1)$ and $W(2)$, namely, the excess electron is concentrated on two water molecules at 50 fs.

At 106.3 fs (point *c*), the excess electron is fully localized on one water molecule $W(1)$, while a dipole of $W(1)$ orients toward the excess electron. The structure of the water trimer anion is slightly deformed from the triangle form by thermal activation due to excess energy, but the triangle form and the hydrogen bond still remained. The energy is minimized at this point. By the internal rotations of water molecules in the cluster, the end of the hydrogen bond is located in $W(1)$. The spin densities on $W(1)$, $W(2)$, and $W(3)$ are 1.081, −0.119, and 0.038, respectively, indicating that the excess electron is trapped on one water molecule $W(1)$. After the electron localization, the hydrogen bond between $W(1)$ and $W(3)$ is gradually broken, while the triangle form is varied to a linear form (for example, the structure at time =319.8 fs).

Potential energy of the system is plotted as a function of time in Fig. 3. Zero level corresponds to the energy at the
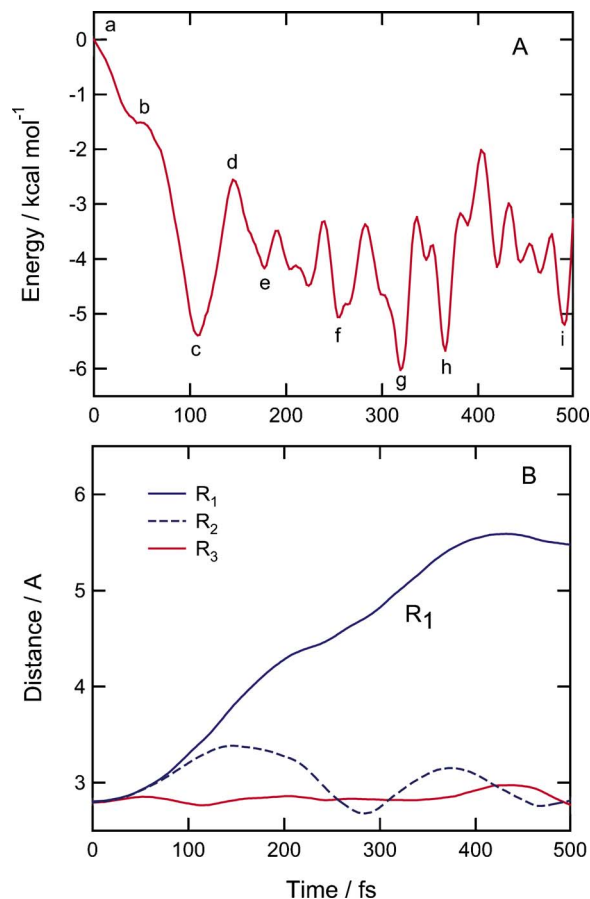

FIG. 3. (Color online) (A) Potential energy and (B) intermolecular distances of the water trimer anion after an electron attachment to neutral water trimer, obtained by direct *ab initio* MD calculation. The corresponding snapshots are illustrated in Fig. 2.

vertical transition point in electron attachment to neutral water trimer (point *a*). After the electron attachment, the energy of the water trimer anion decreases gradually due to the structural relaxation (solvent reorientation). The potential energy curve (PEC) shows a shoulder at 50 fs (point *b*), where the excess electron is concentrated on two water molecules, $W(1)$ and $W(2)$. The energy becomes lower by −5.3 kcal/mol at 106.3 fs (point *c*). At this point, the excess electron is fully localized on one water molecule $W(1)$. However, the triangle form composed of three water molecules is still retained at this time. After that, the energy rebounds up to −2.7 kcal/mol at 144 fs (point *d*), and then it vibrates around −4.0 kcal/mol (points *e* and *f*). The time period of the vibration is significantly long (~40 fs). The triangle form is gradually deformed during the vibration. This deformation is due to the fact that the hydrogen bond between $W(1)$ and $W(3)$ is broken, whereas the hydrogen bonds for $W(1)-W(2)$ and $W(2)-W(3)$ still remained. At 319.8 fs (point *g*), the triangle form becomes a linear form composed of three water molecules. The energy of the system is lowest at this point.

B. Spin densities on water molecules

Spin densities summarized into the water molecules are plotted in Fig. 4 as a function of time. At time zero (point *a*), the densities on $W(1)$, $W(2)$, and $W(3)$ are calculated to be
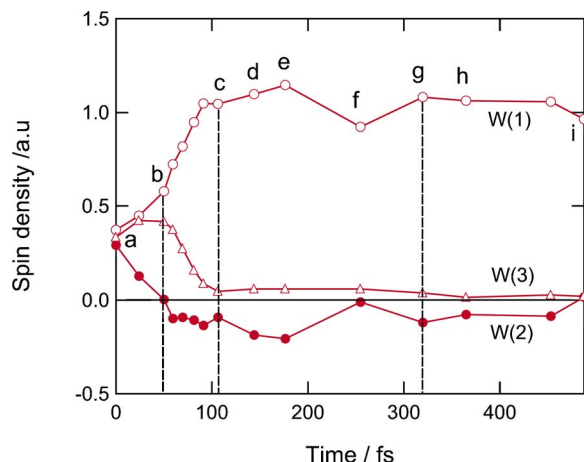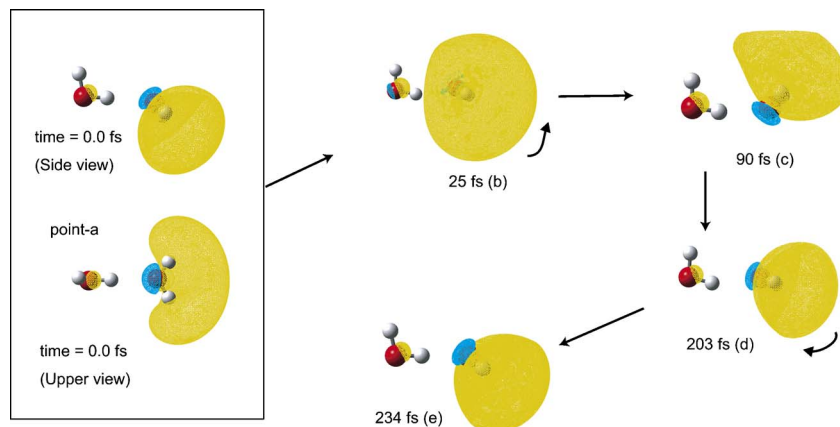
FIG. 4. (Color online) Spin densities summarized into the water molecules plotted as a function of time. The calculation is carried out at the MP2/6-311++G(d,p) level.
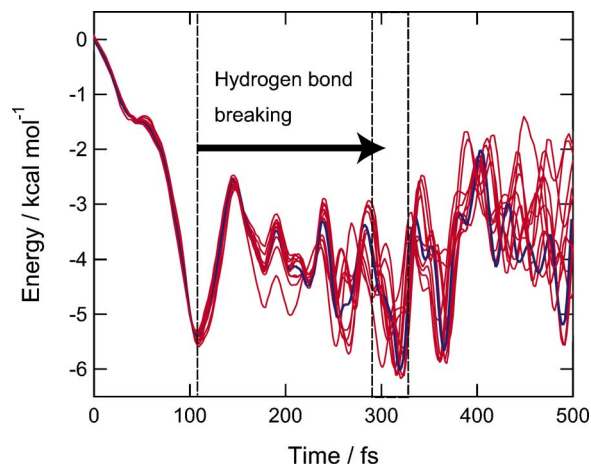

FIG. 5. (Color online) Effects of initial conditions on the dynamics of water trimer. Potential energies of water trimer anion after an electron attachment to neutral water trimer, obtained by direct *ab initio* MD calculation. Ten trajectories are run from selected points generated randomly around the optimized structure. The arrow indicates time period of hydrogen breaking time.

0.373, 0.293, and 0.335, respectively, indicating that the excess electron is equivalently distributed around three water molecules. The electron is concentrated on two water molecules, $W(1)$ and $W(3)$, at 50 fs (point b). The spin densities on $W(1)$, $W(2)$, and $W(3)$ are 0.579, 0.003, and 0.418, respectively. At 106.3 fs (point c), the excess electron is fully localized on only one water molecule, $W(1)$ (spin density is 1.045). After that, the hydrogen bond breaking takes place, but the spin density on $W(1)$ is still close to 1.0. At 319.8 fs (point g), the spin densities on $W(2)$ and $W(3)$ are negative and almost zero, respectively, and positive ($\sim +1.0$) on $W(1)$. At this point, the dipole bound state is formed on the water trimer anion.

C. Effects of initial structures of the water trimer on the dynamics

In actual system, the structure of the water trimer is fluctuated around the equilibrium structure. To include the effects, geometrical configurations are randomly generated around the optimized structure of the water trimer, and then ten dynamics calculations are run from the selected points. The geometries are selected so that the energy differences from that of the optimized geometry are lower than 0.12 kcal/mol.

The results of direct *ab initio* MD calculations from the

ten geometrical configurations are given in Fig. 5 together with that of the optimized geometry. All trajectories pass along the same route up to 100 fs. From this region (100 fs), routes of the trajectories are slightly different from each other. In the region around 300 fs formation of a linear form dipole bound state of the water trimer anion after the deformation of the triangle form occurs. It is found that the hydrogen bond breaking time is distributed in the range of 290–330 fs, but almost all trajectories show the breaking time of about 300 fs.

D. Electron capture dynamics in the water dimer

For comparison, the electron attachment process to the water dimer is also investigated in the same manner. The electron attachment to the water dimer at the optimized geometry is calculated. Figure 6 shows snapshots for structural conformations of $(H_2O)_2^-$ and spin densities of the excess electron in the water dimer anion. Notations of Wd and Wa mean the water molecules as proton donor and acceptor, respectively. At time zero (point a), the excess electron is localized in the direction of the dipole moment of Wa, and also it is distributed around the hydrogen atoms of Wa, meaning

FIG. 6. (Color online) Snapshots of water dimer anion after an electron attachment to neutral water dimer, obtained by direct *ab initio* MD calculation. The trajectory was started from the optimized geometry of neutral water trimer. The calculation was carried out by MP2/6-311++G(d,p) level. Isosurface indicates the spin density around water trimer.
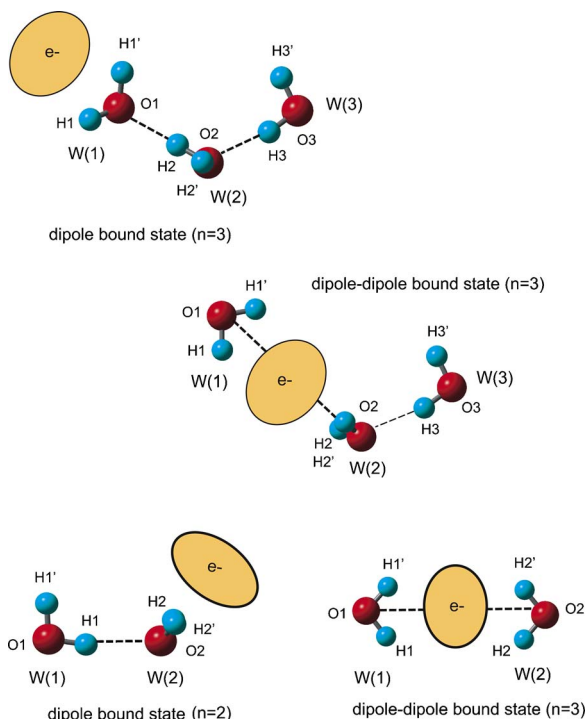
FIG. 7. (Color online) Optimized structures of neutral water trimer and water dimer anion (dipole bound state and dipole-dipole bound state) calculated at the QCISD/6-311++G(d,p) level.

that the excess electron is trapped as a dipole bound state. At 90 fs (point c), Wa has a bent structure where H–O–H plane turns to the upper part. After that, the vibration of the bending mode of Wa continuously takes place.

The energies of the system and the intermolecular distance R_{OO} are monitored as a function of time. After the

TABLE I. Optimized geometrical parameters of water trimer and water trimer anions. Basis set is 6-311++G(d,p). Bond lengths and angles are in Å and in degrees, respectively.

	Parameter	MP2	QCISD
Neutral	$r(O1-O2)$	2.7917	2.8253
	$r(O2-O3)$	2.7960	2.8207
	$r(O3-O1)$	2.8037	2.8320
	$\angle O1-O2-O3$	60.2	60.2
	$\angle O2-O3-O1$	59.8	60.0
	$\angle O3-O1-O2$	60.0	59.8
Dipole bound state	$r(O1-O2)$	2.7777	2.8112
	$r(O2-O3)$	2.8285	2.8594
	$r(O1-O3)$	4.6524	4.6721
	$\angle O1-O2-O3$	112.2	111.0
	$\angle H1-O1-H1$	101.3	101.6
	$\angle H2-O2-H2'$	101.2	101.4
	$\angle H3-O3-H3'$	101.3	101.6
Dipole-dipole bound state	$r(O1-O2)$	5.0943	5.1460
	$r(O1-O3)$	2.8702	2.8994
	$r(O1-O3)$	6.7413	6.7213
	$\angle O1-O2-O3$	112.6	110.1
	$\angle H1-O1-H1'$	100.2	100.5
	$\angle H2-O2-H2'$	100.4	100.8
	$\angle H3-O3-H3'$	101.0	101.3

TABLE II. Relative energies (in kcal/mol) and total energies (in a.u.) of neutral and anion states of water trimer. Basis set is 6-311++G(d,p).

	MP2	MP4SDQ	QCISD
	Relative energy		
$[(H_2O)_3^-]_{ver}$[a]	0.0	0.0	0.0
Dipole bound	−7.7	−7.7	−7.5
Dipole-dipole bound	−6.7	−7.0	−6.8
	Total energy		
Neutral	−228.853 103 1	−228.871 005 8	−228.871 955 6
$[(H_2O)_3^-]_{ver}$[a]	−228.819 961 4	−228.831 031	−228.839 296 8
Dipole bound	−228.832 157 4	−228.850 044 9	−228.851 291 7
Dipole-dipole bound	−228.830 565 7	−228.849 018 7	−228.850 202 3

[a]Water trimer anion with the optimized structures at neutral state.

electron attachment to the water dimer, the energy of the system suddenly decreases to −1.15 kcal/mol because the structural relaxation of each water molecule occurs in the initial step. The intermolecular distance is shortened from 3.0 to 2.85 Å. After that, both water molecules rotated each other, and the R_{OO} distance is elongated as a function of time (3.0 Å at 60 fs, and 5.35 Å at 210 fs). This feature is the nature of the electron trapping in the water dimer. A total of ten trajectory calculations are carried out from the selected points, but all calculations give similar dynamics feature, namely, the dipole bound state is obtained as a product.

E. Structures and energetics of the present systems

In order to check the reliability of the level of theory used in the dynamics calculation, more accurate static *ab initio* calculations are carried out for stationary points for $n=3$. The present direct *ab initio* MD calculation at the MP2/6-311++G(d,p) level gave the dipole bound state as a product of electron capture. In addition to the dipole bound state, we found a new structure for the water trimer anion (denoted by dipole-dipole bound state).

The optimized structures and geometrical parameters of the neutral water trimer and water trimer anions are given in Fig. 7 and Table I. The calculations are carried out at the MP2, MP4SDQ, and QCISD levels of theory with a 6-311++G(d,p) basis set. All calculations give similar structures. The neutral water trimer has a triangle form with an oxygen-oxygen distance $r(O-O)=2.80$ Å. The dipole bound state is composed of a linear hydrogen bond between water molecules. The electron is trapped in the end of the hydrogen bonding network. In the dipole-dipole bound state, the electron is trapped in the dipole field made by both water dimer $W(1)-W(2)$ and monomer $W(3)$. The electron is located in the middle of $W(1)$ and $W(3)$. As clearly shown in Table I, the MP2 calculations give reasonable structures for the water trimer anions.

The relative energies are calculated at several levels of theory and the results are given in Table II. The dipole bound state and dipole-dipole bound state are 7.7 and 6.7 kcal/mol lower in energy than that of vertical electron attachment point $[(H_2O)_3^-]_{ver}$ at the MP2/6-311++G(d,p) level. The MP4SDQ and QCISD calculations give significantly similar energies for the present system.

TABLE III. Harmonic vibrational frequencies for neutral water trimer and water trimer anions (dipole bound state and dipole-dipole bound state). Basis set is 6-311++G(d,p).

	Frequency (cm^{-1})					
			Neutral			
QCISD	3970	3968	3965	3800	3795	3754
	1699	1680	1676	797	668	533
	423	338	328	255	212	204
	183	177	170			
MP2	3965	3964	3961	3747	3739	3688
	1679	1659	1654	829	699	560
	443	359	347	266	219	215
	199	185	177			
			Dipole bound state			
QCISD	3930	3887	3728	3696	3669	3606
	1752	1730	1631	832	752	467
	392	339	295	241	230	178
	171	72	40			
MP2	3939	3889	3665	3656	3624	3513
	1733	1708	1602	870	783	484
	407	348	305	251	240	184
	168	68	42			
			Dipole-dipole bound state			
QCISD	3920(a')	3864(a')	3798(a'')	3798(a')	3764(a')	3726(a')
	1733(a')	1686(a')	1671(a')	724(a'')	456(a')	326(a')
	323(a'')	269(a'')	189(a'')	187(a')	138(a')	108(a'')
	51(a')	26(a'')	26(a')			
MP2	3928(a')	3854(a')	3779(a'')	3776(a')	3725(a')	3677(a')
	1711(a')	1661(a')	1645(a')	751(a'')	459(a')	335(a')
	324(a'')	277(a'')	194(a')	182(a'')	139(a')	105(a'')
	52(a')	24(a')	13(a'')			

To elucidate the potential energy surface for the neutral water trimer and its anion, harmonic vibrational frequencies for all stationary points are calculated and the results are given in Table III. All vibrational frequencies give positive values, indicating that the structures are located in local minima. Comparing the MP2 result with that of the QCISD calculation, it is found that the MP2 calculations give reasonable vibrational frequencies for all species.

The optimized structures of the water dimer anions are given in Fig. 7. As well as the water trimer anion, both dipole bound and dipole-dipole bound states are found as stable structures of the water dimer anion. Both forms have no imaginary frequency. The energy difference between both forms are calculated to be 0.29 (MP2), 0.01 (MP4SDQ), and 0.13 kcal/mol (QCISD), indicating that the dipole bound state is slightly more stable in energy than the dipole-dipole bound anion.

IV. DISCUSSION

A. Summary and a proposed model for electron capture in the water trimer

Although the static structures of hydrated electron have been almost understood previously, the initial process and solvation dynamics for the electron capture in water cluster have been still unclear because the process is too fast to observe experimentally. In the present study, the hydration dynamics in small sized water clusters was clearly visualized by means of *ab initio* MD calculation.

Model of the electron capture dynamics in the water trimer is schematically illustrated in Fig. 8. It is noted that dangling hydrogen atoms of $W(1)$, $W(2)$, and $W(3)$ are located in up, down, and up positions from the molecular plane at time zero, respectively. When an excess electron is injected into the water trimer, the electron is distributed equivalently around three water molecules. During the internal rotation of one of the water molecule (time=10–50 fs), $W(3)$, the electron is concentrated on two water molecules at 50 fs. The internal rotations of $W(1)$ and $W(2)$ further occur within 50–100 fs, and then the excess electron is localized on one water molecule $W(1)$ at 100 fs. The triangle form is still retained in this electron localization because the electron localization is caused by the internal rotation of water molecules. After the electron localization, the hydrogen bond is gradually broken. Time scale of hydrogen bond breaking is estimated to be 200 fs. After 300 fs in the electron attachment, the dipole bound state composed of three water molecules is completed.

It is known that formations of water trimer anion and tetramer anion are low efficiency in direct electron attachment to the neutral cluster because of small dipole moments
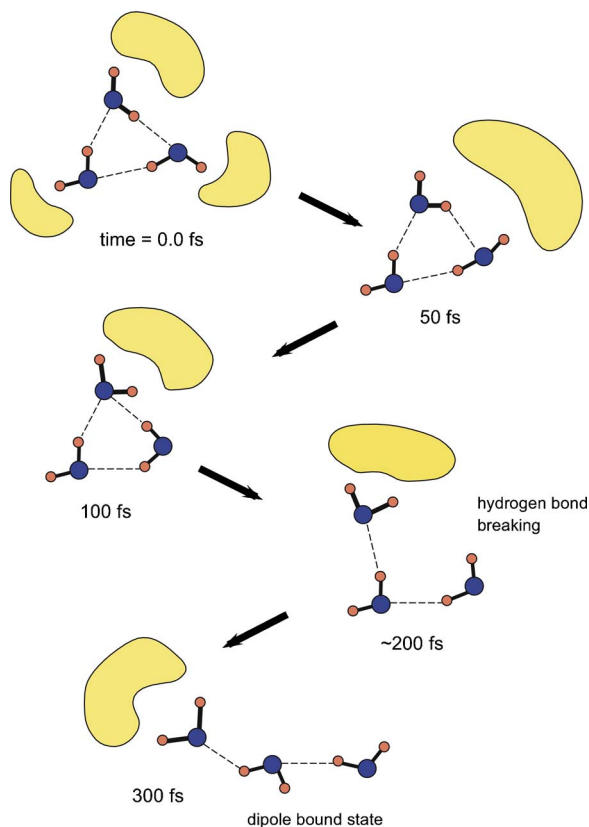
FIG. 8. (Color online) A schematic illustration for a model of an electron attachment process to neutral water trimer.

of neutral systems ($n=3$ and 4). In addition to small dipole moments, the present calculation showed the problem of structural changes. The present calculations show that structural change before and after the electron attachment is large in the water trimer, whereas it is significantly small in the water dimer. This means that the equilibrium point of the water trimer anion is largely shifted from the Franck-Condon (FC) region for electron attachment in water trimer. On the other hand, the FC region in the water dimer is significantly close to the structure of water dimer anion. These results strongly suggest that the efficiency of yield of the water dimer anion is larger than that of the water trimer. This feature is in good agreement with the experiments and previous static DFT calculations by Kim.[23]

B. Comparison with previous studies

In a previous paper,[26] we showed the preliminary result for an electron attachment dynamics in water dimer using the Hartree-Fock (HF) method with a small basis set. After the electron attachment, the dipole bound state is formed. Also, some trajectories give the dipole-dipole bound state structure. The present MP2 dynamics calculation for $n=2$ gives only dipole bound state as a product channel in direct electron attachment to water dimer. This result is slightly different from that of previous calculation. The difference may be caused by the underestimation of the activation barrier from dipole bound state to dipole-dipole bound state in the previous work.

Recently, Hammer $et\ al.$ have observed sharp vibrational bands of small water cluster anion $(H_2O)_n^-$ ($n=4-6$).[16] They generated the water cluster anion by the reaction of $(H_2O)_2^-$ with a neutral water dimer:

$$(H_2O)_2^-(Ar)_n + (H_2O)_2 \rightarrow (H_2O)_4^-(Ar)_m + (n-m)Ar.$$
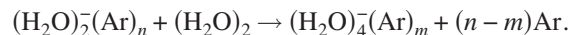
This technique gives a large efficiency for the formation of tetramer anion because water dimer anion is efficiently formed by electron attachment to neutral water dimer. In the present study, we considered only the direct electron attachment to water trimer: $e^- + (H_2O)_3 \rightarrow (H_2O)_3^-$. As the other pathway, it may be possible that the reaction of a water dimer anion with a neutral water molecule

$$(H_2O)_2^-(Ar)_n + H_2O \rightarrow (H_2O)_3^-(Ar)_m$$
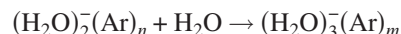
takes place in the case of larger water clusters. Such calculations for a bimolecular reaction is now in progress.

C. Remarks

In the present calculations, several approximations were introduced. First, the excess energy of the system at vertical electron attachment point $[e^-(H_2O)_n]_{ver}$ was assumed to be zero and zero-point energy was neglected. These approximations may cause a slight change of the dynamics feature. In particular, if $[e^-(H_2O)_3]_{ver}$ has an excess energy, the dipole bound state of the water trimer anion may be changed to the dipole-dipole bound state. Next, we used MP2/6-311++G(d,p) level for the $ab\ initio$ MD calculations throughout. Potential energy surface calculated by this method is in good agreement with that of QCISD calculation. However, more accurate wave function would be necessary to obtain deeper insight for the dynamics. Also, inclusion of zero-point energy (ZPE) may give a slight change of the branching ratios of the products. Despite the several assumptions introduced here, the results enable us to obtain valuable information on the mechanism of the electron hydration in small sized water clusters.

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