

# Ab Initio Molecular Orbital Study of Na(H<sub>2</sub>O)<sub>n</sub> (n = 1–6) Clusters and Their Ions. Comparison of Electronic Structure of the “Surface” and “Interior” Complexes

Kenro Hashimoto<sup>\*,†,§</sup> and Keiji Morokuma<sup>§,‡</sup>

Contribution from the Computer Center, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji-shi, Tokyo 192-03, Japan, The Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama 350-01, Japan, Institute for Molecular Science, Myodaiji Okazaki 444, Japan, and Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received June 9, 1994<sup>Ⓢ</sup>

**Abstract:** The stability and structure of Na(H<sub>2</sub>O)<sub>n</sub> (n = 1–6) as well as their ions have been investigated with the *ab initio* MO method. Both the surface structure where Na is situated on the surface of the water cluster and the interior structure where Na is surrounded by water molecules are minima on the potential surface. They are very close in energy, though the surface structure becomes dominant as *n* increases. The surface structure is stabilized mainly by the solvent–solvent interaction, while the interior structure is stabilized by the Na–solvent interaction. In the surface structure the SOMO electron is localized in the vicinity of Na opposite to the hydrating water molecules, whereas in the interior structure the SOMO density spreads into the region between water molecules. This difference is responsible to the difference in the *n* dependency of the ionization potential.

## I. Introduction

Chemistry and physics of clusters have recently been very actively investigated from both experimental and theoretical points of view.<sup>1–3</sup> The cluster consisting of an alkali metal atom and polar solvent molecules has been extensively studied by photoionization spectroscopy, often from the interest related to solvated electrons. With the recent advent of experimental techniques for measurement of the photoionization threshold, the *n* dependency of the ionization potential (IP) for small Na(H<sub>2</sub>O)<sub>n</sub><sup>4</sup> and Na(NH<sub>3</sub>)<sub>n</sub><sup>5</sup> clusters has attracted a renewed attention. Hertel and co-workers have reported that the ionization potential of Na(H<sub>2</sub>O)<sub>n</sub> clusters becomes constant for *n* ≥ 4, while that of Na(NH<sub>3</sub>)<sub>n</sub> decreases monotonically with *n*.<sup>6</sup> Similar results have been reported for Cs(H<sub>2</sub>O)<sub>n</sub> and Cs(NH<sub>3</sub>)<sub>n</sub> by Misaizu et al.<sup>7</sup> This surprising behavior of the *n* dependency of IP's of solvation clusters of alkali atoms has sometimes been considered as a sign of the existence of two-center localized states in these microclusters.<sup>6</sup>

These experimental findings have stimulated active theoretical interest.<sup>8–10</sup> The local spin density functional (LSD) study by Barnett and Landman<sup>8</sup> has shown that the structure of the neutral Na(H<sub>2</sub>O)<sub>n</sub> clusters resembles that of [Na(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> and the onset of the IP's as a function of *n* reflects the formation of the molecular shell where Na is surrounded by water molecules at *n* = 4.

On the other hand, we have reported our preliminary results of *ab initio* Hartree–Fock (HF) molecular orbital (MO) calculations on Na(H<sub>2</sub>O)<sub>n</sub> and Na(NH<sub>3</sub>)<sub>n</sub> systems<sup>9</sup> that Na tends to be located on the surface of the (H<sub>2</sub>O)<sub>n</sub> cluster in Na(H<sub>2</sub>O)<sub>n</sub> for *n* ≥ 4, while Na is surrounded by NH<sub>3</sub> molecules in Na(NH<sub>3</sub>)<sub>n</sub>, and that this structural difference results in the different behavior of their IP's. We have also studied the characteristic structures of Na(H<sub>2</sub>O)<sub>4</sub> and [Na(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> clusters and compared them at the correlated level of theory with large basis sets.<sup>10</sup> The total energy of the “surface” structure where Na is located on the surface of the water cluster and that of the “interior” structure where Na is surrounded tetrahedrally by water molecules are very close even when the basis set superposition error (BSSE) is taken into account at the correlated level of theory.

Though the question concerning the competition between the surface and the interior structures for *n* > 4 has remained unsolved in our previous paper,<sup>10</sup> for better understanding of the problem it is essential to clarify the similarities and dissimilarities between these structural isomers. In the present paper, we will report and discuss the comparison between the “surface” and the “interior” structure of Na(H<sub>2</sub>O)<sub>n</sub> (n = 1–6) and their ions for their geometry, energetics, and electron distribution based on *ab initio* MO calculations.

## II. Method

The molecular structures of Na(H<sub>2</sub>O)<sub>n</sub> (n = 1–6) and their ions were optimized by using the energy gradient method with the 6-31+G(d)

\* Address correspondence to this author at Tokyo Metropolitan University.

† The Institute of Physical and Chemical Research.

§ Institute for Molecular Science.

‡ Present and permanent address: Emory University.

Ⓢ Abstract published in *Advance ACS Abstracts*, November 1, 1994.

(1) Jena, P.; Khanna, S. N.; Rao, B. K., Eds. *Physics and chemistry of finite systems: from clusters to crystal*; NATO ASI Series, Vol. C374; Kluwer: Dordrecht, 1992; Vols. 1 and 2.

(2) Echt, O.; Recknagel, E., Eds. *Proceedings of the fifth International Meeting on Small Particles and Inorganic Clusters*; Konstanz, Federal Republic of Germany, September 10–14, 1990 (*Z. Phys. D* **1991**, *19*, 20).

(3) Berry, R. S.; Burdett, J.; Castleman, A. W., Eds. *Proceedings of the sixth International Meeting on Small Particles and Inorganic Clusters*; Chicago, USA, 16–22 September 1992, (*Z. Phys. D* **1993**, *26*).

(4) Schulz, C. P.; Gerber, A.; Nitsch, C.; Hertel, I. V. *Phys. Rev. Lett.* **1986**, *57*, 1703; *Z. Phys. D* **1988**, *10*, 279.

(5) Schulz, C. P.; Gerber, A.; Nitsch, C.; Hertel, I. V. *Z. Phys. D* **1991**, *20*, 65.

(6) Hertel, I. V.; Huglin, C.; Nitsch, C.; Schulz, C. P. *Phys. Rev. Lett.* **1991**, *67*, 1767.

(7) Misaizu, F.; Tsukamoto, K.; Sanekata, M.; Fuke, K. *Chem. Phys. Lett.* **1992**, *188*, 241.

(8) Barnett, R. N.; Landman, U. *Phys. Rev. Lett.* **1993**, *70*, 1775.

(9) Hashimoto, K.; He, S.; Morokuma, K. *Chem. Phys. Lett.* **1993**, *206*, 297.

(10) Hashimoto, K.; Morokuma, K. *Chem. Phys. Lett.* **1994**, *223*, 423.

basis set<sup>11</sup> and the Hartree-Fock (HF) method, i.e., at the HF/6-31+G(d) level. The diffuse functions on Na and O atoms are expected to provide enough flexibility in the basis set to describe the electronic state of the neutral complexes. The geometries of  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-4$ ) and surface structures of  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 5-6$ ) were optimized starting from the structures optimized at the HF/3-21G level in our previous preliminary study.<sup>9</sup> Geometries of the neutral interior structures of  $n = 4-6$  were optimized by keeping their molecular symmetry unchanged from those of the cation clusters with the same  $n$ . These structures should be more realistic than the assumed structures in a previous report,<sup>8</sup> taken without reoptimization from those of cation clusters.

The vibrational analysis using the analytical second derivative matrix was carried out to characterize the nature of the stationary points. If an optimized structure, usually with some symmetry constraints, has one or more imaginary frequencies, we further optimized the structure following the imaginary normal modes until we obtained the true local minimum structure where all the vibrational frequencies are real. The scale factor of 0.894 obtained from the averaged ratio of the three experimental fundamental frequencies<sup>12</sup> and the HF/6-31+G(d) calculated normal frequencies for an isolated  $\text{H}_2\text{O}$  molecule was utilized to calculate the enthalpy and Gibbs free energy of the Na-water complexes. Single point MP2/6-31+G(d)<sup>13</sup> calculations with frozen core approximation were performed at the HF/6-31+G(d) optimized geometries to assess the effect of electron correlation on the energetics. The Gaussian series of programs<sup>14</sup> was used.

### III. Optimized Structures

**A. Geometries of Neutral  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ).** The optimized geometries of the neutral  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ) are shown in Figure 1. All these structures have been confirmed to have all real vibrational frequencies.  $\text{Na}(\text{H}_2\text{O})$  has a  $C_{2v}$  structure a in which Na is bound to O.  $\text{Na}(\text{H}_2\text{O})_2$  has a  $C_s$  structure b having two Na-O bonds and one hydrogen bond. Although we have found another  $C_s$  structure with a large O-Na-O angle at the HF/3-21G level, the geometry optimization starting from either of the HF/3-21G geometries finally converged to one structure b at the HF/6-31+G(d) level. Hydrogen bond formation between two water molecules gives a small O-Na-O bond angle of less than  $90^\circ$ . The  $C_2$  structure with two equivalent Na-O bonds and no hydrogen bond was a transition state, though its energy is only 0.5 kcal/mol higher than that of b at this level of theory.

We have found three equilibrium structures (c-e) for  $\text{Na}(\text{H}_2\text{O})_3$ . The most stable one among them is  $C_3$  structure c. It is a surface structure where the Na atom is situated on the surface of the cyclic  $(\text{H}_2\text{O})_3$  cluster bound by three equivalent hydrogen bonds. Structure d, which is in  $C_1$  symmetry with three Na-O bonds and one hydrogen bond, is the complex where one water molecule is bound to structure b of  $\text{Na}(\text{H}_2\text{O})_2$  and can be regarded as a beginning of an interior structure, though only three water molecules are surrounding the Na atom. Structure e is a  $C_s$  structure where one  $\text{H}_2\text{O}$  molecule bridges two other  $\text{H}_2\text{O}$  molecules and has two Na-O bonds and two hydrogen bonds. The energies of the three isomers are close

and the differences are at most only 1.7 kcal/mol at the HF level and 2.0 kcal/mol at the MP2 level.

For  $\text{Na}(\text{H}_2\text{O})_4$ , we have found four structural isomers. One can see a clear difference in structure for the first time at  $n = 4$  between surface and interior structures. The most stable one is structure f with  $C_4$  symmetry. It is also a member of the surface structures with four Na-O bonds and four hydrogen bonds. The  $S_4$  symmetry structure, which was a minimum for the  $[\text{Na}(\text{H}_2\text{O})_4]^+$ , was not the minimum for the neutral complex. Isomer g was obtained by following the imaginary modes at the  $S_4$  symmetry structure, and it is a true interior structure at the HF/6-31+G(d) level as we have discussed in the previous study.<sup>10</sup> Na is surrounded tetrahedrally by four water molecules in this structure. Structures h and i are regarded as analogues of the structure reported for the isoelectronic  $[\text{Mg}(\text{H}_2\text{O})_4]^+$  system.<sup>15</sup> In these structures, one  $\text{H}_2\text{O}$  molecule is bound to  $\text{Na}(\text{H}_2\text{O})_3$  through two hydrogen bonds. The energy differences between these three types of structures, in particular between the surface and interior structures, are very small, at most 1.3 kcal/mol at the HF and 3.4 kcal/mol at the MP2 level.

The optimized equilibrium structures obtained for  $\text{Na}(\text{H}_2\text{O})_5$  are j-l. The first isomer j is the surface structure with three Na-O bonds and five hydrogen bonds. Na is situated on the  $(\text{H}_2\text{O})_3$  cluster and the two water molecules are bound to  $(\text{H}_2\text{O})_3$  from the opposite side of Na. The other two isomers k and l are interior structures. These structures were obtained by following the imaginary modes at the structure optimized with  $C_2$  symmetry, which gave a minimum for the  $[\text{Na}(\text{H}_2\text{O})_5]^+$  ion as discussed in the preceding section. These two isomers have four Na-O bonds and three hydrogen bonds and can be regarded as the complexes where one water molecule bridges two of the four water molecules in the interior  $\text{Na}(\text{H}_2\text{O})_4$  complex. Surface complex j is more stable than interior complex l by 2.1 kcal/mol at the HF level and 3.5 kcal/mol at the MP2 level and than k by 2.7 kcal/mol at the HF level and 4.2 kcal/mol at the MP2 level.

The optimized structures of  $\text{Na}(\text{H}_2\text{O})_6$  are shown in Figure 1 (m-o). Structures m and n are the surface structure and o is the interior structure. The most stable isomer m has a  $C_3$  symmetry structure with three Na-O bonds and six hydrogen bonds. Na atom is situated on the surface of the  $(\text{H}_2\text{O})_6$  cluster which consists of two layers of  $\text{H}_2\text{O}$  molecules, one directly interacting with Na and the other not. In the other surface structure n, there are four Na-O bonds and six hydrogen bonds. Na is on the  $(\text{H}_2\text{O})_4$  cluster and two other water molecules are bound to  $(\text{H}_2\text{O})_4$  as the second hydration shell. The  $D_{2d}$  symmetry structure is the minimum for the ion complex but not for the neutral complex. Interior structure o was obtained by following the imaginary modes at the  $D_{2d}$  symmetry structure and is a true interior structure for the neutral system. The energy lowering from the  $D_{2d}$  structure to the  $C_2$  structure is 2.1 (HF) kcal/mol. The energy of the Th symmetry structure where Na is surrounded by six equivalent  $\text{H}_2\text{O}$  molecules is higher than that of structure o by 4.4 kcal/mol (HF). Structure o and the Th symmetry structure correspond to the "4 + 2" and the "6" structure, respectively, found by Barnett and Landman with their LSD calculation,<sup>8</sup> though at the present level of calculation the former is a minimum but the latter is not. In structure o, there are four Na-O bonds and four hydrogen bonds. It can be regarded as the structure in which two  $\text{H}_2\text{O}$  molecules are bound to the interior  $\text{Na}(\text{H}_2\text{O})_4$  complex or one  $\text{H}_2\text{O}$  molecule is bound to the interior  $\text{Na}(\text{H}_2\text{O})_5$  complex, in either case via hydrogen

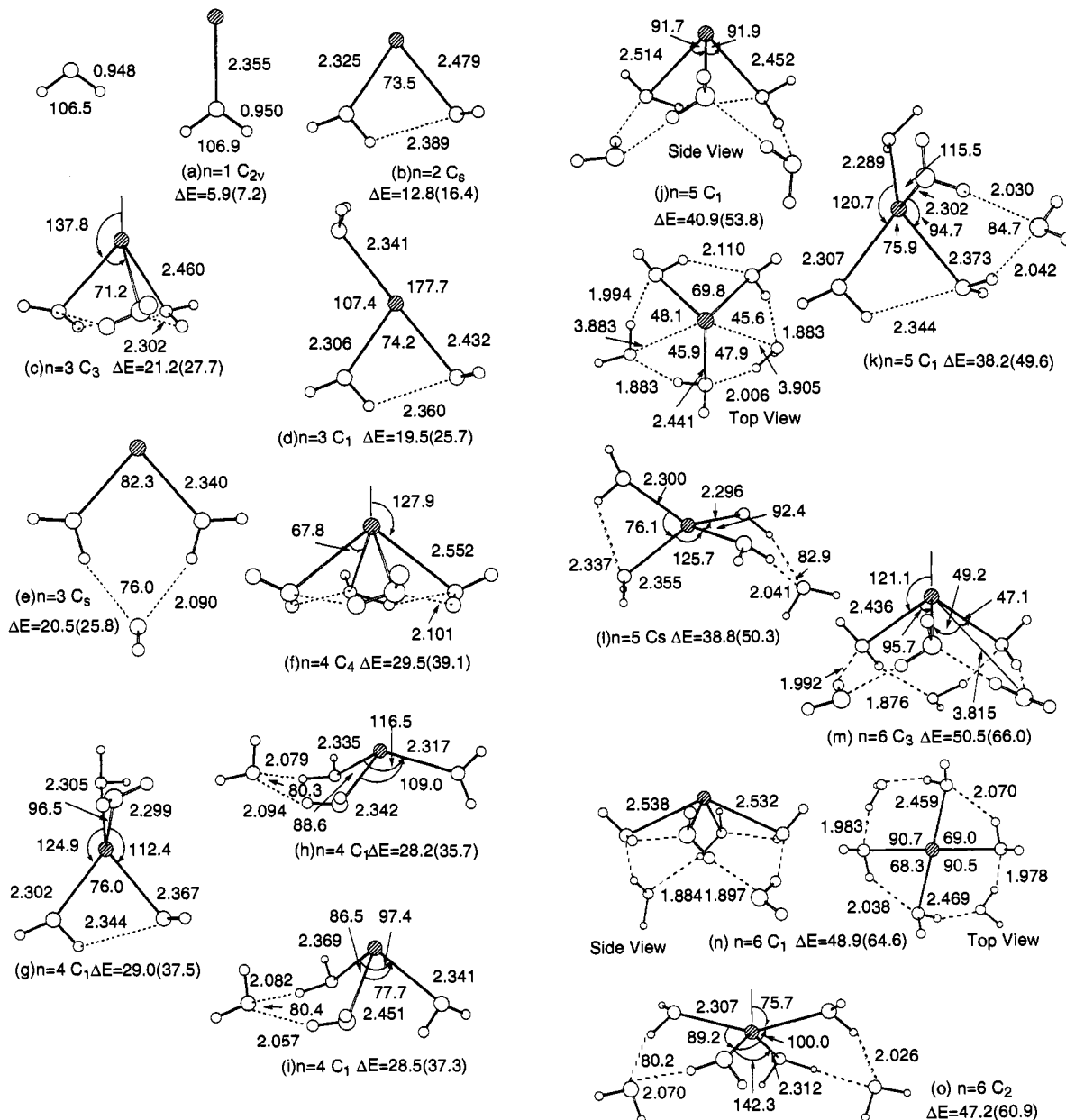
(11) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio molecular orbital theory*; Wiley: New York, 1986.

(12) Strey, G. J. *Mol. Spectrosc.* **1967**, *24*, 87.

(13) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(14) (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992. (b) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian Inc.: Pittsburgh, PA, 1990.

(15) Bauschlicher, C. W., Jr.; Partridge, H. *J. Phys. Chem.* **1991**, *95*, 9694.



**Figure 1.** Optimized structures of  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ) calculated at the HF/6-31+G(d) level. Geometrical parameters are given in Å and deg. Total binding energies in kcal/mol are also given. The values in parentheses are at the MP2/6-31+G(d)//HF/6-31+G(d) level.

bonds. Surface complex m is more stable than interior complex o by 3.3 kcal/mol at the HF level and 5.3 kcal/mol at the MP2 level.

**B. Geometries of  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ( $n = 1-6$ ) Ions.** The optimized geometries of the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ( $n = 1-6$ ) ions are shown in Figure 2. All these structures also have been confirmed to have all real vibrational frequencies. The molecular symmetries for  $n = 1-4$  are the same as those reported in the previous study.<sup>16</sup> Water molecules are bound directly to the  $\text{Na}^+$  ion by oxygen atoms avoiding the repulsion among the water molecules, as can be seen in a-d. As a result, in  $[\text{Na}(\text{H}_2\text{O})_4]^+$  four equivalent water molecules tetrahedrally surround the  $\text{Na}^+$  ion without forming a hydrogen bond. Bauschlicher et al.<sup>16</sup> have reported the geometrical parameters at the HF/DZ+d and TZ+2P levels. The Na-O distances they reported are 2.222 ( $n = 1$ ), 2.244 ( $n = 2$ ), 2.273 ( $n = 3$ ), and 2.304 ( $n = 4$ ) Å with the DZ+d basis set and 2.228 ( $n = 1$ ),

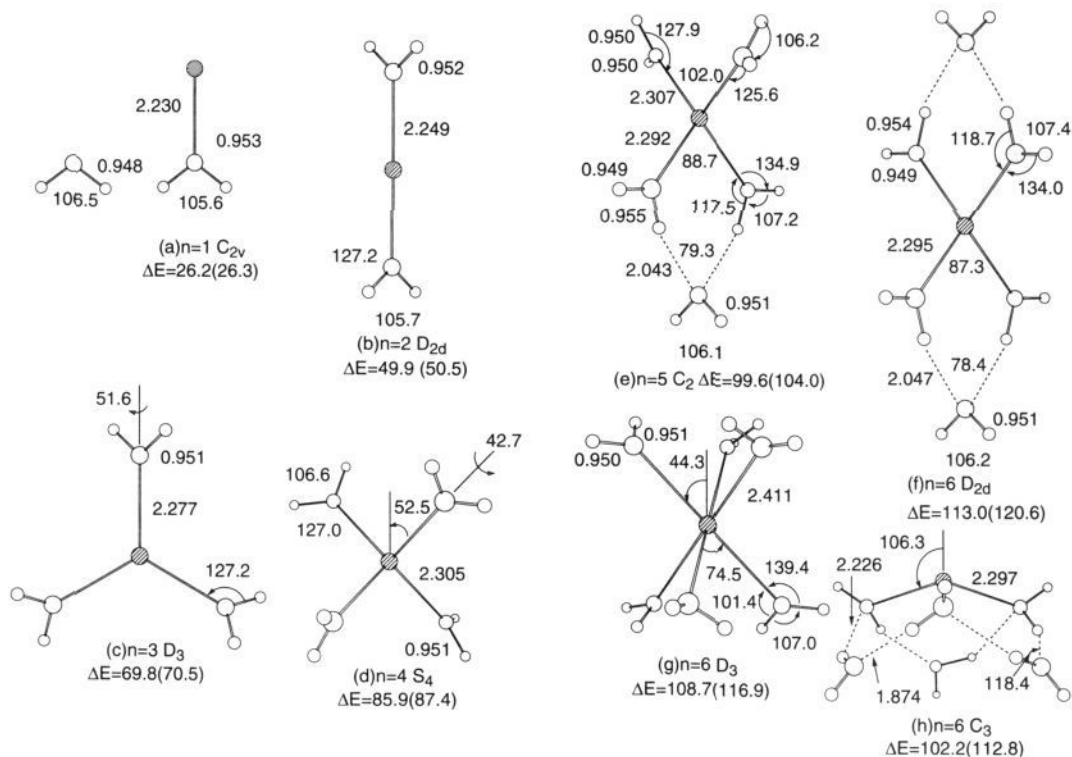
2.253 ( $n = 2$ ), 2.282 ( $n = 3$ ), and 2.317 ( $n = 4$ ) with the TZ+2P. They have shown that these parameters are not much affected by electron correlation at the MP2 level. Our distances obtained at the HF level with a smaller basis set but still with diffuse and polarization functions are in good agreement with theirs.

For the cation complexes with five or more water molecules, we find that the most stable structure is derived from the tetrahedral arrangement in  $[\text{Na}(\text{H}_2\text{O})_4]^+$  with more water molecules hydrating on the outside, as seen in e for  $[\text{Na}(\text{H}_2\text{O})_5]^+$  and f for  $[\text{Na}(\text{H}_2\text{O})_6]^+$ . Thus, the first hydration shell of the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ion can be considered to be closed at  $n = 4$ , which is similar to the case of the smaller isoelectronic system,  $\text{Be}^{2+}$ , we studied previously.<sup>17</sup>

For  $n = 6$ , in addition we have found the  $D_3$  symmetry structure g which can be considered to be of deformed  $T_h$

(16) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H.; Rice, J. E.; Konorovich, A. *J. Chem. Phys.* **1991**, *95*, 5142.

(17) (a) Hashimoto, K.; Yoda, N.; Iwata, S. *Chem. Phys.* **1987**, *116*, 193. (b) Hashimoto, K.; Iwata, S. *J. Phys. Chem.* **1989**, *93*, 2165. (c) Hashimoto, K.; Yoda, N.; Iwata, S.; Osamura, Y. *J. Am. Chem. Soc.* **1990**, *112*, 7189.



**Figure 2.** Optimized structures of  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ( $n = 1-6$ ) calculated at the HF/6-31+G(d) level. Geometrical parameters are given in Å and deg. The total binding energies in kcal/mol are also given. The values in parentheses are at the MP2/6-31+G(d)//HF/6-31+G(d) level.

**Table 1.** Total Binding Energy,  $\Delta E(n)$ ,<sup>a</sup> Solvent-Solvent Contribution,  $\Delta E_S(n)$ ,<sup>a</sup> and Solute-Solvent Contribution,  $\Delta E_M(n)$ ,<sup>a</sup> in kcal/mol for Neutral  $\text{Na}(\text{H}_2\text{O})_n$  and  $[\text{Na}(\text{H}_2\text{O})_n]^+$  Ion Complexes ( $n = 1-6$ ) Calculated at the HF/6-31+G(d) Level by the MP2/6-31+G(d)//HF/6-31+G(d) Method (Values in Parentheses)

n	neutral $\text{Na}(\text{H}_2\text{O})_n$						$[\text{Na}(\text{H}_2\text{O})_n]^+$ ion interior structure <sup>c</sup>		
	surface structure <sup>b</sup>			interior structure <sup>b</sup>			$\Delta E(n)$	$\Delta E_S(n)$	$\Delta E_M(n)$
	$\Delta E(n)$	$\Delta E_S(n)$	$\Delta E_M(n)$	$\Delta E(n)$	$\Delta E_S(n)$	$\Delta E_M(n)$			
1	5.9 (7.2)	0.0 (0.1)	5.9 (7.1)	5.9 (7.2)	0.0 (0.1)	5.9 (7.1)	26.2 (26.3)	0.0 (0.3)	26.2 (26.0)
2	12.8 (16.4)	0.3 (1.8)	12.5 (14.6)	12.8 (16.4)	0.3 (1.8)	12.5 (14.6)	49.9 (50.3)	-1.5 (-0.9)	54.1 (51.4)
3	21.2 (27.7)	5.2 (9.1)	16.0 (18.6)	19.5 (25.7)	-2.7 (-0.4)	22.2 (26.1)	69.8 (70.5)	-5.3 (-3.9)	75.1 (74.4)
4	29.5 (39.1)	12.7 (18.9)	16.8 (20.2)	29.0 (37.5)	-7.3 (-3.8)	36.3 (41.3)	85.9 (87.4)	-11.1 (-8.5)	97.0 (95.5)
5	40.9 (53.8)	24.7 (34.7)	16.2 (19.1)	38.8 (50.3)	-3.6 (2.9)	42.4 (47.4)	99.6 (104.0)	-6.9 (-1.2)	106.5 (106.2)
6	50.5 (66.0)	31.6 (44.3)	18.9 (21.7)	47.2 (60.7)	-2.6 (6.3)	49.8 (54.4)	113.0 (120.6)	-3.3 (5.3)	116.3 (115.3)

<sup>a</sup>  $\Delta E(n)$ ,  $\Delta E_S(n)$ , and  $\Delta E_M(n)$  are defined by eqs 1-3. See text. <sup>b</sup> For the neutral complex, the values for the most stable surface and interior structures are presented. <sup>c</sup> The values of the ion complexes are for the most stable interior structure.

symmetry where six equivalent water molecules are directly bound to the central  $\text{Na}^+$  ion. Although this deformation should provide an additional stabilization via hydrogen bonds, the energy of structure g is higher than that of tetrahedral structure f by 4.3 kcal/mol at the HF level and 3.7 kcal/mol at the MP2 level. We have also found another structure h starting optimization from the neutral surface structure in Figure 1 (m).  $\text{C}_3$  structure h, a local minimum, is higher in energy than the most stable complex f by about 10 kcal/mol. This structure h can be regarded as the surface structure of the  $[\text{Na}(\text{H}_2\text{O})_6]^+$  ion. The distance between Na and three oxygen atoms in the first layer is much shorter in the ion complex than in the neutral complex shown in Figure 1 (m). Probably as a result of this stronger Na-O interaction, the three weaker hydrogen bond distances are elongated from 1.992 (neutral) to 2.226 Å (ion), while the other three shorter and thus stronger hydrogen bond distances remain unchanged at around 1.875 Å. In general, the Na-O bond distances in  $[\text{Na}(\text{H}_2\text{O})_n]^+$  are shorter than those in the neutral  $\text{Na}(\text{H}_2\text{O})_n$  with the same  $n$ , as expected from the strong electrostatic interaction between  $\text{Na}^+$  ion and  $\text{H}_2\text{O}$  molecules.

#### IV. Energetics

**A. Energetics of Neutral  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ).** Total binding energies  $\Delta E(n)$  of both neutral  $\text{Na}(\text{H}_2\text{O})_n$  and ion  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ( $n = 1-6$ ) complexes are given in Figures 1 and 2 for each structural isomer. They are given by

$$-\Delta E(n) = E[\text{M}(\text{H}_2\text{O})_n] - E[\text{M}] - nE[\text{H}_2\text{O}]$$

$$(\text{M} = \text{Na and Na}^+) \quad (1)$$

The values of  $\Delta E(n)$  for the neutral  $\text{Na}(\text{H}_2\text{O})_n$  and  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ion are given in Table 1. For the isomers of the neutral complex with more than three  $\text{H}_2\text{O}$  molecules, the values of the most stable surface and interior complexes of each  $n$  are shown. The binding energy of the water dimer was calculated to be 5.4 and 6.9 kcal/mol with HF and MP2 methods, respectively, without correction for the basis set superposition error. These values are in reasonable agreement with the experimental value,  $5.44 \pm 0.7$  kcal/mol.<sup>18</sup> The total binding energies for both surface

(18) Curtiss, L. A.; Frurip, D. L.; Blander, M. J. *Chem. Phys.* **1979**, *71*, 2703.

and interior complexes are almost additive against the number of solvent water molecules,  $n$ . The slope of the total binding energies as a function of  $n$  is slightly larger for the surface complexes than for the interior complexes. That is the surface complex becomes more and more stable relative to the interior complex as  $n$  increases, and for the neutral  $\text{Na}(\text{H}_2\text{O})_n$  with larger  $n$  the surface complex is expected to be the dominant structure.

We will examine the relative energetics between two structural isomers in detail. For  $\text{Na}(\text{H}_2\text{O})_4$  we have reported that the energy difference between the two isomers is very small even if we take the BSSE (basis set superposition error) and the zero-point vibrational energies into account with a larger basis set.<sup>10</sup> At the present MP2/6-31+G(d)//HF/6-31+G(d) level (HF/6-31+G(d) level in parentheses), the  $n = 4$  surface complex *f* in Figure 1, which is more stable than the interior complex *g* by 1.6 (0.5) kcal/mol, is slightly less stable by 0.1 (1.2) kcal/mol when the zero-point vibrational correction (ZPC) is taken into account by the HF harmonic frequencies scaled by 0.894. The Gibbs free energy of surface complex *f* at 1 atm, 298.15 K, is even higher than that of interior complex *g* by 3.6 (4.7) kcal/mol. For  $\text{Na}(\text{H}_2\text{O})_5$ , the energy of surface complex *j* in Figure 1 is lower than that of interior complex *l* in Figure 1 by 3.6 (4.7) kcal/mol, and with the zero-point vibrational correction, the relative stability is reduced to 1.6 (0.3) kcal/mol. At 298.15 K and 1 atm, the Gibbs free energy of the surface complex is only 0.1 (1.4) kcal/mol higher than that of the interior complex. For  $\text{Na}(\text{H}_2\text{O})_6$ , for the first time a clear superiority of the surface structure emerges at all levels of calculation and at all temperatures: surface complex *m* in Figure 1 is more stable than interior complex *o* in Figure 1 by 5.3 (3.3) kcal/mol without ZPC and by 3.9 (1.9) kcal/mol with ZPC and has a lower Gibbs free energy by 3.2 (1.2) kcal/mol at 1 atm and 298.15 K.

Although the total stabilization energies of the surface and interior complexes are close to each other, their structures are very different and therefore the origin of stability could be quite different. Thus it is instructive to analyze the components of the total binding energies. Here, following our previous study,<sup>9</sup> we define the solvent-solvent contribution,  $\Delta E_S(n)$ , and the solute-solvent contribution,  $\Delta E_M(n)$ , by eqs 2 and 3, respectively.

$$-\Delta E_S(n) = E[(\text{H}_2\text{O})_n^\#] - nE[\text{H}_2\text{O}] \quad (2)$$

$$-\Delta E_M(n) = E[\text{M}(\text{H}_2\text{O})_n] - E(\text{M}) - E[(\text{H}_2\text{O})_n^\#] \\ (\text{M} = \text{Na and Na}^+) \quad (3)$$

Here,  $E[(\text{H}_2\text{O})_n^\#]$  is the energy of a complex of  $n$   $\text{H}_2\text{O}$  molecules whose structure is fixed at that of the  $\text{Na}(\text{H}_2\text{O})_n$  or  $[\text{Na}(\text{H}_2\text{O})_n]^+$  complex, and  $\Delta E_S(n)$  gives the interaction energy among the  $\text{H}_2\text{O}$  molecules in the Na or  $\text{Na}^+$  complex. The  $\Delta E_M(n)$  is the interaction energy between the prepared  $\text{H}_2\text{O}$  cluster and the Na atom or ion, and the sum of the two components gives the total binding energy  $\Delta E(n)$ :

$$\Delta E(n) = \Delta E_S(n) + \Delta E_M(n) \quad (4)$$

The values of  $\Delta E_S(n)$  and  $\Delta E_M(n)$  of both neutral and ion complexes are presented in Table 1.

In the neutral surface complex, the solute-solvent contribution,  $\Delta E_M(n)$ , increases up to  $n = 4$  and becomes almost constant for  $n \geq 4$ , while the solvent-solvent contribution,  $\Delta E_S(n)$ , increases monotonically even after  $n \geq 4$ . As a result, the surface complex is stabilized mainly by the solvent-solvent contribution in the case of  $n \geq 5$ . This feature in energetics is

closely related to the structure of the surface complex. In the stable surface complexes of  $n \geq 5$  the number of water molecules directly interacting with the Na atom is three and further hydration takes place onto these first-shell water molecules giving rise to the second solvation shell, as seen in Figure 1. On the other hand, the solute-solvent contribution,  $\Delta E_M(n)$ , is the main contributor of the total binding energy for the interior complex for all  $n$  examined. The solvent-solvent stabilization is always less than 10 kcal/mol and is negative or repulsive for  $n \geq 5$  at the HF level because the repulsion energy among the water molecules is larger than the stabilization energy by the hydrogen bonds in the "prepared"  $(\text{H}_2\text{O})_n^\#$  complex mentioned above. In other words, the stabilization gained by the new hydrogen bonds of the additional water molecule is upset by extra repulsion of this additional water molecule with other water molecules in the cluster. The SOMO, in which the diffuse nature of the Na 3s orbital is well retained, has a bonding character between that of the central Na and the surrounding water molecules. This orbital is considered to be responsible for the binding energy of the interior complexes. It changes almost proportionally to the number of Na-O bonds until the first shell closes.

It is interesting to notice that  $\Delta E_M(n)$  still increases for  $n \geq 5$  for the neutral interior complex though the slope becomes smaller than that for  $n \leq 4$ . It corresponds to the formation of the second solvation shell at  $n = 5$ . In order to understand the situation more clearly, we further divide the binding energy at  $n = 5$  by the following formula:

$$\Delta E(5) = \Delta E(\text{Na}-\text{W}_4^{\#1\text{st}}) + \Delta E(\text{Na}-\text{W}_1^{\#2\text{nd}}) + \\ \Delta E(\text{Na}-\text{W}_4^{\#1\text{st}}-\text{W}_1^{\#2\text{nd}}) + \Delta E(\text{W}_4^{\#1\text{st}}-\text{W}_1^{\#2\text{nd}}) + \\ \Delta E(\text{W}_4^{\#1\text{st}}) + \Delta E(\text{W}_1^{\#2\text{nd}}) \quad (5)$$

Here,  $\Delta E(\text{Na}-\text{W}_4^{\#1\text{st}})$  is the interaction energy between Na and the  $(\text{H}_2\text{O})_4$  part in the first shell of  $\text{Na}(\text{H}_2\text{O})_5$  and  $\Delta E(\text{Na}-\text{W}_1^{\#2\text{nd}})$  is that between Na and an  $\text{H}_2\text{O}$  in the second shell.  $\Delta E(\text{W}_4^{\#1\text{st}}-\text{W}_1^{\#2\text{nd}})$  is the interaction energy between the first shell  $(\text{H}_2\text{O})_4$  and the second shell  $\text{H}_2\text{O}$ .  $\Delta E(\text{Na}-\text{W}_4^{\#1\text{st}}-\text{W}_1^{\#2\text{nd}})$  is the three-body interaction term among Na, the first shell  $(\text{H}_2\text{O})_4$ , and the second shell  $\text{H}_2\text{O}$  molecule.  $-\Delta E(\text{W}_4^{\#1\text{st}})$  and  $-\Delta E(\text{W}_1^{\#2\text{nd}})$  are the energies of the  $(\text{H}_2\text{O})_4$  part and the second shell  $\text{H}_2\text{O}$  molecule relative to the isolated water molecules. The sum of the first three terms in (5) is equal to  $\Delta E_M(5)$  and that of the last three terms is equal to  $\Delta E_S(5)$ .  $\Delta E(\text{Na}-\text{W}_4^{\#1\text{st}})$ ,  $\Delta E(\text{Na}-\text{W}_1^{\#2\text{nd}})$ , and  $\Delta E(\text{Na}-\text{W}_4^{\#1\text{st}}-\text{W}_1^{\#2\text{nd}})$  are 41.5 (36.5), 1.1 (0.6), and 7.7 (5.3) kcal/mol, respectively, at the MP2(HF) level.  $\Delta E(\text{Na}-\text{W}_4^{\#1\text{st}})$  is larger than  $\Delta E_M(4)$  of the interior  $\text{Na}(\text{H}_2\text{O})_4$  by only 0.2 kcal/mol and  $\Delta E(\text{Na}-\text{W}_1^{\#2\text{nd}})$  is very small. The three-body term among Na and the two hydration shells is responsible for the increment of  $\Delta E_M$  for  $n \geq 5$ .

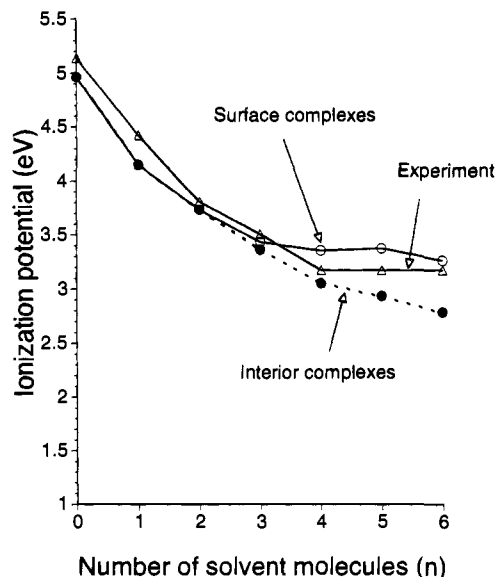
Thus we have shown that the total binding energy as a function of the number of  $\text{H}_2\text{O}$  molecules,  $n$ , increases almost linearly for both surface and interior complexes. The origin of stability, however, is very different between the complexes, reflecting their structural features.

**B. Energetics of  $[\text{Na}(\text{H}_2\text{O})_n]^+$  Ion ( $n = 1-6$ ).** The  $\Delta E(n)$ ,  $\Delta E_S(n)$ , and  $\Delta E_M(n)$  of  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ions are shown in the last three columns of Table 1. The total binding energy increases almost linearly with  $n$  and the slope is much larger than for the neutral complex, due to the strong electrostatic interaction between the  $\text{Na}^+$  ion and solvent molecules. As expected from their structures, the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ions are stabilized only by the solute-solvent interaction up to  $n = 4$ , causing the solvent molecules to be repulsive among themselves. The solvent-solvent repulsion decreases from  $n = 4$  to 6 due to the hydrogen

**Table 2.** Successive Binding Energy,  $\Delta E_{n-1,n}$ ,<sup>a</sup> and Successive Enthalpy Change,  $\Delta H_{n-1,n}$ ,<sup>b</sup> (1 atm, 298.15 K), Shown in *Italic*, of  $[\text{Na}(\text{H}_2\text{O})_n]^+$  in kcal/mol at Various Levels of Calculation and by Experiment

$n$	HF/6-31+G(d) (this work)	MP2/6-31+G(d)//HF/6-31+G(d) (this work)	HF/TZ+2P (ref 16)	HF/6-31G (ref 19)	experiment (ref 20)
1	26.2/24.1	26.3/24.2	24.7	33.7	24.0
2	23.7/21.7	24.2/22.1	22.1	31.0	19.8
3	19.9/17.8	20.0/18.0	18.4	29.6	15.8
4	16.1/14.2	16.9/14.9	15.0	27.1	13.8
5	13.7/11.1	16.6/14.0		21.3	12.3
6	13.4/10.8	16.6/14.0		17.8	10.7

<sup>a</sup>  $-\Delta E_{n-1,n} = E([\text{Na}(\text{H}_2\text{O})_n]^+) - E([\text{Na}(\text{H}_2\text{O})_{n-1}]^+) - E(\text{H}_2\text{O})$ . <sup>b</sup>  $-\Delta H_{n-1,n} = H([\text{Na}(\text{H}_2\text{O})_n]^+) - H([\text{Na}(\text{H}_2\text{O})_{n-1}]^+) - H(\text{H}_2\text{O})$ . Calculated using the harmonic vibrational frequencies calculated at the HF/6-31G(d) level and scaled by 0.894.



**Figure 3.** The calculated vertical ionization potentials in eV of  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ) complexes by the  $\Delta$ MP2 method at HF/6-31+G(d) geometries together with the experimental values. Solid lines are for the most stable surface complex and dashed lines are for the most stable interior complex for each  $n$ .

bond formation between the first shell and the second shell water molecules. The effect of electron correlation is very small, especially for  $n \leq 4$ , suggesting the dominant electrostatic nature of interaction in the first solvation shell.

For the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ions, theoretical successive hydration energies have been reported by two groups. Probst<sup>19</sup> has reported the values at the HF/6-31G level for  $n = 1-6$  and Bauschlicher et al.<sup>16</sup> have reported the values by the HF method with an extended basis set for  $n = 1-4$ . The experimental incremental enthalpy change under the condition of 1 atm and 298 K has been reported by Dzidic and Kebarle.<sup>20</sup> The values obtained in the present study are compared to these results in Table 2. The binding energy gradually decreases from about 26 (26) kcal/mol to about 17 (13) kcal/mol at the MP2 (HF) level as  $n$  grows, and it becomes almost constant at  $n = 5$  when water molecules start forming the second shell. The absolute values themselves are improved very much by adding the diffuse and polarization functions to the basis set and in good agreement with the previous theoretical results with the extended basis set.<sup>16</sup> The effect of the electron correlation estimated by the single point MP2 calculation is slightly larger for  $n \geq 5$  than for  $n \leq 4$ , presumably reflecting the fact that the second shell interaction is less electrostatic and the dispersion energy contribution is more important. The calculated enthalpy changes are also in good agreement with experiment.<sup>20</sup>

## V. Ionization Potentials of $\text{Na}(\text{H}_2\text{O})_n$ ( $n = 1-6$ ) Clusters

The vertical ionization potentials of  $\text{Na}(\text{H}_2\text{O})_n$  clusters calculated by the  $\Delta$ MP2 method as functions of  $n$  are shown in Figure 3. The calculated vertical ionization potentials of the surface  $\text{Na}(\text{H}_2\text{O})_n$  complexes decrease up to  $n = 4$  and become almost constant for  $n \geq 4$ . This peculiar behavior is considered to result from the structural feature of the surface  $\text{Na}(\text{H}_2\text{O})_n$  clusters. Only three or four water molecules interact directly with Na and further indirect hydration does not much affect the local electronic structure around Na, and the first ionization takes place from the singly occupied molecular orbital (SOMO) which is essentially localized at the Na atom as will be shown later. Therefore, the IP's of the Na complex should remain almost unchanged after it becomes a surface complex at around  $n = 4$ . On the other hand, the vertical ionization potentials of the interior  $\text{Na}(\text{H}_2\text{O})_n$  complexes as functions of  $n$  decrease monotonically with  $n$  though the slope of the function for  $n \geq 4$  becomes much smaller than that for  $n \leq 4$ . This behavior is understood by considering that the electronic structure around the Na atom is still affected by the fifth and sixth water molecules after the first hydration shell is completed at  $n = 4$ .

## VI. Electron Distribution

**A. Mulliken Population Analysis.** Mulliken atomic charges<sup>21</sup> of  $\text{Na}(\text{H}_2\text{O})_n$  and their ions are shown in Figures 4 and 5, respectively. For the neutral complexes, the results of the most stable surface and interior complexes are presented. Compared to the free state, the  $\text{H}_2\text{O}$  molecules in the complex are more polarized. The Na atom seems to be acting as a positive center, with the directly interacting oxygens more negatively charged and the hydrogens becoming more positively charged. Hydrogen bonds in the cluster are even more strongly polarizing the water molecules; hydrogen atoms taking part in hydrogen bonding are more positively charged than those without hydrogen bonds. The amount of charge transfer to the Na atom in the surface complexes is small, while that in the interior complexes is substantially larger.

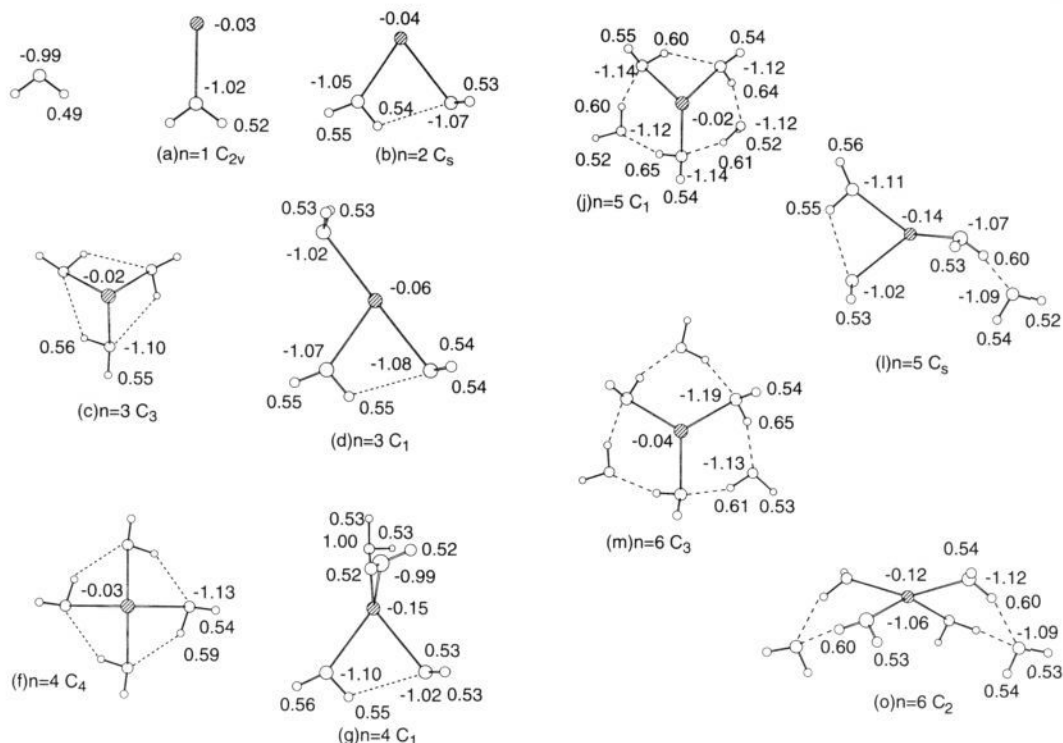
In the cation complexes, water molecules are more polar than the isolated  $\text{H}_2\text{O}$  as in the neutral complexes. No large difference can be found in the charge distribution of  $\text{H}_2\text{O}$  molecules between the neutral and cation complexes. This may provide some support to the model of small clusters in which the electron is trapped around the cation embedded in a polarizable media rather than to other models where the electron is separated from the cation and both are screened individually by the solvent. The charge on Na changes from 0.99 to 1.11 as the number of hydrating water molecules increases. Thus, Na in the cation complexes seems to become more positively charged by hydration. This counterintuitive result may possibly be an artifact of the Mulliken population analysis, but we have not pursued this further at this stage.

(19) Probst, M. M. *Chem. Phys. Lett.* **1987**, *137*, 229.

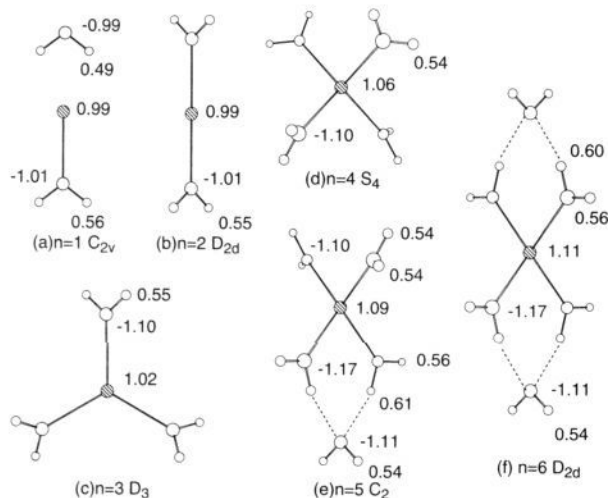
(20) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

(21) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.





**Figure 4.** Mulliken atomic charge distribution of  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ) at the HF/6-31+G(d) level. The alphabetical labels correspond to the structures shown in Figure 1.



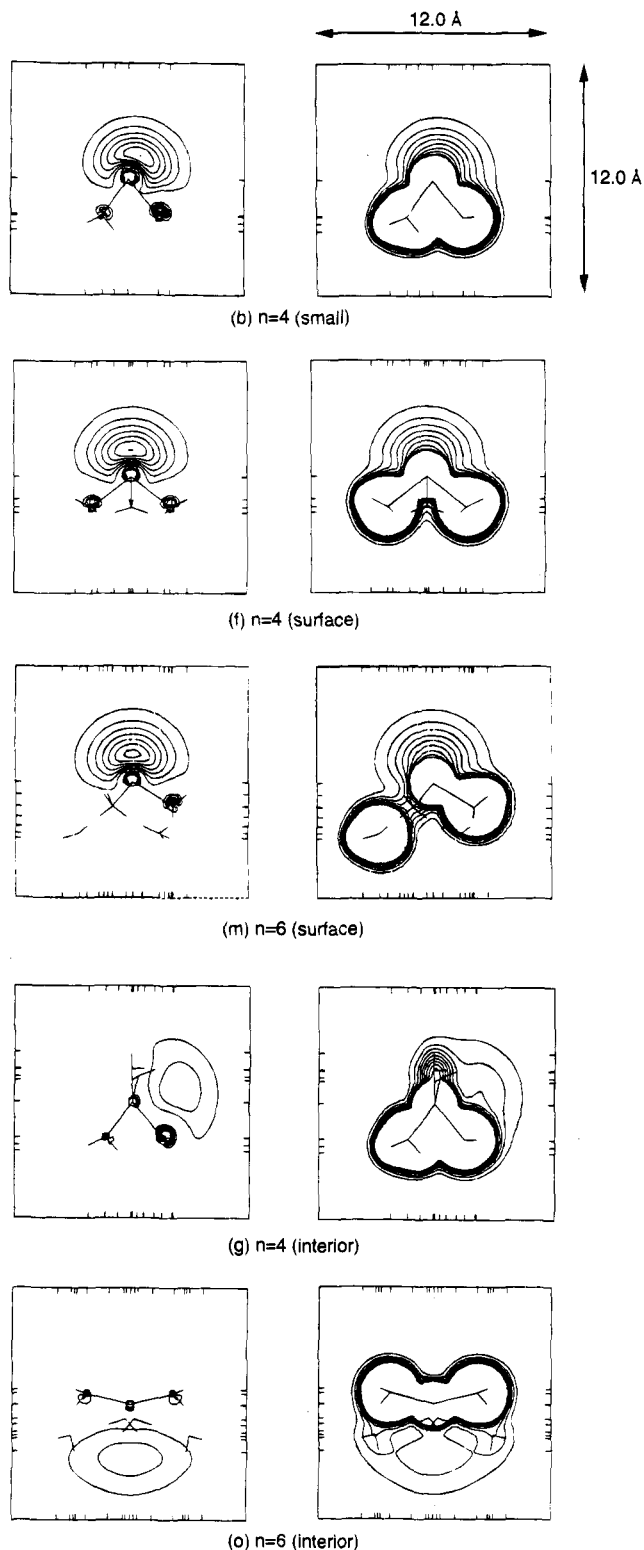
**Figure 5.** Mulliken atomic charge distribution of  $[\text{Na}(\text{H}_2\text{O})_n]^+$  ( $n = 1-6$ ) at the HF/6-31+G(d) level. The alphabetical labels correspond to the structures shown in Figure 2.

**B. SOMO and Total Electron Distribution in Neutral  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ) Complexes.** Shown in Figure 6 are the SOMO and the total electron density maps of  $\text{Na}(\text{H}_2\text{O})_n$  for the most stable surface and interior complexes with  $n = 2, 4$  and 6. Those for  $n = 1, 3$ , and 5 appear in the supplementary material. Looking at the left side of Figure 6, parts b through m corresponding to small ( $n \leq 2$ ) or surface ( $n \geq 3$ ) complexes, one can easily notice that the SOMO electron density is mostly localized in the vicinity of the Na atom and extends widely in space in the directions where hydrating  $\text{H}_2\text{O}$  molecules do not exist. The SOMO density distributions around the Na atom resemble one another from  $n = 1$  to 6. They are even quantitatively nearly unchanged for  $n = 4-6$ ; one can put all three plots in one without recognizing a difference. This similarity of the SOMO density distribution, especially for  $n =$

4-6, is considered to give rise to the peculiar  $n$  dependence of the ionization potential of the surface complexes; the IP decreases up to  $n = 4$  and becomes almost constant for  $n \geq 4$ .<sup>6</sup> For larger  $n$ , additional water molecules will interact directly with the water molecules but not with Na, and thus the constancy of the IP will be maintained.

The total electron density on the right side of Figure 6, parts b through m, is heavily concentrated in the bulk region, or the region on and between the Na and  $(\text{H}_2\text{O})_n$  cluster. On the other hand, the SOMO electron distribution, as just discussed, is concentrated in the surface region of the cluster, i.e., in the vicinity of Na opposite to hydrating  $\text{H}_2\text{O}$  molecules. Actually in this region, the total density agrees nearly completely with the SOMO density, indicating that no other electrons exist here. Since the SOMO is responsible to the first ionization, we may say that the surface ionization takes place in the surface complex of  $\text{Na}(\text{H}_2\text{O})_n$ .

On the other hand, the electron distributions in the interior complexes presented in parts g and o in Figure 6 are quite different from those in the surface complexes. Some SOMO density is found on Na and O atoms. Some space between hydrating water molecules is filled with an electron distribution. A comparison of the SOMO density and the total electron density for each interior  $\text{Na}(\text{H}_2\text{O})_n$  complex in Figure 6 shows that the SOMO density in the interior complex concentrated more inside the total electron cloud than for the corresponding surface complex. Thus, one may say that in the interior complex an interior ionization takes place. However it is important to notice in part o of Figure 6 for  $\text{Na}(\text{H}_2\text{O})_6$  that the SOMO density is not completely shielded inside the total electron cloud but extends in the region between the first and second solvation shells. As  $n$  increases through 6 and over, additional water molecules forming the second solvation shell will still be able to interact with the SOMO and thus give rise to an  $n$  dependency of the ionization potential for interior  $\text{Na}(\text{H}_2\text{O})_n$  complexes. Of



**Figure 6.** Contour maps of the SOMO and the total electron density for  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 2, 4$ , and  $6$ ) at the HF/6-31+G(d) level. The SOMO and the total density are shown on the left side and the right side, respectively. The alphabetical labels correspond to the structures shown in Figure 1. The spacing of the contour is  $0.0005 \text{ e}/\text{Bohr}^3$ , with those of over  $0.005$  are omitted. The Na atom is placed at the origin in each figure. The plot is made in the molecular plane for b. In f, the  $C_4$  axis and two oxygen atoms define the plotting plane. In m, the  $C_3$  axis and one of the oxygen atoms in the first shell are placed on the plotting plane. In g, the Na atom and two oxygen atoms drawn in the lower part of the figure are on the plotting plane. In o, the  $C_2$  axis and two upper oxygen atoms are in the plotting plane.

course, as  $n$  increases further, the slope of the  $n$  dependency of IP is expected to diminish.

## VII. Concluding Remarks

In the present paper, we have investigated the  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ) complexes as well as their ions with the *ab initio* MO method. We have focused on the similarities and differences of the "surface" and "interior" structures of  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1-6$ ), both of which are minima on the potential energy surface. In the neutral complexes, the surface structure has the Na atom situated on the surface of the  $(\text{H}_2\text{O})_n$  cluster. On the other hand, in the interior structure, the Na atom is surrounded by four  $\text{H}_2\text{O}$  molecules in the first solvation shell and more on the second shell. Although the total solvation energy is nearly linear with respect to the number of solvent molecules in both isomers, the origin of the stabilization energy is quite different. The solvent-solvent interaction due to the hydrogen bonds is the main contributor in the surface complexes for  $n = 4-6$ , while the solute-solvent interaction is dominant in the interior complexes. A balance between Na-O bonds and hydrogen bonds is important for stabilization of the interior structure. The interior structure of the neutral complex is slightly different from that of the ion complex in the orientation of water molecules with hydrogen bonds.

The total energies of the surface and of the interior structures are very close. At the present level of calculation, a clear superiority of the surface structure is first seen at  $n = 6$ , though the exact value of  $n$  will depend on the accuracy of the calculation. Though the Mulliken population analysis shows that the odd electron in the neutral complex can be regarded as trapped in the polarizable media for both structures, a comparison of the spatial distribution of the SOMO density clearly shows their differences. The surface structure has the SOMO electron localized in the region of Na opposite to hydrating water molecules, whereas the interior structure has the SOMO electron distributed on and between Na and hydrating water molecules. This difference in the SOMO distribution gives rise to the difference in  $n$  dependency of the IP between two structures.

It would be interesting and important to make a systematic comparison of the  $\text{Na}(\text{NH}_3)_n$  cluster with  $\text{Na}(\text{H}_2\text{O})_n$  whose ionization potential has been reported to show a different  $n$  dependency. The results of such a comparison will be presented in a separate paper.

**Acknowledgment.** This work was financially supported by the Grants-in-Aid in Priority Areas, "Molecular Approaches to Non-equilibrium Processes in Solutions" (Nos. 02245108, 03231106, and 04215225) and "Theory of Chemical Reaction" (No. 05227228) from the Ministry of Education, Science and Culture, Japan. K.H. is grateful to the support from the special researchers' basic science program in the Institute of Physical and Chemical Research (RIKEN) at the early stage of this work. The IBM3090/30J and RS/6000 computers were used at the computer center in Tokyo Metropolitan University (TMU).

**Supplementary Material Available:** Contour maps of the SOMO and the total density for  $\text{Na}(\text{H}_2\text{O})_n$  ( $n = 1, 3$ , and  $5$ ) at the HF/6-31+G(d) level (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.