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Theoretical Studies of the Aluminum–Water Clusters $Al(H_2O)_n$ and Their Ions $[Al(H_2O)_n]^+$

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With the *ab initio* molecular orbital calculations, the structures of the neutral clusters $Al(H_2O)_n$ were optimized, and the vertical ionization energy was evaluated. Two types of the stable clusters are found; the one has a structure $[Al(H_2O)](H_2O)_{n-1}$ and the other has $[Al(H_2O)_2](H_2O)_{n-2}$. The former type of the clusters, in which only one water molecule is directly bonded, is more stable than the latter. The calculated ionization energy with the multi-reference configuration interaction is in very good agreement with the experimental energy determined recently by Fuke's group, only for the series of the former type of clusters. The structures of the $[Al(H_2O)_n]^+$ were determined, and the incremental stability energy was evaluated. A very stable ring structure is found in $[Al(H_2O)_4]^+$. The ring structure persists in $[Al(H_2O)_5]^+$, but only substantial deformation. The extremely stable structure of $[Al(H_2O)_4]^+$ explains the observed product distribution of the photo-dissociation recently reported by Fuke's group.

In recent years, the clusters of a metal atom and its ion with water molecules have been studied extensively both experimentally and theoretically. In particular, the detailed studies of clusters of the group 1 and 2 metal atom with water molecules have been reported by Hertel's group and by Fuke's group.[1—5] Very recently Fuke's group extended the study to the group 3 element, aluminum.[6] From the theoretical side, there are numerous *ab initio* molecular orbital studies reported on the group 1, 2, and 3 metal clusters with water molecules. The works of Bauschlicher and his coworkers are most extensive.[7—12] Recently Hashimoto, He, and Morokuma studied the structures of $Na(H_2O)_n$ and $Na(NH_3)_n$,[13] and found that a strong hydrogen bonding network of water molecules determines the structure of the sodium–water clusters. The similar finding is reported by Barnett and Landman with the density functional theory.[14] We also systematically studied on the interaction of a beryllium atom and its ions Be^+ and Be^{2+} with water molecules.[15—17]

In the present study, the structures of the neutral hydrated aluminum clusters ($Al(H_2O)_n$; $n=1$ to 4) and cationic hydrated aluminum clusters ($[Al(H_2O)_n]^+$; $n=1$ to 5) are determined with the *ab initio* molecular orbital method. In particular, the structures of the second hydration are examined. The hydration energy and its dependence on the cluster size n are also evaluated. The ionization energies of hydrated aluminum clusters are evaluated and compared to the experimental result.

1. Method

The structures of the neutral and cation aluminum–water clusters ($Al(H_2O)_n$ $n=1$, 2, 3, 4 and $[Al(H_2O)_n]^+$ $n=1$, 2, 3, 4, 5) are optimized with the unrestricted self-consistent-field (UHF), and closed shell restricted self-consistent-field (RHF) methods, respectively. To confirm the true stability, the harmonic frequencies at the optimized structures are evaluated. For $n=1$ and $n=2$ of neutral clusters, and $n=1$, $n=2$, and $n=3$ of cation clusters, the structures are re-optimized with the second order Møller–Plesset (MP2) method to examine the effect of the electron correlation on the Al–O distance. At the optimized structures, the full fourth order MP (MP4SDTQ) energy is evaluated. The basis set used in the optimization is 6-31G.

The program used in GAUSSIAN88[18] registered at the computer center of Institute for Molecular Science (IMS). The computations were carried out on S820 at IMS.

At the optimized structures, the configuration interaction (CI) calculations are carried out to evaluate the vertical ionization energies. The basis sets used in the CI study are [43111/411/1] for Al, [521/41] for O, [61] for H. The active orbitals for the multi-reference CI calculations are four molecular orbitals of $3s_{Al}$ and $3p_{Al}$ nature of an aluminum atom. The vacant $3p_{Al}$ orbitals are determined by the VAL-VAC method of Iwata.[19] The reference configuration state functions (CSF) are all of the configurations of $[3s_{Al}, 3p^x_{Al}, 3p^y_{Al}, 3p^z_{Al}]^3$ for the neutral clusters and $[3s_{Al}, 3p^x_{Al}, 3p^y_{Al}, 3p^z_{Al}]^2$ for the cation clusters. The single and double excitation configurations from the reference CSF's are then generated with $1s_O$, $1s_{Al}$, $2s_{Al}$, and $2p_{Al}$ orbitals frozen. The program used is our MOLYX-QDCI package.

2. Results and Discussion

2.1 Structure and Stability of Neutral Clusters. The optimized structures of neutral $Al(H_2O)_n$ ($n=1$—4) clusters are shown in Figs. 1, 2, and 3. The values under figures are the relative energy in $kJ\,mol^{-1}$ among the isomers; they are evaluated with the MP4SDTQ method.

Figure 1 **a** shows the structure of $Al(H_2O)$. The geometrical parameters of each structure are given in the figure; the parameters determined with the SCF method are in parentheses. There is little difference between the parameters of the SCF and MP2 methods. The neutral cluster $Al(H_2O)$ is planar and has C_{2v} symmetry. The most stable isomer of $AlOH_2$, however, is not a Al–water complex. As recently studied by Sakai,[20] the product of the insertion reaction H–Al–

#The paper is dedicated to the late professor Hiroshi Kato.

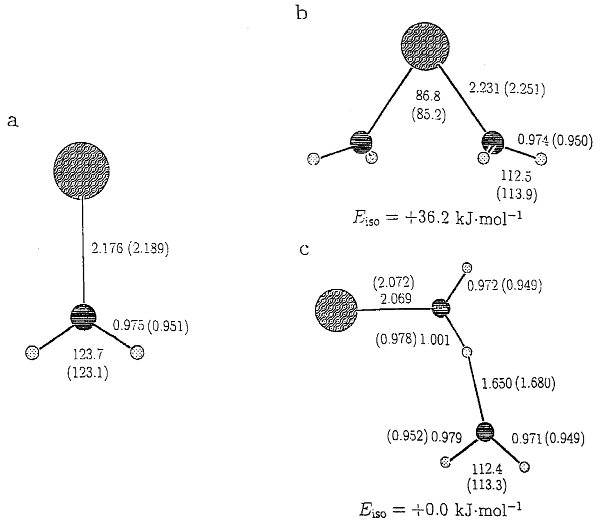


Fig. 1. The optimized structures of $Al(H_2O)$ (**a**) and of two isomers of $Al(H_2O)_2$ (**b** and **c**). The geometrical parameters are determined with the UHF MP2-(SCF) method. The energy E_{iso} is the isomerization energy evaluated with the MP4SDTQ method. In the following figures, the true stability of the optimized structures are confirmed by evaluating the harmonic frequencies.

OH is the most stable. The reaction barrier, however, of the insertion reaction is as high as 32.0 kJ mol^{-1} at HF/6-31G** level.$^{20)}$

Figure 1 **b** and **c** shows the structures of $Al(H_2O)_2$. Hereafter, for instance, the structure depicted in Fig. 1a is referred as structure.

There are two stable structures in $Al(H_2O)_2$. Structure **1b** has two water molecules directly bonding to an aluminum atom. All four hydrogen atoms are equivalent. Structure **1c** has only one water directly bonding to the aluminum atom, and the second water is hydrogen-bonding to the first water. The cluster is planar and has C_s symmetry. The electronic correlation, taken into account with the MP2 method, does not affect the optimized structures also for the neutral complexes of $n=2$. Although the hydrated neutral aluminum clusters are supposed to be van der Walls complexes, the effect of electronic correlation is not so large. It implies that the bond between the Al and O atom has more or less covalency; in other words a non-bonding orbital of water's oxygen coordinates to a vacant $3p_{Al}$ atomic orbital Al.

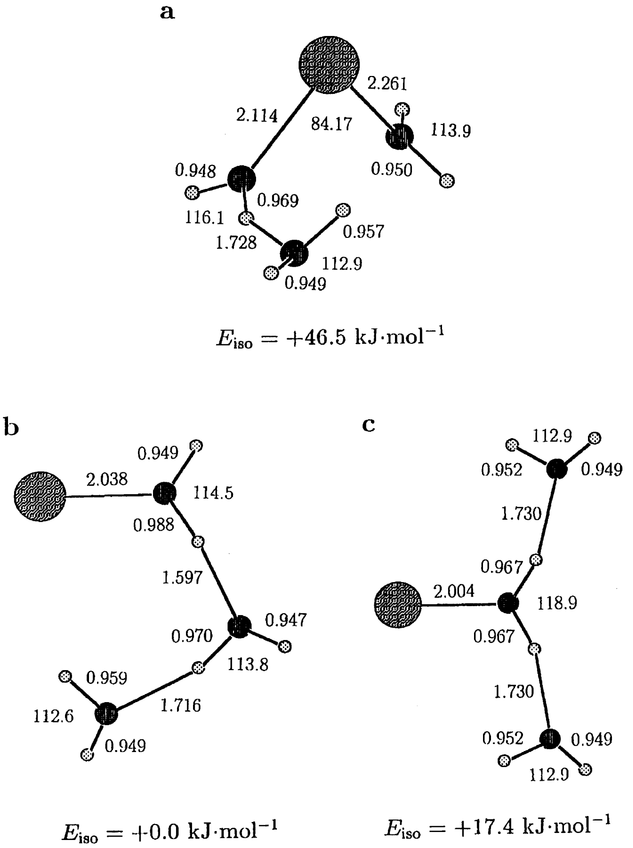


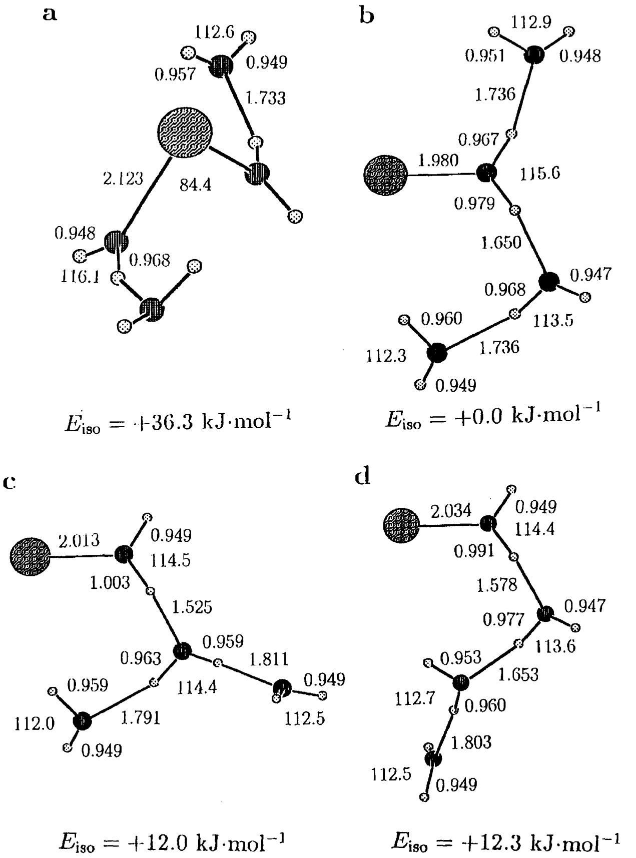
Fig. 2. The optimized structures of the neutral cluster $Al(H_2O)_3$. The structures are optimized with the UHF method. The energy E_{iso} is evaluated with the MP4SDTQ method.

Figure 2 shows the structures of $Al(H_2O)_3$. The three isomers are found. In structure **2a**, two water molecules are bonded to the aluminum atom directly, and the second hydration starts to form. The third water is hydrogen-bonding to one of the first shell's water molecules. In the other structures, only one water is bonded to the aluminum atom. Structure **2b** has a simple chain of water, and structure **2c** has a branch. Both chain and branch of Al–O–H–O lie nearly on a plane. We have tried to make the third water molecule approach to the aluminum atom of structure **2b** of $Al(H_2O)_2$ to form $Al(H_2O)_3$ which has three waters directly bonded to the Al atom. But the third water goes away and is not bonded to the aluminum. The saturation of the bonds Al–O at $n=2$ is consistent with the view that the vacant $3p_{Al}$ atomic orbitals are coordinated by the non-bonding orbitals of waters.

In the following discussion, we will call the structure **2a** "dimer-core", and the structure like **2b** and **2c** "monomer-core". Both two monomer-core structures are more stable than the dimer-core isomer.

The structures of four isomers of $Al(H_2O)_4$ are shown in Fig. 3. Structure **3a** has a dimer-core and its symmetry is C_2; two water molecules of the second shell are equivalent to each other. Structures **3b**, **3c**, and **3d** have a monomer-core. Structures **3b** and **3c** have branch, and **3d** has a linear chain of hydrogen-bonded water molecules. The most stable isomer is **3b**, which has the structural units of both **2b** and **2c**. Structures **3c** and **3d** are the next stable isomers, and the least stable is structure **3a** of the dimer-core isomer.

In summary, the monomer-core isomers are more stable than the dimer-core clusters for $n \geq 2$. Among the monomer-core isomers, the chained-isomers are more



$E_{\text{iso}} = +36.3\ \text{kJ·mol}^{-1}$ $E_{\text{iso}} = +0.0\ \text{kJ·mol}^{-1}$

$E_{\text{iso}} = +12.0\ \text{kJ·mol}^{-1}$ $E_{\text{iso}} = +12.3\ \text{kJ·mol}^{-1}$

Fig. 3. The optimized structures of the neutral cluster $Al(H_2O)_4$. The structures are optimized with the UHF method. The energy E_{iso} is evaluated with the MP4SDTQ method.

stable than the branched ones.

But the other type of the metal-water clusters was recently reported for the sodium–water clusters $Na(H_2O)_n$ by K. Hashimoto et al.[13] In $n=2$, 3, 4, all water molecules are apparently bonded to the sodium atom directly. In these clusters the water molecules make a strong hydrogen bonding network by themselves and a sodium atom resides on the network. They called the clusters the surface-isomers.

The structures and energy difference of the clusters are mostly understood in terms of the large polarization of the water molecules and the hydrogen bonding. Figure 4 shows the Mulliken population analysis of the neutral clusters. Although the Mulliken population with the split-valence basis set has to be used with care, the net charges in Fig. 4 are suggestive of the change of the electron distribution in the clusters. It is noticed that almost no charge transfer between the metal and water(s) and among the waters is found in the Mulliken population analysis. But, the polarization within each water molecule is remarkable. The water directly bonded to the metal (the first shell water) becomes strongly polarized within the molecule, and when the molecule is hydrated with the other water, it becomes more polarized. The second hydration also influences the electron distribution. The oxygen atom of the water bonded to the next shell water becomes more negative than that of the other water. Especially, the oxygen atom of the water, which is bonded to two water molecules in the monomer-core structure, is more negative than -1.0. The second hydration also influences the gross charge of hydrogen of the first shell water. In the first shell waters, the charge of a hydrogen atom bonded to the oxygen atom of the second shell becomes more positive than that of the hydrogen atoms other than that.

2.1.1 The Effects of SOMO: Another interesting finding in the electron distribution in the cluster is the spin density distribution. In the monomer $Al(H_2O)$, the singly occupied molecular orbital SOMO is a $3p\pi$ orbital of Al perpendicular to the molecular plane. The SOMO in the dimer-core clusters is always also the $3p\pi$ orbital perpendicular to the plane of O–Al–O. On the other hand, the SOMO of the monomer-core isomers of $n \geq 2$ is the in-plane 3p orbital. The odd electron looks interacting with the positively charged hydrogen atom(s) of the second and third shell water(s). The SOMO influences the structure and stability of the monomer-core isomers. The SOMO apparently interacts with a hydrogen atom of the water molecule, and makes the water molecule be on a plane or near in-plane. Especially, the hydrogen of water of the third shell in a chained $Al(H_2O)_3$ (structure **2b**) is very close to the SOMO. The chained $Al(H_2O)_3$ is, therefore, more stable than the branched $Al(H_2O)_3$ (structure **2c**). Similarly, structure **3b** is the most stable isomer among the $Al(H_2O)_4$. Structures **3c** and **3d** have a water molecule which is apart from the SOMO and is not even near on the molecular plane.

2.1.2 Angle of O–Al–O in Dimer-Core: Table 1 summarizes the angle of O–Al–O in the dimer-core. In neutral clusters, the angles are about 84°—86°. They are systematically smaller than 90°, which is expected if the non-bonding electrons of waters hydrate to the vacant 3p orbitals of Al. As is shown below, the cation clusters, the angles O–Al–O become about 80° (see Table 1). The single O–Al–O in $[Al(H_2O)_4]^+$ becomes even smaller than 80°, because of the stable six-membered ring (see below). For the $Na(H_2O)_n$ clusters, Hashimoto et al. found much smaller angle for O–Na–O;[13] they attributed it to the inter-cluster water–water hydrogen bonding.

2.1.3 The Effect on the Al–O Distance of the Second Hydration: Table 2 shows the size dependence of the bond length $R_{\text{Al–O}}$ between aluminum and oxygen atom of the first hydrating water. In the neutral monomer-core structures, the larger the cluster size, the shorter $R_{\text{Al–O}}$ (see also Figs. 1, 2, and 3). While in the neutral dimer-core structure, the larger the cluster size, the longer the Al–O distance. An interesting finding is that the bond length $R_{\text{Al–O}}$ becomes short, where the second shell forms. The second hydration shortens both

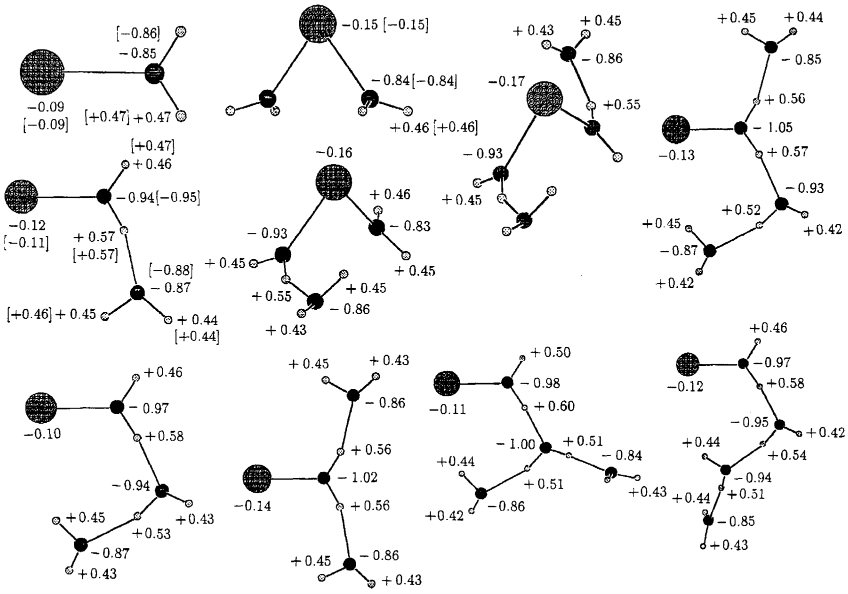


Fig. 4. The net Mulliken charge of the neutral cluster $Al(H_2O)_n$ (n=1, 2, 3, 4). The values are determined with the SCF[MP2] method.

R_{Al-O}, and also R_{H-O} between the hydrogen of the first shell ane the oxygen of the second shell. In the dimer-core structures, R_{Al-O} distance is also shortened with the second hydration (see Figs. 2 and 3).

2.2 Structure and Stability of Cation Clusters. Figure 5 **a** shows the structure of $[Al(H_2O)]^+$. The cation monomer cluster is planar and has C_{2v} symmetry. The difference in the structural parameters of the neutral and cation complexes is small. The parameters in parentheses are those determined with the SCF method. There is little difference in two approximations, as in the neutral clusters. Table 3 compares our parameters with those Sdoupe and Bauschlicher, who used the double zeta polarization basis set.[8] The polarization functions on aluminum and oxygen are not crucial in the structural parameters of the present complexes.

Table 1. The Angles O–Al–O (/degree) of $Al(H_2O)_n$ (dimer-core) and $[Al(H_2O)_n]^+$

	Neutral		Cation		
n	SCF	MP2	SCF		MP2
2	85.2	86.8	80.9		80.9
3	84.2		81.0		80.1
4	84.4		79.1[a)]	86.3	
5			80.5[a)]	85.5[b)]	

a) Inside of the six-membered ring. b) Inside of the eight-membered ring.

Table 2. Size Dependence of the Bond Distances R_{Al-O} (/Å) in $Al(H_2O)_n$ and $[Al(H_2O)_n]^+$

	Neutral			Cation	
n	Monomer-core[a)]	Dimer-core			
1	2.189	2.189[b)]		2.091[b)]	
2	2.072	2.251[b)]		2.113[b)]	
3	2.038	2.261[b)]	2.114[c)]	2.140[b)]	
4	1.980		2.123[c)]	2.116[b)]	2.090[d)]
5				2.093[e)]	2.065[d)]

a) The most stable structure. b) The water without the second hydration. c) The water with the second hydration. d) The water in the six-membered ring. e) The water in the eight-membered ring.

Figure 5 **b** shows the structure of $[Al(H_2O)_2]^+$. Two water molecules are bonded to an aluminum atom directly. On the contrary to n=1, the structure of cation cluster is different from that of the neutral dimer-core structure. The water molecules are staggered, and has only C_2 axis. This structure is similar to that of Sdoupe

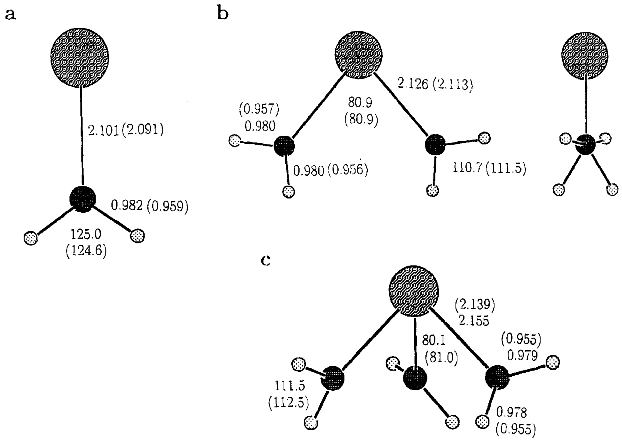


Fig. 5. The optimized structures of $[Al(H_2O)_n]^+$. (**a**) n=1, (**b**) n=2, (**c**) n=3. The geometrical parameters are determined with the MP2(SCF) method. The side view is shown for n=2.

Table 3. Comparing Our Structural Parameters of $[Al(H_2O)]^+$ and $[Al(H_2O)_2]^+$ with Those of Sdoupe and Bauschlicher[a)]

			SCF(DZP) (Sdoupe and Bauschlicher's)	SCF(6-31G)	MP2(6-31G)
				(Our parameters)	
$[Al(H_2O)]^+$	Al–O	(/Å)	2.080	2.091	2.101
$[Al(H_2O)_2]^+$	Al–O	(/Å)	2.12	2.251	2.231
	O–H	(/Å)	0.95	0.957	0.980
	O–Al–O	(/deg)	80.2	80.9	80.9
	H–O–H	(/deg)	108.3	111.5	110.7

a) Ref. 8.

and Bauschlicher,[8,12)] and the structural parameters are also very close to theirs (see Table 3).

Figure 5 **c** shows the structure of $[Al(H_2O)_3]^+$. Contrary to the neutral cluster (n=3), the third water in the cation cluster is directly bonded to the aluminum atom, and three water molecules become equivalent. The symmetry of $[Al(H_2O)_3]^+$ is C_3. Apparently three vacant 3p orbitals of the aluminum atom accept the non-bonding electrons of three water molecules.

Figure 6 shows the structure of $[Al(H_2O)_4]^+$ and its side view. The first hydration of cation cluster is saturated with three water molecules, and thus in $[Al(H_2O)_4]^+$, the fourth water molecule is combined with two of the first shell waters and forms the second hydration shell. Three waters form a six-membered ring structure with the aluminum atom. Two waters in the first shell are equivalent, and the cluster ion has C_s symmetry. Sdoupe and Bauschlicher also obtained the ring structure. Their structure has also C_s symmetry, but not completely same as our structure. In the structure obtained by Sdoupe and Bauschlicher, two hydrogens of the water without the second hydration are out of the mirror plane.[12)] We have confirmed the true stability by evaluating the harmonic frequencies. The six-membered ring in this cation cluster is very stable, which is also seen in the incremental hydration energy discussed below. In the cation $[Al(H_2O)_4]^+$, we have also tried to make the fourth water molecule approach to the Al^+ ion directly, in vain, as in the case of the neutral $Al(H_2O)_3$.

Figure 7 shows the structure of $[Al(H_2O)_5]^+$, in which the six-membered ring structure of $[Al(H_2O)_4]^+$ is kept, but with a substantial deformation of the ring. The fifth water is bonded to two water molecules: One is the first shell's water and the other is the second shell's, and, thus, the fifth water forms a new eight-membered ring. To form the new ring, two types of deformation from the structure $[Al(H_2O)_4]^+$ are found. One is the rotation of the water in the first shell, to which the fifth water is hydrogen-bonded. The other is a large deformation of the six-membered ring (compare the side views of Figs. 6 and 7). The six-membered ring in $[Al(H_2O)_5]^+$ becomes less stable than in $[Al(H_2O)_4]^+$.

The second hydration induces the similar effect on the structural parameters of the cation clusters as in the neutral clusters. When the first shell water is hydrogen-bonded, R_{O-Al} is shortened as is seen in Table 2. The effect, however, is less profound in the cation clusters.

Figure 8 shows the size dependence of Mulliken population analysis of cation clusters. The oxygen of the first-shell water bonded to the other water(s) becomes more negative, and the hydrogen atoms become more positive. The second hydration influences upon the net Mulliken population of cation clusters as in the neutral cluster.

2.2.1 Relevance to the Photodissociation Reaction:

Recently Misaizu et al. studied the photodissociation reaction of the ion clusters;

$$[Al(H_2O)_n]^+ + h\nu \rightarrow [Al(H_2O)_m]^+ + (n-m)H_2O \qquad (1)$$

In their experiment, the $[Al(H_2O)_n]^+$ clusters are dis-

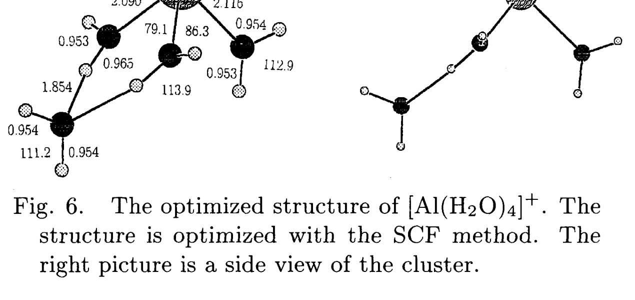


Fig. 6. The optimized structure of $[Al(H_2O)_4]^+$. The structure is optimized with the SCF method. The right picture is a side view of the cluster.

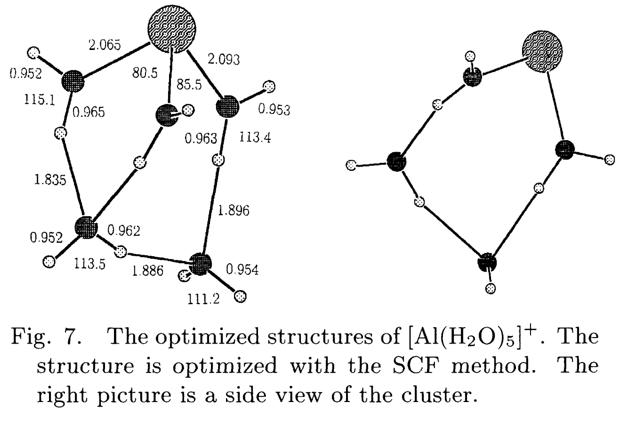


Fig. 7. The optimized structures of $[Al(H_2O)_5]^+$. The structure is optimized with the SCF method. The right picture is a side view of the cluster.

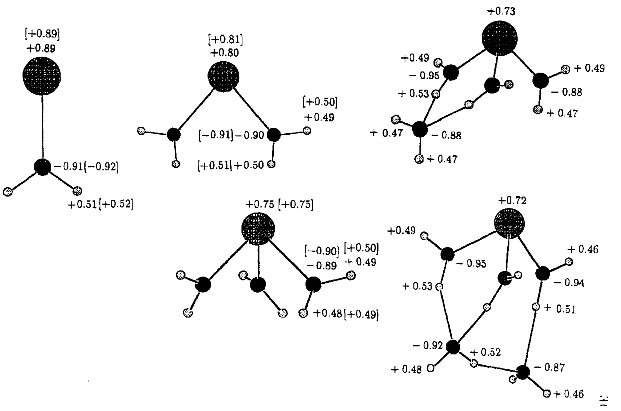


Fig. 8. The net Mulliken charge of the cation clusters $[Al(H_2O)_n]^+$ (n=1, 2, 3, 4, 5). The values are determined with the SCF[MP2] method.

sociated by the photoexcitation at a fixed wavelength 248 nm (5.00 eV=482 kJ mol^{-1}), and the smaller clusters are detected with the time-of-flight (TOF) mass spectroscopy. They succeeded in analyzing the size of the product ions, m, for each mass-selected parent cluster $[Al(H_2O)_n]^+$. If the evaporation reaction proceeds on the ground state surfaces, the excess energy is 482 kJ mol^{-1}, which is enough to evaporate at least four water molecules (see Fig. 9 **c**). One of the characteristics in the product distribution is that for the clusters of $n \geq 6$, the $n-m$ water molecules evaporate by the photoexcitation to form the smaller stable ion clusters $[Al(H_2O)_m]^+$, $4 \geq m \geq 1$. This finding is consistent with the special stability of $[Al(H_2O)_4]^+$ with a six-membered ring structure. When $n=5$, however, the peak of $m=4$ is missing in the mass-spectrum. This results strongly suggests that the cluster ions of $n \geq 6$ contain the six-membered ring structure $[Al(H_2O)_3]^+(H_2O)$ as a core. In $[Al(H_2O)_5]^+$, however, the six-membered ring structure is stained and becomes less stable. Thus, the evaporation of a water induces another water to evaporate successively.

2.3 Size Dependence of Hydration Energy. The incremental hydration energy is defined in the following reaction:

$$Al(H_2O)_{n-1} + H_2O \rightarrow Al(H_2O)_n \qquad (2)$$

$$[Al(H_2O)_{n-1}]^+ + H_2O \rightarrow [Al(H_2O)_n]^+ \qquad (3)$$

and the internal energy change is:

$$\Delta E^{\mathrm{inc}}(n) = E(n) - \{E(n-1) + E(H_2O)\} \qquad (4)$$

$$\Delta E_+^{\mathrm{inc}}(n) = E_+(n) - \{E_+(n-1) + E(H_2O)\} \qquad (5)$$

where $\Delta E^{\mathrm{inc}}(n)$ and $\Delta E_+^{\mathrm{inc}}(n)$ are the incremental hydration energies of the neutral and cation clusters, $E(n)$ and $E_+(n)$ are the total energies of $Al(H_2O)_n$ and $[Al(H_2O)_n]^+$, and $E(H_2O)$ is the total energy of H_2O.

The hydration energies are evaluated with the SCF, MP2, and MP4SDTQ methods. There is a slight difference in values, depending on the methods, but the tendency is independent of all the methods. Figure 9 **a** and **b** shows the incremental hydration energies of the neutral clusters of monomer-core and dimer-core structures, respectively for each of the most stable isomer.

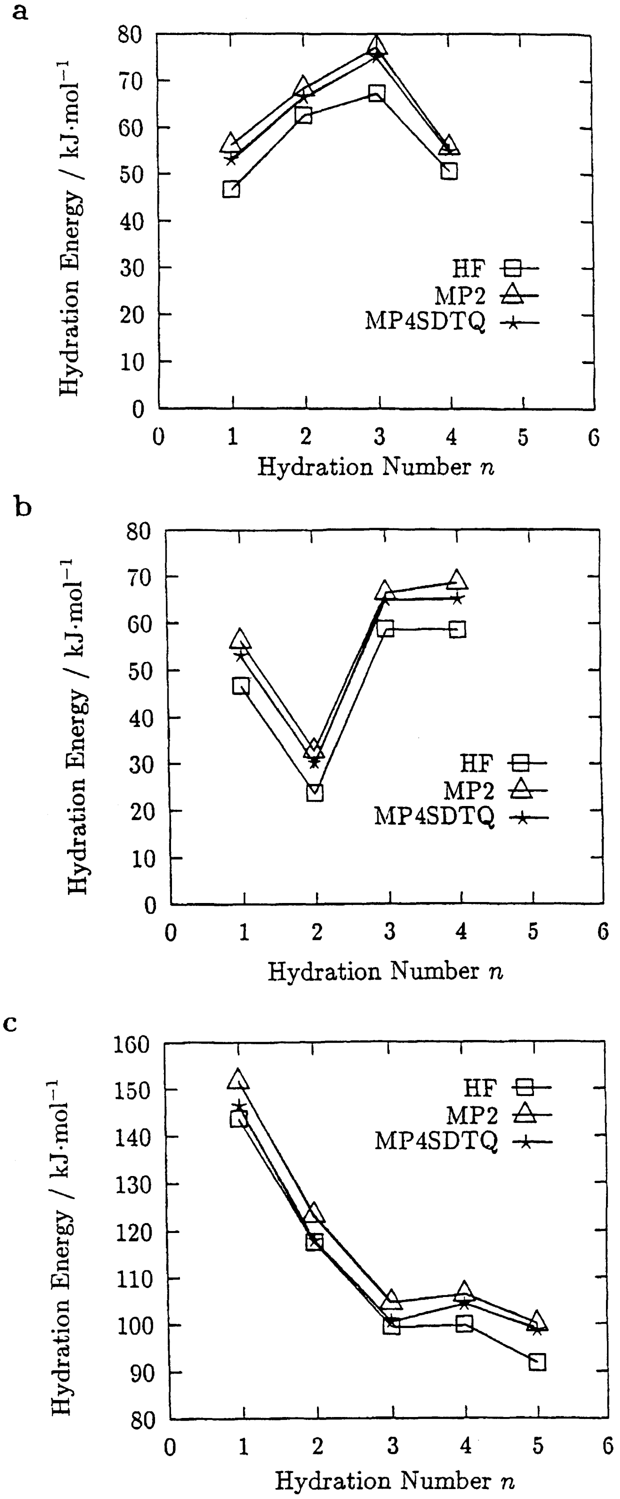


Fig. 9. The incremental hydration energies of Al–water clusters. (**a**) The neutral monomer-core clusters. (**b**) The neutral dimer-core clusters. (**c**) The cation clusters.

In both monomer-core and dimer-core structures, the non-additivity of the hydration energy is clearly seen. In the dimer-core, $\Delta E^{\mathrm{inc}}(2)$ is almost half of $\Delta E^{\mathrm{inc}}(1)$, but $\Delta E^{\mathrm{inc}}(3)$ is larger than $\Delta E^{\mathrm{inc}}(1)$, because of formation of the second shell. Similarly in the monomer-core, $\Delta E^{\mathrm{inc}}(2)$ is larger than $\Delta E^{\mathrm{inc}}(1)$. In the monomer-core isomers $\Delta E^{\mathrm{inc}}(3)$ is even larger than $\Delta E^{\mathrm{inc}}(2)$. This is because a positively charged hydrogen of the second shell water interacts with an odd electron in $3p_{\mathrm{Al}}$ (see Fig. 2 **b**).

The incremental hydration energies of cation clusters are shown in Fig. 9 **c**. In the cation clusters, $\Delta E_{+}^{\mathrm{inc}}(1)$ is nearly three times of $\Delta E^{\mathrm{inc}}(1)$. Up to n=3, $\Delta E_{+}^{\mathrm{inc}}(n)$ decreases almost linearly, but because of the stable six-membered ring $\Delta E_{+}^{\mathrm{inc}}(4)$ is as large as $\Delta E_{+}^{\mathrm{inc}}(3)$.

2.4 Size Dependence of Ionization Energy. The calculated vertical ionization energy with the CI and MP4SDTQ methods is given in Fig. 10 **a** for the monomer-core and **b** for the dimer-core clusters. It is known that the ΔSCF method underestimates the ionization energy. This general tendency is also seen in the MP4SDTQ method. Experimentally the ionization energy of the clusters is determined by the appearance photon energy of the mass-spectrum.[6] In the usual sense, this energy is more close to the adiabatic ionization energy than the vertical ionization energy, but the geometry of the cation cluster is, in most cases, so different from that of the corresponding neutral cluster that the appearance energy of the cation in the mass spectrum is expected to be much higher than the adiabatic energy difference. In the present study the experimental energy is compared with the vertical energy. The evaluated ionization energies of CI calculation for an Al atom and $Al(H_2O)$ are agreed with the experimental energy. In the dimer-core structure, however, the CI vertical ionization energy for $Al(H_2O)_n$ becomes substantially smaller than the corresponding experimental one. On the other hand, in the monomer-core structure, the calculated ionization energy for n=2 and 3 is almost very close to the experimental energy. Because we have carried out the same type of MRSDCI calculations for n=0 to n=3 of both monomer- and dimer-core clusters, we might expect the similar accuracy for n=2 and 3 as for n=0 and 1. A slight overestimate for n=3 may suggest the existence of a more stable isomer than **2b**. Another possibility of the cause of the small error is that in the experimental condition a few of the isomers are mixed in the molecular beam.

The general agreement in the calculated ionization energies for the monomer-core clusters and the systematic disagreement for the dimer-core clusters strongly suggest that the monomer-core clusters are formed in the molecular beam.

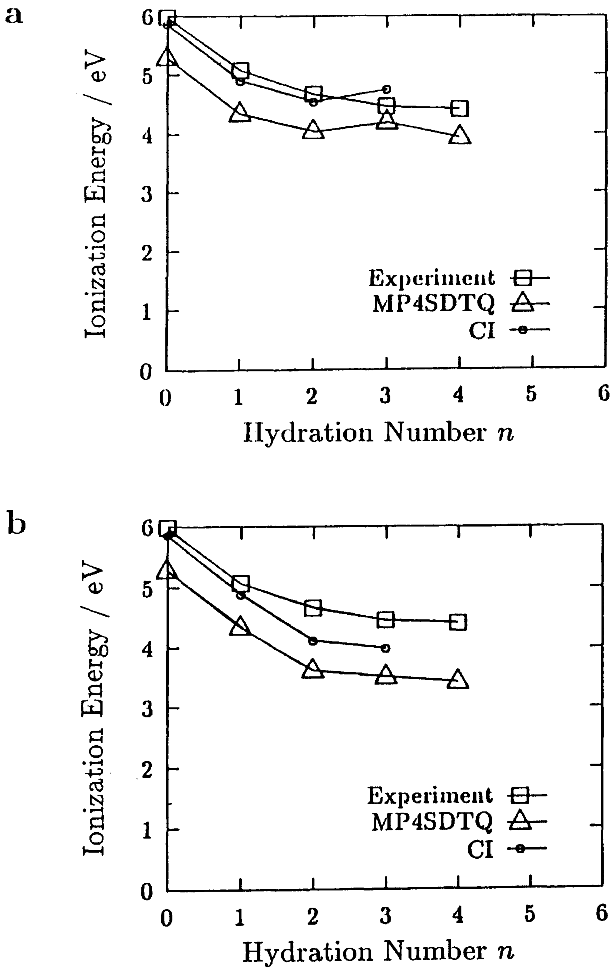


Fig. 10. Comparison of the experimental and the calculated vertical ionization energies. The experimental energies are from Ref. 6. 1 eV=96.485 kJ mol^{-1}. (**a**) The calculated energies for the most stable isomer of the monomer-core clusters. (**b**) The calculated energies for the dimer-core clusters.

2.5 Saturation of the First Layer. In the neutral clusters, the first shell is saturated with two water molecules, while in the cation clusters the first shell is with three waters molecules. The shell closing may be explained in terms of the classical octet rule. When non-bonding electrons of the three water molecules try to coordinate to a neutral Al atom, which has three valence electrons, the number of valence electrons around the Al atom becomes nine, and three waters cannot combine with an Al atom directly. Similarly, since an Al^+ ion has two valence electrons, when three water molecules coordinate to a cation Al^+, the number of valence electrons around the Al^+ ion is eight, and, thus no more waters can be combined with the Al^+ ion directly. The fourth water forms the second hydration shell. On the other hand, Hashimoto et al. reported that all water molecules in the most stable $Na(H_2O)_4$ are bonded to the sodium atom directly.[13] Four water molecules form a ring through a network of hydrogen bonds, and the sodium atom lies on the top of the ring of four water molecules. The $Na(H_2O)_4$ cluster has C_4 symmetry. We have examined the similar structure for $[Al(H_2O)_4]^+$; the stationary structure is found, in which all four water molecules are directly bonded to the aluminum atom, has several imaginary frequencies, although the structure has C_4 symmetry and the four waters are equivalent. Obviously the water molecules in this structure are not enough close to each other, to form a ring of waters. Bauschlicher and Partridge recently reported two isomers of $[Mg(H_2O)_4]^+$;[12] the one has a similar structure with $[Al(H_2O)_4]^+$ and the other with $Na(H_2O)_4$. The former is more stable than the latter. These results suggests that when a metal atom of groups 1, 2, and 3 is neutral or singly charged, the maximum number of possible waters directly coordinated to the metal is guessed by octet rule, except for the complexes with strong hydrogen bonding network of waters.

3. Conclusion

In the neutral aluminum–water clusters $Al(H_2O)_n$, the monomer-core isomers are more stable than the dimer-core isomers. The agreement of the calculated ionization energies for the monomer-core isomers with the experimental energies suggests that the monomer-core isomers are formed in the experiments of Misaizu et al.[6] The hydration energy is non-additive. The hydrogen-bonds between the water hydrating to the Al atom and the water of the second shell is very strong, which results in the stabilization to the monomer-core isomers. The bond length and charge density are also affected with the hydrogen bonding of the first and second shell waters. The SOMO in the monomer-core isomers interacts with a hydrogen atom of the second and third shell waters. It is this interaction that determines the most stable isomer among the monomer-core isomers.

In the cation clusters $[Al(H_2O)_n]^+$, the second hydration starts at $n=4$. It has a stable six-membered ring structure. $[Al(H_2O)_5]^+$ has also a six-membered ring, which, however, is strained, because of a new formation of a eight-membered ring. The existence of the very stable $[Al(H_2O)_4]^+$ cluster explains the product distribution of the photo-dissociation reaction of $[Al(H_2O)_n]^+$.

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