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Theoretical Studies of Structures and Ionization Threshold Energies of Water Cluster Complexes with a Group 1 Metal, $M(H_2O)_n$ ($M = $ Li and Na)

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Water cluster complexes with a group 1 metal atom, $M(H_2O)_n$ ($M = $ Li and Na), for $n = 3-6$ were studied with ab initio MO methods. The singly occupied molecular orbitals (SOMOs) are classified into three types: surface, quasi-valence, and semi-internal. It is the isomers of structures with semiinternal SOMO that are responsible for the observed convergence of the ionization threshold energy. They are the ion-pair complexes, $M^+(H_2O)_m{\cdot}(H_2O)_l{\cdot}(H_2O)^-_{n-m-l}$, and their vertical ionization energies (VIEs) are determined by the local structure of $(H_2O)^-_{n-m-l}$ and the electrostatic potential from the cation $M^+(H_2O)_m$. The model also explains why the experimental ionization threshold energy converges at $n = 4$.

Introduction

The ionization threshold energies (ITEs) of water clusters containing a group 1 metal atom, $M(H_2O)_n$ ($M = $ Li, Na, and Cs) have been reported by Takasu et al.,[1] Hertel et al.,[2] and Misaizu et al.[3] The observed ionization threshold energies of these clusters show several interesting features. For $n \leq 3$, the ITE decreases rapidly as n increases. But for $n \geq 4$, it becomes constant, and the converged value is nearly equal to the ionization energy of bulk water (about 3.2 eV[4]); the value is common for Li, Na, and Cs. To explain this behavior, the experimentalists assumed that the solvated metal atom is completely ionized and screened by four water molecules. In their model, the excess electron is ejected outside the first solvation shell, and the state of the excess electron is not affected by the solvated metal ion. Theoretical calculations were also performed to explore the anomalous features. Barnett et al.[5] showed using the local spin density functional method for $Na(H_2O)_n$ that the Na atom becomes ionized at $n = 4$ and that for $n \geq 4$ the structures of $Na(H_2O)_n$ resemble $Na(H_2O)_n^+$ with a Rydberg-like excess electron. Hashimoto and Morokuma (HM) also performed calculations for $Na(H_2O)_n$ using ab initio MO methods.[6−8] They showed that the most stable structure was the surface-metal structure, where an Na atom sits on the cluster surface. Because this type of structure cannot have more than four water molecules in the first solvation shell, the behavior of the ionization threshold changed at $n = 4$. The excess electron distribution in the surface structure is localized near the Na atom and opposite the water molecules. Hashimoto and Kamimoto (HK)[9,10] have also reported ab initio calculations for $Li(H_2O)_n$. They showed that the interior-metal structure is most stable, where the metal is surrounded by four water molecules, and that it cannot have more than four water molecules in the first solvation shell. They suggested that this is the origin of the change in the ionization threshold of $Li(H_2O)_n$ at $n = 4$. However, the excess electron density is distributed on and between the water molecules in the second solvation shell, which is different from that in $Na(H_2O)_n$. Most of the theoretical works indicated that the clusters have four water molecules in the first solvation shell and the metal atom becomes ionized at $n = 4$. But until now, the reason why the ionization threshold is independent of the metal element has not been explained, and the reasons for size independence have not been explored.

Recently, we have performed a series of ab initio MO calculations on the water cluster anions, $(H_2O)_n^-$, and showed that the excess electron can be trapped inside water clusters as small as $n = 2$, 3, and 4.[11,12] The electron cloud is surrounded by two or more H−O bonds of water molecules, whose structure we denote O−H{e} H−O hereafter. Kim et al.[13,14] also found a similar structure in the excess electron of the most stable isomer of $(H_2O)_6^-$. These results suggest the stability of this type of structure for the excess electron and encourage us to think that the O−H{e}H−O structure might be present also in a group 1 metal-water clusters, $M(H_2O)_n$. If $M(H_2O)_n$ is an ion pair with a O−H{e}H−O structure and a solvated metal atomic ion, the ionization energy might not be affected by the metal cation. Furthermore, the structure O−H{e}H−O might remain unchanged when n increases, and consequently the ionization energy could become n-independent.

In this paper, we reexamine $M(H_2O)_n$ ($M = $ Li and Na) in a consistent way, keeping a O−H{e}H−O structure in mind. We first describe the geometric structures of the optimized isomers and their relative energies. The isomers are classified by introducing a set of measures to characterize the singly occupied molecular orbital (SOMO). The determining factor of the vertical ionization energy is analyzed. Finally, we present a model to explain why the ionization threshold energy converges at an energy beyond $n = 4$, independent of the metal element.

Computational Details

For the geometry optimization, the MP2/6-311++G(d,p) level of approximation is used. In our previous study for water cluster anions, which have a O−H{e}H−O structure,[11] we have found it necessary to work at least at the MP2 level of approximation. Some of the isomers determined by Hashimoto and Kamimoto,[10] and by Hashimoto and Morokuma, are reoptimized at the MP2 level. The harmonic vibrational frequencies are also calculated to confirm the stable structures, and they will be reported in a separate paper.[12] To estimate the total binding energy, the basis set superposition error (BSSE) has to be corrected. In the present

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TABLE 1: Distance between $R_{\{e\}}$ and the Metal Atom, the Shortest Four Distances between $R_{\{e\}}$ and the Hydrogen Atoms, SEM, VIE, and ΔE_{ISO}

	type	M*n*W	R({e}−M)[a]	R({e}−H)[a]	SEM[b]	VIE[c]	ΔE_{ISO}[d]
Li3a	S	M3W	1.50	2.42, 2.42, 2.42, 2.85	115	3.39	0.00
Li3b	S	M3W	1.69	1.76, 1.96, 2.11, 2.17	95	3.43	0.09
Na3b	S	M3W	1.65	2.03, 2.33, 2.42, 2.84	101	3.40	0.00
Li3c	V	M2W	1.41	2.63, 2.81, 3.06, 3.33	40	3.78	5.49
Na3c	V	M2W	1.34	3.05, 3.22, 3.32, 3.84	48	3.68	0.93
Li4a	S	M4W	2.13	1.74, 1.78, 2.29, 2.47	96	3.31	0.00
Li4b	S	M4W	2.21	1.34, 1.34, 2.44, 2.44	93	3.30	0.09
Na4b	S	M4W	2.68	1.39, 1.39, 2.48, 2.48	83	3.36	0.00
Li4c	I	M3W	2.71	1.48, 1.66, 2.68, 2.90	63	3.53	2.77
Na4c	I	M3W	2.94	1.48, 1.60, 2.77, 3.02	69	3.40	1.58
Li4d	I	M3W	2.55	1.07, 1.24, 2.23, 2.85	75	3.42	4.26
Na4d	I	M3W	2.49	1.17, 2.08, 2.21, 3.04	63	3.55	1.95
Li4e	V	M2W	1.90	1.98, 1.98, 2.95, 2.95	28	3.97	9.05
Na4e	V	M2W	1.92	2.12, 2.12, 3.18, 3.18	36	3.90	3.01
Li5a	I	M4W	2.99	1.52, 1.59, 1.82, 2.90	67	3.36	0.00
Na5a	I	M4W	3.47	1.49, 1.57, 1.95, 3.01	65	3.37	0.00
Li5b	I	M4W	2.98	1.53, 1.58, 2.75, 2.83	62	3.33	0.50
Li5c	I	M4W	2.51	1.62, 1.92, 2.01, 2.53	63	3.48	0.60
Li5d	I	M3W	3.34	1.16, 1.73, 2.70, 2.74	51	3.50	3.42
Na5d	I	M3W	3.40	1.23, 1.78, 2.74, 2.80	48	3.51	2.19
Li5e	I	M3W	3.12	1.51, 1.70, 2.01, 2.70	36	3.72	4.87
Na5e	I	M3W	3.18	1.61, 1.72, 2.00, 2.98	36	3.70	3.77
Li6a	I	M5W	3.27	1.38, 1.57, 1.87, 2.70	66	3.34	2.66
Na6a	I	M5W	3.69	1.25, 1.74, 1.97, 2.77	61	3.44	0.00
Li6b	I	M4W	3.73	1.07, 1.76, 2.60, 2.67	53	3.35	1.18
Na6b	I	M4W	4.05	1.02, 1.88, 2.53, 2.75	53	3.37	0.57
HK−VIa	I	M4W	3.15	1.52, 1.58, 1.71, 3.01	55	3.49	0.00
HM-m	V	M3W	1.38	3.59, 3.59, 3.59, 3.96	52	3.35	0.57

[a] In Å. [b] In Å^3. [c] In eV. [d] In kcal/mol.

paper we discuss only the relative energy among the isomers of the same size *n*. In most cases the energy differences are small, and the identification of the most stable isomer is difficult. All calculations are carried out with Gaussian94[15] registered at the computer center of the Institute for Molecular Science.

Three measures are defined to characterize the electron distribution of the singly occupied molecular orbital (SOMO).

1. SOMO extent measure (SEM): The volume (in Å^3) of the sphere, which contains a half of electron in SOMO. To define the sphere, we first calculate $\psi_{SOMO}(\mathbf{r}_{ijk})$ at the cubic grids $\mathbf{r}_{ijk} = (x_i, y_j, z_k)$ for $i = 1, ..., L$, $j = 1, ..., M$, and $k = 1, ..., N$. The spacings of these grids are fixed as Δx, Δy, and Δz. Next, we sort them in descending order such that $|\psi_{SOMO}(1)| \geq |\psi_{SOMO}(2)| \geq ... \geq |\psi_{SOMO}(p)| \geq ... \geq |\psi_{SOMO}(LMN)|$. Finally, we search the index P such that $\sum_{p=1}^{P}|\psi_{SOMO}(p)|^2 \times \Delta x\Delta y\Delta z \approx 0.5$. The sphere so defined is unique and has a volume $P \times \Delta x\Delta y\Delta z$.

2. *R*({e}−M): The distance between the center of the electron density of SOMO ($\mathbf{R}_{\{e\}}$) and the metal atom. $\mathbf{R}_{\{e\}}$ is evaluated as $\mathbf{R}_{\{e\}} = \sum_{ijk}|\psi_{SOMO}(\mathbf{r}_{ijk})|^2\Delta x\Delta y\Delta z \times \mathbf{r}_{ijk}$.

3. *R*({e}−H): The distance between $\mathbf{R}_{\{e\}}$ and the hydrogen atom.

We have also examined the effect of adding a set of diffuse sp type functions on the vertical ionization energy (VIE) and on the SEM of three isomers of $Li(H_2O)_4$ (Li4b, Li4c, and Li4e), which correspond to three types of isomer as we will show later. These diffuse functions are added only on the oxygen atom, and their exponents are 0.017, 0.003, 0.0006, and 0.00012. As a result, VIEs increase by at most 0.01 eV and are almost converged with the 6-311++G(d,p) basis set. SEMs also increase slightly by at most 3 Å^3. Because both changes are small and do not influence the following discussion, we have used 6-311++G(d,p) basis set in the present calculation.

Results and Discussion

The optimized structures for $Li(H_2O)_n$ and $NaH_2O)_n$ for $n = 3-6$ are given in Figures 1−4. The surface of the sphere, defined in the previous section, is also shown. The SEM in our definition is the volume of the sphere in the figures. In Table 1 three measures defined above as well as the VIE and the relative isomer energy are summarized. The geometric structures of isomers are classified in terms of the number of water molecules *m* in the first solvation shell, "M*m*W" isomer. The electronic structures of $M(H_2O)_n$ are classified using two measures (SEM and R({e}−M)) into three types, surface (S), semiinternal (I), and quasi-valence (V). The definition is as follows;

1. Surface (S): SEM is larger than 75 Å^3. In this type of isomers, an electron is detached from the metal atom, and the ejected electron is delocalized on the surface of the cluster.

2. Semiinternal (I): SEM is smaller than or equal to 75 Å^3 and R({e}−M) is longer than 2.0 Å^3. The electron is detached from the metal atom and captured internally by O−H bonds of the water molecules. The structure O−H{e}H−O plays a key role in localizing the ejected electron.

3. Quasi-valence (V): SEM is smaller than 55 Å^3 and R({e}−M) is shorter than 2.0 Å. The SOMO electron is not yet completely detached from the metal atom. The SOMO is a sp hybrid orbital, though it is more diffuse than the ordinal valence s and p orbitals. This type of isomers has a larger VIE than those of the other types.

The correlations of SEM with VIE (a) and with R({e}−M) (b) are shown in Figure 5, which demonstrates the appropriateness of the classification.

$M(H_2O)_3$. Three isomers are found for $Li(H_2O)_3$, and two isomers are for $Na(H_2O)_3$ (see Figure 1). Isomer Li3a has C_3 symmetry, and all oxygen atoms lie nearly on a plane. Hydrogen bonds among the water molecules are not formed, because of

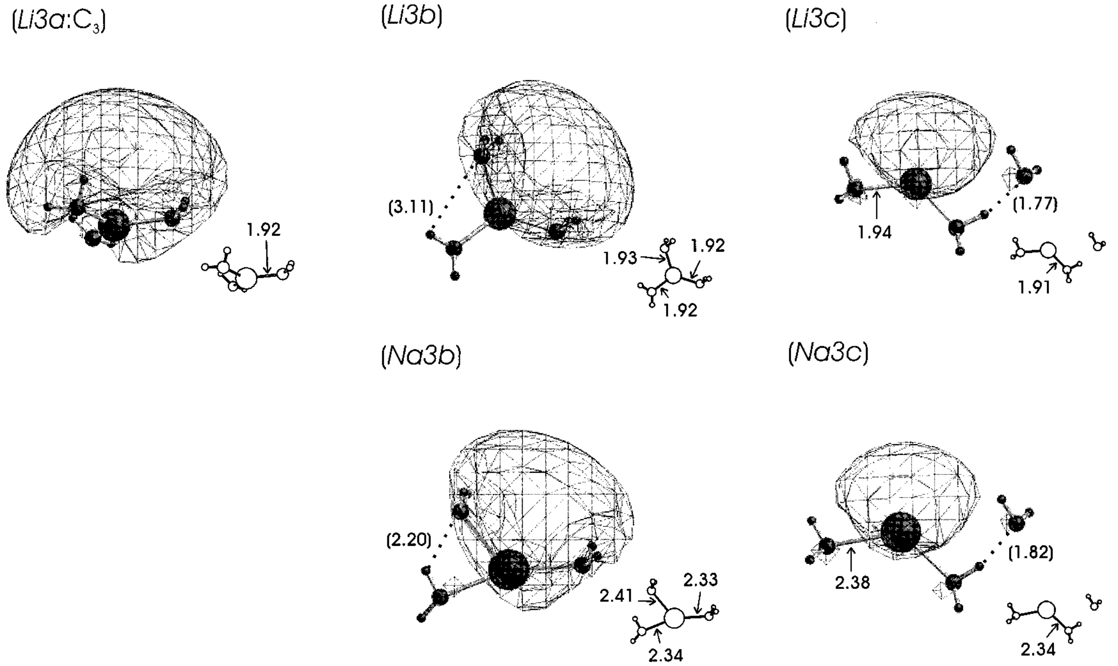

Figure 1. Optimized structures for $Li(H_2O)_3$ and $Na(H_2O)_3$. The surface of the sphere, inside of which a half of the SOMO electron is contained, is drawn. The hydrogen bonds are shown by dotted lines. The metal-oxygen bond lengths and the hydrogen bond lengths are given in angstroms. The hydrogen bond lengths are in parentheses.

short Li−O distances. We also found a similar planar C_3 structure for $Na(H_2O)_3$, which turned out to have two imaginary frequencies and collapsed to isomer Na3b by forming a hydrogen bond between a pair of water molecules. Isomers Li3b and Na3b have a pair of hydrogen-bonded water molecules. The difference in the hydrogen bond strength of Li3b and Na3b, which is seen in the metal−oxygen bond distances, results from the ionic radius of Li^+ and Na^+. Isomer Li3a, having no hydrogen bonds, is as stable as isomer Li3b. The electronic structures of Li3a, Li3b, and Na3b are of typical surface type; the SEMs are as large as 115, 95, and 101 Å^3, respectively. In these isomers the metal atom is ionized, and the ejected electron is distributed on the surface of the cluster. One of the interesting findings in the surface type electron is that $\mathbf{R}_{\{e\}}$ is closer to the metal ion than to the hydrogen atoms of water molecules, although some of OH bonds are directed toward {e}, as seen in the figure.

Isomers Li3c and Na3c are of M2W. The energy difference of isomers Li3c and Li3a is as large as 5.49 kcal/mol. On the other hand, the corresponding difference of Na3c and Na3b is less than 1 kcal/mol. The Na−O bond energy is similar to the hydrogen bond between the first and second shell water molecules, and they are smaller than the Li−O bond energy. The characteristics of isomers of Li3c and Na3c are small SEM, short R({e}−M) and long R({e}−H), as is shown in Table 1. The electron in SOMO is bound to the metal atom, and therefore, we classify the isomers quasi-valence type. It might be worth emphasizing that the interaction between {e} and HO bonds determines the direction of the second shell water molecule and one of the first shell water molecules.

Hashimoto and Kamimoto (HK) examined isomers of $Li(H_2O)_3$ with several basis sets.[10] Hashimoto and Morokuma (HM) also reported the structures of isomers of $Na(H_2O)_3$.[8] Some of their isomers are similar to Li3a, Li3b, and Na3b. They also found a few isomers of M2W having two hydrogen bonds. The quasi-valence type isomers Li3c and Na3c are not reported, probably because they expected that the isomers of this type are less stable than the isomers having two hydrogen bonds.

$M(H_2O)_4$. The isomers of $Li(H_2O)_4$ and $Na(H_2O)_4$ in Figure 2 have similar structures except the metal−oxygen distances. An exception is Li4a; the counterpart Na4a collapses to Na4b as Na3a does to Na3b. Isomers Li4b and Na4b have C_2 symmetry and have two hydrogen bonds. Because of a larger ionic radius of the Na^+ ion, the Na−O bonds in Na4b are much longer and weaker than the Li−O bonds in Li4b, and thus the water molecules in Na4b can be reoriented to form stronger hydrogen bonds. The SOMOs of three isomers are of surface type, as their SEMs indicate, although the distances R({e}−M) are substantially larger than in Li3b and Na3b. Besides, some of R({e}−H) are short, which suggests stronger OH and {e} interaction.

Two pairs of M3W isomers, M4c and M4d, are found in our study. In M4c, the water molecule in the second solvation shell is a double proton-acceptor water molecule; one of OH bonds of the molecule interacts with an electron cloud {e}. In M4d, a pair of water molecules in the first shell is hydrogen-bonded. The energy difference between M4c and M4d is 1.49 kcal/mol for M = Li and 0.37 kcal/mol for M = Na. The SOMO electron of both M3W isomers is semiinternal, as their SEMs range from 63 to 75 Å^3. There are noticeably short R({e}−H)s. It should be noticed that even though M4d has the first shell structure of M3b, the electron distribution {e} of M4d is different from that of M3b. This implies that the second shell water molecule in M4d substantially reduces the electron distribution {e}.

One M2W isomer M4e is found for both metals. Both have C_2 symmetry, and a pair of water dimers coordinate to the metal atom. The isomer is less stable than the others. The SEM and R({e}−M) indicate the character distinct from the other isomers, and the SOMO is a typical quasi-valence orbital. The water molecules in the second shell interact strongly with the electron.

$M(H_2O)_5$ and $M(H_2O)_6$. For $M(H_2O)_5$, three M4W isomers for Li and one for Na are found (Figure 3). There is a double proton-acceptor water molecule in the second shell in Li5a, Li5b, and Na5a, which share a similar electronic structure. The SOMO is of semiinternal type, and the ejected electron {e} interacts with the double proton-acceptor water molecule and with one

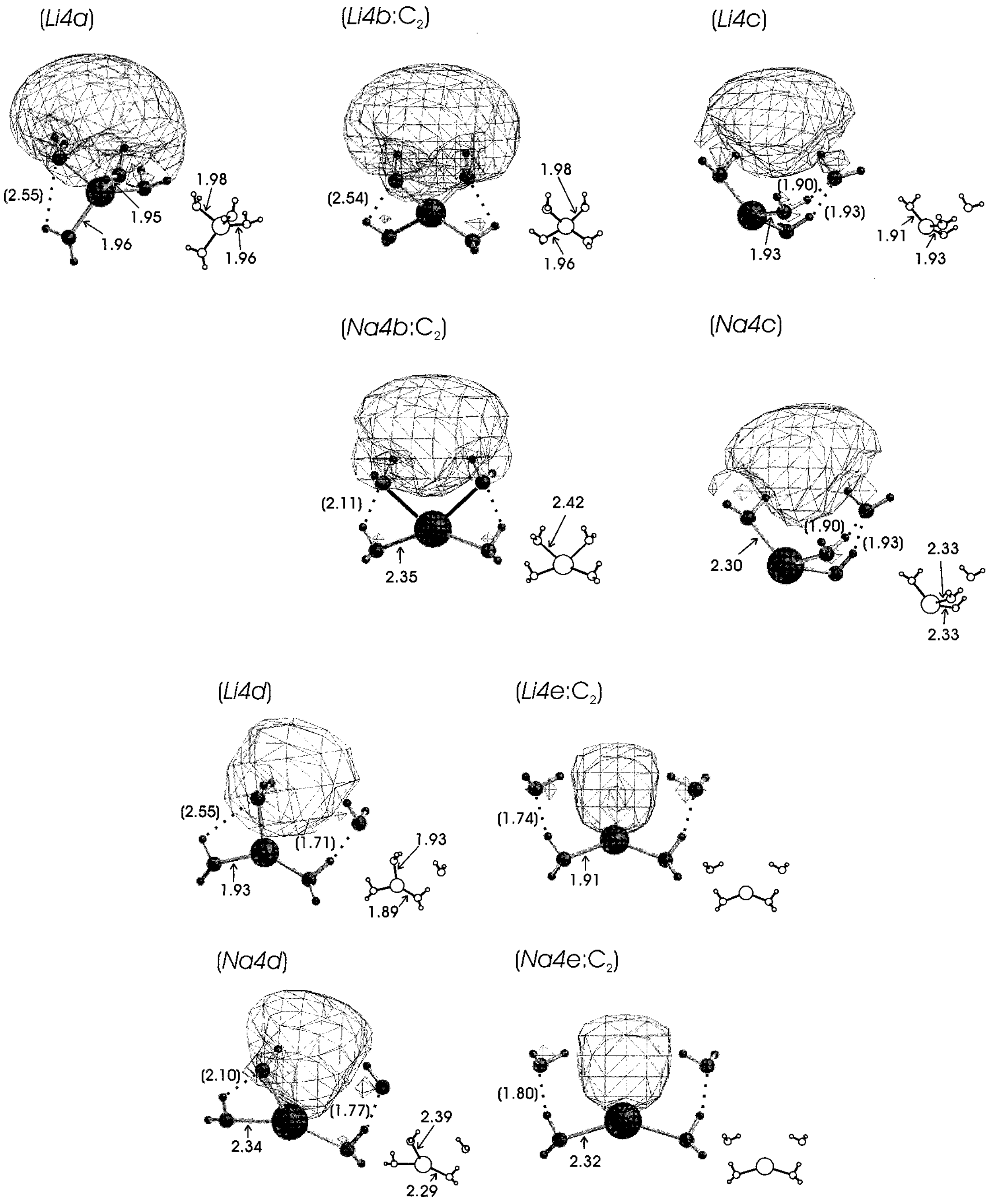

Figure 2. Optimized structures for $Li(H_2O)_4$ and $Na(H_2O)_4$.

of the first shell water molecules. The number of OH bonds strongly interacting with {e} in isomer Li5b is two, while it is three in isomer Li5a. This difference comes from the position of the hydrogen bond within the first solvation shell. The energy difference of the isomers, however, is merely 0.50 kcal/mol. The attempt to locate the corresponding isomer Na5b has failed.

There is a large free space in the other side of water molecules in M5a, which suggests that one more water molecule can hydrate to the metal atom; in fact, isomers Li6a and Na6a are found as shown in Figure 4. The SEMs become smaller and R({e}−M) longer than the corresponding M5a. It is, however, worth noticing that the three shortest R({e}−H)s are not much changed; the structure (OH_2)\{e\}(HO) is almost common in M5a and M6a. Most of the M4W form of $M(H_2O)_n$ ($n > 4$) have the structure of M4b as an ion core, which has two strong intrashell hydrogen bonds of the four-membered ring. In M5a, one of the rings is replaced with a six-membered hydrogen bond ring. If two of the four-membered rings are replaced, it becomes one of the isomers found for $Na(H_2O)_6$ by Hashimoto and Morokuma.[8] It is expected that a similar core structure persists both for $K(H_2O)_n$ and $Cs(H_2O)_n$.

Isomer Li5c is also M4W, and its first shell structure is similar to Li4a. But, the character of the SOMO is changed to semiinternal in our classification; R({e}−M) becomes longer, and the SEM is as small as 63 Å^3. The change of SOMO results from stronger interaction of the ejected electron with the proton acceptor water molecule. The energy difference from the other M4W isomer Li5a is only 0.60 kcal/mol, though the structure is very different.

Two isomers (M5d and M5e) of M3W are examined for $M(H_2O)_5$. The SOMO of both isomers is of semiinternal type. A large R({e}−M) clearly indicates the ion-pair formation in these isomers. Isomers M5d have three hydrogen bonds, and

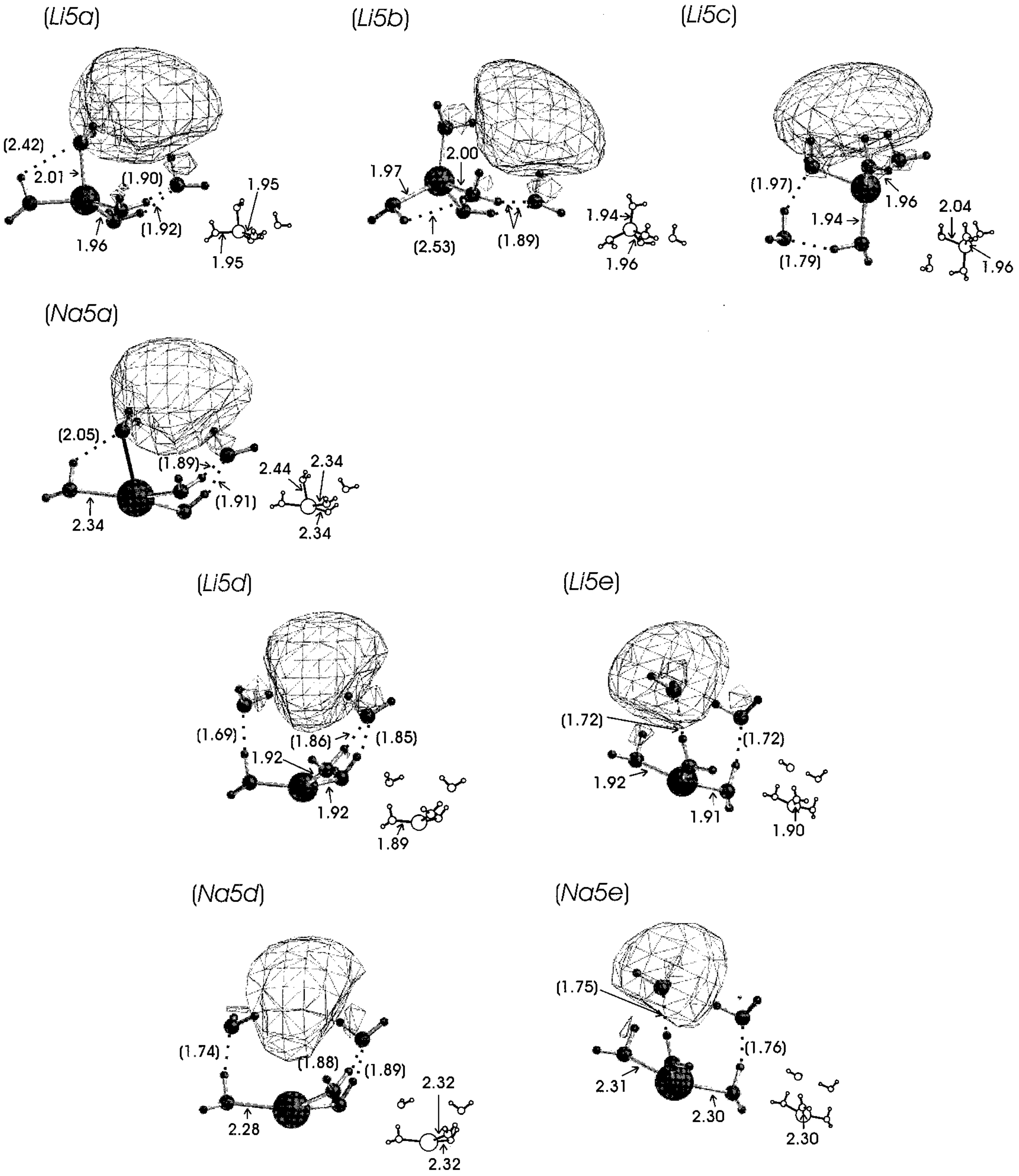

Figure 3. Optimized structures for Li(H_2O)$_5$ and Na(H_2O)$_5$.

two OH bonds of the second shell molecules interact with the ejected electron {e}. On the other hand, isomers M5e have only two hydrogen bonds, but three OHs strongly interact with {e}. The SEMs are small, in particular, for isomers M5e. There are more isomers of M3W and M2W types expected, with different hydrogen-bonding networks of water molecules.

There are many more isomers in M(H_2O)$_6$ than in M(H_2O)$_5$; some of them are reported by HK for M = Li[10] and HM for M = Na.[8] We have chosen two isomers of M5W and M4W of M(H_2O)$_6$ to examine the structural dependence of the vertical ionization energy. As already mentioned above, isomers M6a are derived from M5a by adding a water molecule at the other side of {e}. This extra water molecule lengthens R({e}−M), but the character of SOMO is not much affected, as both SEM and R({e}−H) are similar to each other in M6a and M5a. Isomers M6b are representatives of M4W; they are derived from isomers M5d of M3W by adding a water molecule to the metal ion. In Li6b, four of the oxygen atoms in the first shell are nearly tetrahedrally coordinated, while in Na6b they are distorted from the tetrahedral configuration, because of a hydrogen bond within the first shell. Even with this difference, the characteristic measures of SOMO are very similar to each other as is seen in Table 1. Isomer Li6a is slightly less stable (1.48 kcal/mol.) than isomer Li6b, while isomer Na6a is a little more stable than isomer Na6a. The energy difference is in any case insignificant. Hashimoto and co-workers reported several isomers for M(H_2O)$_6$ in their papers. Isomers HK-VIa and HM-m in Figure 4 and Table 1 are their most stable isomers for Li(H_2O)$_6$[10] and for Na(H_2O)$_6$,[8] respectively. To compare the relative stability, the structures were reoptimized with MP2/6-311++G(d,p) level of calculations. Isomer Li6b is a little less stable than HK-VIa. It is probably because the latter has two six-membered rings. Isomer Na6a of M4W is slightly more stable than isomer HM-m of M3W. The SOMOs of all isomers are semiinternal, except for HM-m, whose SOMO is quasi-valence in our definition, as a very short R({e}−M) indicates.

Concluding the subsection, we should emphasize that for $n \geq 4$ there are several (or many) isomers within 2 kcal/mol. The

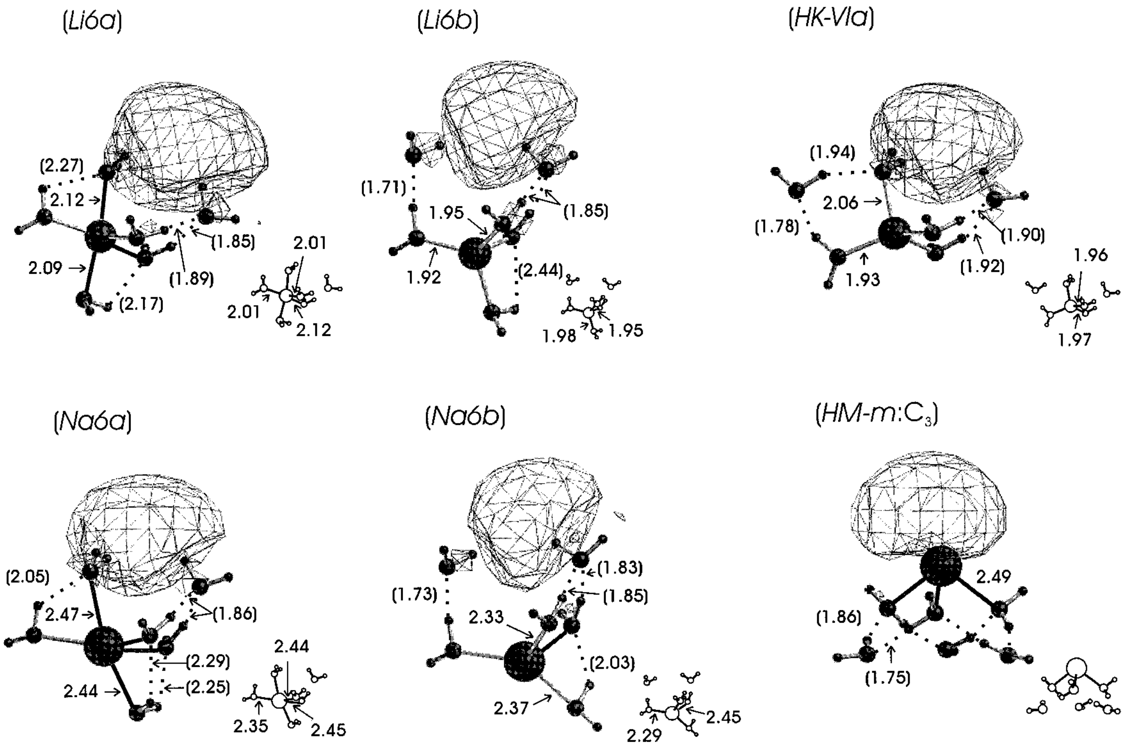

Figure 4. Optimized structures for Li$(H_2O)_6$ and Na$(H_2O)_6$.

ordering of the calculated stability energy among the isomers might be sensitive to the basis set superposition correction. Experimentally, it is most likely that a few of isomers coexist in the molecular beam, as was recently found in $(H_2O)_6^-$ [16] and $Mg^+(H_2O)_n$.[17]

Vertical Ionization Energies (VIEs), and Their Size and Metal Dependencies. Table 1 summarizes the calculated VIEs, which are evaluated by taking the difference of MP2 energies of the neutral and cation clusters at the optimized geometry for the neutral cluster. Before discussing the calculations, it is worth noticing what is experimentally known. Photoelectron spectra have not been measured for these neutral clusters because of the difficulty in size selection. Instead, the threshold photon energy, where the ions start to be detected in the mass spectrometer, is experimentally determined. The ITE would be close to the VIE, only if the geometries of the initial (neutral) and final (cation) clusters were similar to each other. In this case, both should be close to the adiabatic ionization energy. In the clusters we are studying, the cation clusters $M^+(H_2O)_n$ might be more strongly bound than the corresponding neutral clusters. More importantly, the interaction between the electron {e} and the OH bonds influences the geometric structures of hydrated water molecules in the neutral clusters, as we have seen in Figures 1−4. Therefore, it is expected that VIE will be larger than the ITE in most cases. There is another complication; if a few isomers coexist in the experimental beam condition, the observed ITE is determined by the isomer which has the smallest ITE. Table 1 (also the papers of HK and HM) shows that the energy difference among the isomers is small, and that the number of possible isomers increases with the size of clusters. So the direct comparison of the calculated VIE with the observed ITE is not straightforward. With these reservation, the trends in the calculated VIE are still informative in exploring the experimentally observed features in the ITE.

At a glance, the VIEs in Table 1 are almost size- and metal-independent; the values range from 3.3 to 4.0 eV. In Figure 5, the correlation between SEM and VIE (a) and between SEM and R({e}−M) (b) is shown. Distinctively the isomers of quasi-valence type (V) SOMO, M3c and M4e (M = Li and Na), have larger VIE, smaller SEM, and shorter R({e}−M) than the others. The VIE of M4e is larger than that of M3c, which is contrary

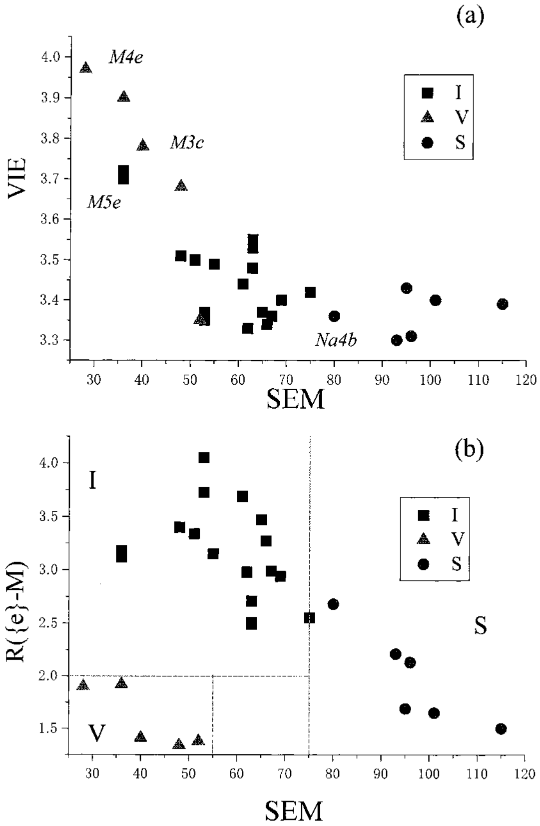

Figure 5. (a) Correlation between SEM (SOMO extent measure) and VIE (vertical ionization energy). (b) Correlation between SEM and R({e}−M). The broken lines indicate the criteria for classification of isomers.

to the experimental trends in ITE. The VIE decreases almost linearly with the SEM, except for HM-m. These isomers, except for Na3c, are less stable than the other isomers. Thus, we may be able to exclude these isomers as candidates for the clusters detected in the experiments.

In Figure 5, the isomers of surface type (S) SOMO, Li3a, M3b, Li4a, and M4b, are clearly distinguished from the others. They have almost same VIE; the VIEs of $M(H_2O)_4$ are slightly smaller than those of $M(H_2O)_3$. Experimental ITEs are 3.36 eV for $Li(H_2O)_3$,[1] 3.25−3.3 eV for $Na(H_2O)_3$,[2] 3.12 eV for $Li(H_2O)_4$,[1] and 3.17 eV for $Na(H_2O)_4$.[2] The calculated VIEs for $M(H_2O)_3$ are close to the experimental ITEs, although a slight difference in the experimental ITE of Li and Na is not reproduced in the calculations. The geometric structures of these isomers are expected not to be changed by the ionization, and the VIE should be close to the adiabatic and threshold ionization energies. The calculated VIE difference of surface type $M(H_2O)_3$ and $M(H_2O)_4$ is nearly 0.1 eV or less than that, which is slightly smaller than the experimental one. Among the isomers of surface type, isomer Na4b may be classified as an intermediate to semiinternal type, as Figure 5 shows. Two of water molecules interacting with {e} are the proton acceptors in the hydrogen bonds, and their hydrogen atoms become more positive. Because of stronger OH−{e} interaction, the SEM is reduced. In larger clusters, the hydrogen-bond network evolves, and the surface type SOMO is not possible to exist.

As Figure 5a shows, the VIEs of isomers having the semiinternal (I) type SOMO range from 3.3 to 3.5 eV, independently of the metal element and the size of clusters; the exception is isomers M5e, whose VIE is 3.7 eV; the reason for this will be discussed below. Even though isomers of the (I) type generally have a restricted range of VIE, SEM, and R({e}−M), the correlation among them is not so straightforward. It is because the structure of water molecules surrounding {e} does play a key role in determining both VIE and SEM; thus we have denoted the structure O−H{e}H−O. To analyze the determining factors of the VIE, more careful examination of the geometric and electronic structures of the clusters is required.

One of characteristics in the isomers of semiinternal type is the similarity of the structure of the corresponding isomer $Li(H_2O)_n$ and $Na(H_2O)_n$. The structures around the ejected electron {e} of the corresponding pairs (Li4c, Na4c), (Li4d, Na4d), (Li5a, Na5a), (Li5d, Na5d), (Li5e, Na5e), (Li6a, Na6a), and (Li6b, Na6b) resemble each other, although the difference in the ionic radii causes the structural change around the metal atom ion and the distance R({e}−M). Their structures have a common form of $M^+(H_2O)_m{\cdot}(H_2O)_m{\cdot}(H_2O)^-_{n-m-l}$ where the metal atom is ionized and becomes a hydrated ion $M^+(H_2O)_m$ ($m = 3-5$) in the clusters. The water cluster $(H_2O)_{n-m-l}$ traps an ejected electron and becomes a water cluster anion $(H_2O)^-_{n-m-l}$, which determines the shape of the SOMO, as are seen in the figures. The structure O−H{e}H−O is the essential part of the anion part. The energy required to ionize an electron is, however, governed not only by the anion part but also by the hydrated metal ion $M^+(H_2O)_m$. The potential (V_{SOMO}) on the SOMO electron could conceptually be written as $V_{\mathrm{SOMO}} = V^{\mathrm{HMI}}_{\mathrm{SOMO}} + V^{\mathrm{WC}}_{\mathrm{SOMO}}$, where $V^{\mathrm{HMI}}_{\mathrm{SOMO}}$ is a long-range potential of the hydrated metal ion (HMI) and $V^{\mathrm{WC}}_{\mathrm{SOMO}}$ is the short-range potential of the water cluster (WC) $(H_2O)_{n-m-l}$. Because of these two factors, the correlation of SEM with VIE and with R({e}−M), shown in Figure 5, looks somewhat weak. Nevertheless, the SEM and VIE of the pairs (Li5a, Na5a), (Li5d, Na5d), (Li5e, Na5e), and (Li6b, Na6b) are close to each other. The common feature among these pairs is that the pair has either long R({e}−M) or nearly equal R({e}−M). To examine the determining factors of the electronic structure of O−H{e}H−O and VIE more in detail, we analyze a few examples below.

Isomers M6b of M4W are derived from isomers M5d of M3W; in the former an extra water molecule hydrates to the metal ion. In all of these four isomers there are a very short (≤1.23 Å) and a short (≤1.88Å) R({e}−H)s. Besides, their SEMs are also close to each other (ranging from 48 to 53 Å^3). So, the local structure of O−H{e}H−O in M6b is similar to that in M5d. On the other hand, R({e}−M)s become longer in M6b than in M5d, which reduce $V^{\mathrm{HMI}}_{\mathrm{SOMO}}$, resulting in smaller VIE by 0.15 eV in M6b than in M5d. The pair (Li4c, Li5b) is another example of this type; they share the similar O−H{e}H−O structure, but VIE of Li5b is 0.20 eV smaller than that of Li4c.

Isomers M6b can be also regarded as derivatives of M5a; both have a M4W structure of the hydrated metal ion $M^+(H_2O)_m$. In M6b, a water molecule is added in the second shell, which causes the rearrangement of the hydrogen bonds in the cluster. As a result, the surrounding structure of the metal ion and the O−H{e}H−O structure undergo large changes. But the calculated VIEs are all nearly equal to each other (3.36−3.37 eV). We may be able to interpret this apparent size and metal independence as a result of the cancellation of $V^{\mathrm{HMI}}_{\mathrm{SOMO}}$ and $V^{\mathrm{WC}}_{\mathrm{SOMO}}$. Because R({e}−M) in M6b is longer than in M5a, $V^{\mathrm{HMI}}_{\mathrm{SOMO}}$ is weaker in M6b. On the other hand, a short R({e}−H) and smaller SEM in M6b suggest stronger {e}−HO interaction and larger $V^{\mathrm{WC}}_{\mathrm{SOMO}}$ than in M5a. A OH bond of the newly added water molecule leads to the stronger interaction; the water molecule is a proton-acceptor molecule in the hydrogen bond, and the hydrogen is more positively charged. Besides, the molecule can freely rotate to maximize the interaction with {e}. As a result, the SEMs of M6b become substantially smaller and $V^{\mathrm{WC}}{}_{\mathrm{SOMO}}$ larger than those of M5a. Two opposite effects are canceled out, and in effect the VIEs of M6b and M5a become nearly equal to each other.

We have seen the SEM is an appropriate measure to characterize the electronic structure of the ejected electron {e} and the O−H{e}H−O structure. Three factors can be identified in determining the O−H{e}H−O structure and $V^{\mathrm{WC}}_{\mathrm{SOMO}}$, and therefore its SEM. One is the strength of the bond dipole of the O−H bonds which directly interact with the ejected electron. It is known that as a hydrogen bond chain becomes longer, the charge on the terminal hydrogen atom becomes more positive and consequently the bond dipole of O−H bond becomes larger as mentioned above. It is also known that the hydrogen atoms of the proton-acceptor water molecules are more positively charged. This is particularly true for the double proton-acceptor molecule.[18] The larger bond dipoles of O−H bonds make SEM smaller. The examples are seen in the SEMs of pairs of isomers; Li5a (67 Å^3) and Li6b (53 Å^3), Na5a (65 Å^3) and Na6b (53 Å^3), Li4c (63 Å^3) and Li5d (51 Å^3), and Na4c (69 Å^3) and Na5d (48 Å^3). As the cluster size of semiinternal electron type becomes large and the hydrogen bond chain becomes long, the bond dipole of O−H bonds in the O−H{e}H−O structure becomes large. As a result, the SEM becomes smaller. Another factor is the number of OH bonds in the O−H{e}H−O structure. The SEM becomes smaller as the number of surrounding OH bonds increases. An example is the SEM of Li5e and Na5e, which have three OH bonds in the O−H{e}H−O structure; two of them are those of the proton-acceptor molecules. Their SEMs are as small as 36 Å^3. Because of the small SEM, their VIEs are as large as 3.70 eV, and in Figure 5a their points are located far from those of the other surface type isomers. The relative orientation of O−H bonds also plays a role. For example, when two dipoles of the opposite direction are collinear, the electrostatic potential well between the dipoles becomes the deepest. The factor may have little effect in the present cases, but it might play a role in the pure water cluster ions.

In our present level of calculations and with the restricted experimental data available, we cannot identify the experimentally detected isomers, which have nearly equal ionization threshold energy for $n \geq 4$ of $M(H_2O)_n$ (M = Li and Na). From the above results, we might, however, be able to deduce the working hypothesis for further studies. The ion-pair structure, $M^+(H_2O)_m{\cdot}(H_2O)_l{\cdot}(H_2O)^-{}_{n-m-l}$, is the basic unit of the clusters of $n > 5$; $m = 3$, 4, or 5. The most probable m is 4. Among the isomers we have studied, M4b, M5a, and M6b, all of which have a M4W core, explain the observed features, the convergence and the metal independence of VIE. They are the most stable or close to the most stable in energy. The metal independence of VIE results from the ion-pair structure as the experimentalists thought. The convergence of VIE is attained by the cancellation of two factors $V_{\mathrm{SOMO}}^{\mathrm{HMI}} + V_{\mathrm{SOMO}}^{\mathrm{WC}}$. In large n, R({e}−M) is long, and consequently the electrostatic potential $V_{\mathrm{SOMO}}^{\mathrm{HMI}}$ becomes weaker. At the same time, the hydrogen bond chain becomes longer and therefore the interaction between the ejected electron and the terminal O−H bonds becomes stronger, and $V_{\mathrm{SOMO}}^{\mathrm{WC}}$ becomes larger.

Conclusion

We have investigated the water clusters containing a group 1 metal atom $M(H_2O)_n$ (M = Li and Na) for $n = 3-6$ with ab initio MO methods. These isomers are classified into three types, and among these types of clusters the semiinternal electron type isomers have the ion-pair structure, $M^+(H_2O)_m{\cdot}(H_2O)_l{\cdot}(H_2O)^-_{n-m-l}$, in the clusters $M(H_2O)_n$, and possibly determine the features of the observed ITE. The structure of $(H_2O)^-_{n-m-l}$ part contains the O−H{e}H−O structure, and the structure around the ejected electron is determined by the interaction within the O−H{e}H−O structure. The calculations indicate that there are a few isomers of nearly equal stabilization energy. The number of those isomers increases substantially with n. Photoelectron spectra and vibrational spectra are more informative than ionization threshold spectra for the structures of the isomers. More theoretical work is in progress.[12] In the present study, we have reached a model to explain the observed convergence of ITEs at $n = 4$ and their metal independence. We cannot, however, say anything yet about why the converged value is the VIE of bulk water. To understand it, further extensive theoretical studies are required.

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