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Ab Initio MO Study of $Na(NH_3)_n$ ($n = 1-6$) Clusters and Their Ions: A Systematic Comparison with Hydrated Na Clusters

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Abstract: Stability and structure of $Na(NH_3)_n$ ($n = 1-6$) clusters as well as their ions have been investigated by the *ab initio* MO method and systematically compared with those of $Na(H_2O)_n$ clusters. Both neutral and ion ammonia complexes with $n \geq 4$ have an interior structure where Na is surrounded by NH_3 molecules rather than a surface structure preferred by $Na(H_2O)_n$ clusters. Both neutral and ion clusters are stabilized by the Na−N bonds; the interior structure allows formation of a maximum number of such bonds in the first solvation shell. The calculated ionization potential as a function of the number of solvent molecules is in good quantitative agreement with experiment and behaves differently from that of the surface structures of $Na(H_2O)_n$ clusters. In the interior structure the SOMO (singly occupied molecular orbital) electron is distributed on and between Na and solvent molecules inside the cluster; interior ionization is expected to take place.

I. Introduction

The solvated electrons, in particular, in polar molecules, have been subjects of continued research from chemical, physical, and biological points of view.[1−3] Recent experimental success[4−6] in observing isolated negative water and ammonia clusters and theoretical progress[7−10] have attracted renewed attention to this celebrated subject. In addition, the experimental development of measuring the photoionization threshold for small $Na(H_2O)_n$[11] and $Na(NH_3)_n$[12] clusters has begun to uncover electronic and structural properties of solvated alkali metal atom clusters and solvated electrons. Measurement of the ionization potentials (IPs) of alkali atoms M (M = Na[13] and Cs[14]) in the size-selected H_2O and NH_3 clusters has found that the IP of $M(H_2O)_n$ clusters decreases monotonically up to $n = 4$ and becomes constant for $n \geq 4$ while that of $M(NH_3)_n$ shows a monotonic decrease with n. Although there have been some theoretical studies on the energetics, spectra, and structures of solvated electrons in pure solvent cluster systems,[15−18] these surprising findings on solvated alkali metal systems have motivated new theoretical challenges on the $Na(H_2O)_n$ system.[19−23] A local spin density functional (LSD) study[19] has suggested that the onset of the IPs of $Na(H_2O)_n$ as a function of n reflects the formation of the molecular shell and the structural similarity between the neutral and ion cluster.

On the other hand, we have performed *ab initio* MO study of the stability and structure of $Na(H_2O)_n$ ($n = 1-6$) as well as their cations, including the electron correlation effect.[21,22] For the neutral complexes, 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 for $n \geq 3$. Though they are very close in energy for $n = 3$ to 5, the surface structure becomes dominant at $n = 6$ and is expected to become more so for higher n. The surface structure is stabilized mainly by solvent−solvent interaction, while the interior structure is stabilized by Na−solvent interaction. In the surface structure, the SOMO electron is localized in the vicinity of Na opposite the hydrating water molecules, whereas in the interior structure the SOMO electron is distributed on and between Na and water molecules within the cluster. This difference is considered to give rise to a difference in the n dependency of the ionization potential between surface and interior structures. For the cation clusters $[Na(H_2O)_n]^+$ ($n = 1-6$), only the interior structure is a local minimum on the potential energy surface. The strong Na^+−

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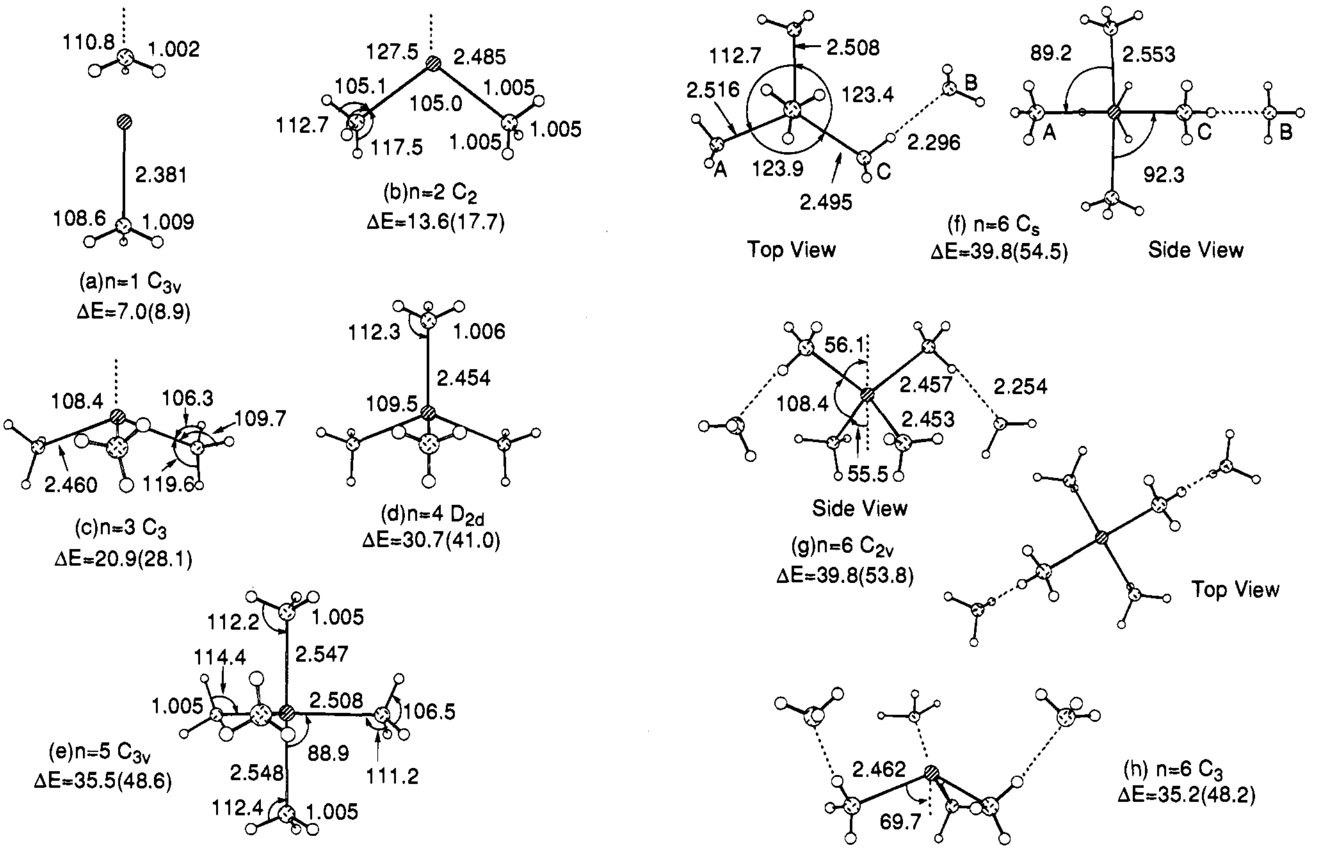

Figure 1. Optimized structures of $Na(NH_3)_n$ (n = 1−6) calculated at the HF/6-31+G(d) level. Geometrical paramaters are given in angstroms and degrees. Total binding energies in kcal/mol are also given. The values in parentheses are at the MP2/6-31+G(d)//HF/6-31+G(d) level.

solvent interaction overshadows the solvent−solvent interaction and dictates the structure.

Very recently, Stampfli and Bennemann have investigated the binding energies and ionization potentials of $Na(H_2O)_n$ and $Na(NH_3)_n$ by the polarizable electropole model.[23] They suggested an asymmetric shape for the former cluster from the discprepancy of the theoretical IPs as functions of n for a spherical model. In order to confirm if the different n dependency of IPs between $Na(H_2O)_n$ and $Na(NH_3)_n$ is actually due to the difference in the preferred structure, it is essential to carry out a calculation including electron correlation for $Na(NH_3)_n$ cluster. In the present paper, we have extended our preliminary study of $Na(NH_3)_n$ (n = 1−6) system[20] to higher levels of the *ab initio* MO calculation to discuss the structure and electronic nature of the clusters and their ions in more detail and make a systematic comparison with the similar results for $Na(H_2O)_n$ clusters and their ions.[22]

II. Method

The molecular structures of $Na(NH_3)_n$ (n = 1−6) and their cations were optimized by using an energy gradient with the Hartree−Fock (UHF for the neutrals and RHF for the ions) method with the 6-31+G(d) basis set,[24] i.e., at the HF/6-31+G(d) level. The 6-31+G(d) basis set, used for the hydrated Na systems in the previous studies,[21,22] contains diffuse s and p functions on Na and N atoms that are expected to provide enough flexibility to describe the electronic state of the neutral complexes. The geometries of neutral $Na(NH_3)_n$ (n = 1−6) were optimized starting from the structures optimized at the HF/3-21G level in our preliminary study.[20] Structures of ion complexes were optimized starting from the initial geometries obtained by replacing the H_2O molecules by NH_3 molecules in the corresponding $[Na(H_2O)_n]^+$ (n = 1−6) system we studied previously.[22] 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 the true local minimum structure is reached where all the vibrational frequencies are real. Single point MP2/6-31+G(d)[25] calculations with frozen core approximation were performed at the HF/6-31G(d)-optimized geometries to assess the effect of electron correlation on the energetics. The scaled HF/6-31+G(d) harmonic vibrational frequencies were utilized to calculate the zero point vibrational corrections and Gibbs free energies of some complexes. The scale factor of 0.879, obtained as the average ratio of the experimental[26] and the calculated frequencies of four normal modes of NH_3, was adopted. The Gaussian series of programs[27] was used.

III. Optimized Structures

A. Geometries of Neutral $Na(NH_3)_n$ (n = 1−6). The optimized geometries of the neutral $Na(NH_3)_n$ (n = 1−6) clusters are shown in Figure 1. All these structures have been confirmed to have all real vibrational frequencies.

$Na(NH_3)$ has a C_{3v} structure (a) in which Na is bound to the N atom. $Na(NH_3)_2$ has a C_2 structure (b) having two equivalent Na−N bonds. Both C_{2v} and C_s structures were transition states for NH_3 rotation, but their energy barriers were nearly zero (less than 0.1 kcal/mol) at the HF level. Consistent with this small

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energy difference, the scaled frequencies for internal rotation of NH_3 molecules in structure (b) are small, i.e., 9 and 16 cm^{-1}. Thus, the two NH_3 ligands can rotate almost freely.

$Na(NH_3)_3$ has a C_3 structure (c) and $Na(NH_3)_4$ has a D_{2d} structure (d). In structure (d), one NH_3 molecule is bound to Na from the open site of $Na(NH_3)_3$ (c) and Na is surrounded tetrahedrally by NH_3 molecules. In structures (c) and (d), all NH_3 molecules are equivalent. The scaled frequencies of NH_3 rotation are 14−16 cm^{-1} for (c) and 26−37 cm^{-1} for (d), and NH_3 ligands can rotate almost freely also in these structures.

$Na(NH_3)_5$ has a C_{3v} structure (e) where one additional NH_3 molecule is bound to Na via an open face of $Na(NH_3)_4$ (d). Structure (e) is trigonal bipyramidal and three equatorial Na−N bonds are shorter than the two axial Na−N bonds. A C_s structure optimized after removal of one of the outer shell NH_3 molecules from the C_{2v} structure of $Na(NH_3)_6$ (g) (vide infra) was not a local minimum. Thus for $Na(NH_3)_n$, $n = 1-5$, only one equilibrium structure for each n has been found. The scaled frequencies of NH_3 rotation for the C_{3v} structure (e) are 12−67 cm^{-1}. Though the maximum frequency of NH_3 rotation becomes a little larger for $n = 5$ than that for the smaller n due to its coupling with the axial N−Na−N bending vibration, these frequencies are still very small and NH_3 ligands can rotate nearly freely.

Three isomers have been found for $Na(NH_3)_6$. The most stable structure is a C_s structure (f) where one NH_3 molecule is hydrogen-bonded as a proton acceptor to an NH bond of one of the NH_3 ligands in $Na(NH_3)_5$. This type of structure can be called a "5 + 1" structure, indicating five first-solvation-shell and one second-shell NH_3 ligands. In structure (f), two "axial" Na−N bonds in the C_{3v}-like first shell are longer than the three "equatorial" bonds are also are longer than the axial Na−N bonds in $Na(NH_3)_5$ (e). The bond between Na and the NH_3 connected with the outer NH_3 through a hydrogen bond becomes shorter than those in $Na(NH_3)_5$ due to the head−tail cooperative effect. In order to examine the rotational effect of NH_3 molecules, we have optimized, in addition to (f), three more "5 + 1" structures where an equatorial first-shell N^AH_3 molecule and the second-shell N^BH_3 molecule are rotated from the structure of (f) by (0, 180°), (180°, 0), and (180°, 180°), respectively. The energies of these structures are only slightly higher, at most 0.11 kcal/mol, than that of (f). Thus, in the "5 + 1" structure, the NH_3 molecule in the first solvation shell as well as that in the second solvation shell rotates nearly freely, obviously except for the rotation of the first shell N^CH_3 molecule, which is the proton donor, where the rotation should be completely suppressed.

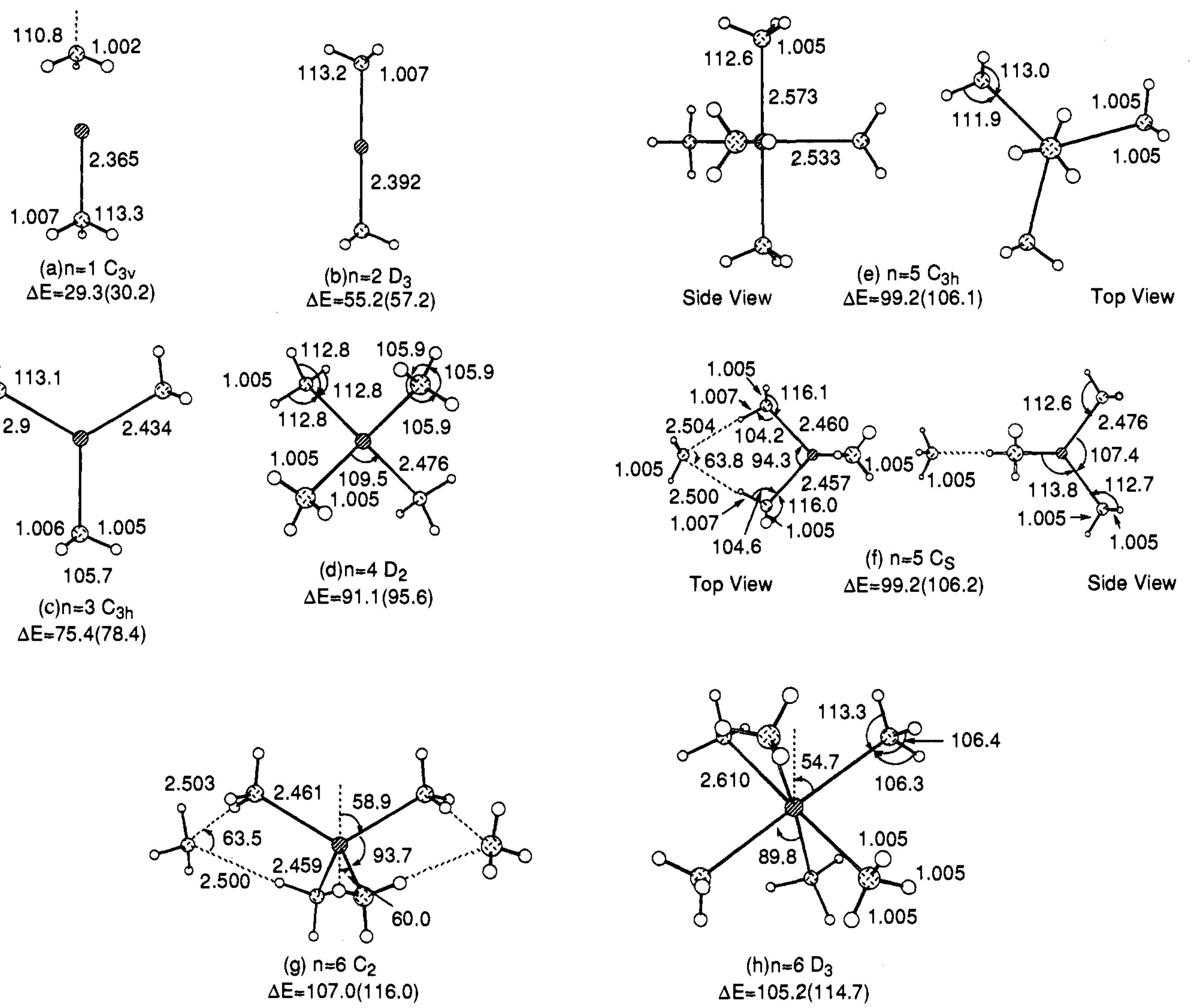
The second most stable structure at the present level of calculation is a C_{2v} structure (g). In structure (g), Na atom is surrounded tetrahedrally by four NH_3 molecules, two of which are further solvated each by a second-shell NH_3 molecule through a hydrogen bond. Thus this is a "4 + 2" structure. As will be discussed, this structure (g) is as stable as (f) at the HF level and only slightly less stable, by 0.7 kcal/mol, than (f) at the MP2 level. Calculation at a substantially higher level than the present level of MP2 energy at HF-optimized geometry would be required to reliably predict the relative stability of the "5 + 1" structure (f) and the "4 + 2" structure (g). The third isomer of $Na(NH_3)_6$ has a C_3 structure (h), where three NH_3 molecules are bound to $Na(NH_3)_3$ (c) through hydrogen bonds forming the second shell. This structure can be called a "3 + 3" structure. The stability of (h) is about 5 kcal/mol lower than that of (f) and (g).

Thus, the most stable structures of $Na(NH_3)_n$ for $n \geq 4$ are the *interior* structures where Na is surrounded by four or five NH_3 molecules forming the inner or first solvation shell. Even structure (h) of $Na(NH_3)_6$ can be regarded more as the structure where three $(NH_3)_2$ complexes are equivalently bound to the Na atom rather than the structure where Na is situated on the surface of the hydrogen-bonded $(NH_3)_6$ cluster. Thus there is no *surface* structure found in our optimization of $Na(NH_3)_n$. Even among the interior structures, NH_3 molecules in the inner shell are so oriented that the repulsion, both electrostatic and exchange, among them is the smallest. This situation is in dramatic contrast with the situation for $Na(H_2O)_n$ for $n \geq 4$, where interior and surface structures are very close in energy, at least up to $n = 6$ which we have studied.[22] In surface structures of $Na(H_2O)_n$, the primary cluster is determined by hydrogen bonds among water molecules, and the Na atom is just attached to it. Even in interior structures, H_2O molecules, while binding to the central Na, try to keep hydrogen bonds among themselves. The structural dissimilarity between $Na(NH_3)_n$ and $Na(H_2O)_n$ is considered to result from the relative importance of hydrogen bonds and metal−ligand bonds. In the $Na(NH_3)_n$ cluster, the metal−ligand interaction is the dominant source of stabilization, while in the $Na(H_2O)_n$ cluster, the H_2O−H_2O hydrogen bond is as important as, if not more than, the metal−ligand interaction. The role of the hydrogen bond in the energetics for $Na(NH_3)_n$ will be discussed in detail in section V.

Since the first solvation shell is completed with four or five NH_3 molecules in $Na(NH_3)_n$ for $n \geq 4$ in their most stable interior structures, there are more electrons around Na than eight expected by the classical octet rule. The bonding nature of Na−N bonds will be discussed in detail in section IV.

B. Geometries of $[Na(NH_3)_n]^+$ ($n = 1-6$) Ions. The optimized geometries of $[Na(NH_3)_n]^+$ ($n = 1-6$) ions are shown in Figure 2. All these structures have been also confirmed to have all real vibrational frequencies. $[Na(NH_3)]^+$ has a C_{3v} structure (a) where Na and N bind directly with each other. $[Na(NH_3)_2]^+$ has a D_3 symmetry structure (b) where two NH_3 molecules bind directly to Na in the trans disposition. $[Na(NH_3)_3]^+$ has a C_{3h} symmetry structure (c) where all N atoms are bound directly to the central Na^+ ion in a plane. $[Na(NH_3)_4]^+$ has a D_2 structure (d) where the Na^+ ion is surrounded tetrahedrally by four NH_3 molecules. For $[Na(NH_3)_5]^+$, we have found two stable structural isomers. One is a C_{3h} structure (e) with a trigonal bipyramidal arrangement, which can be regarded as the structure where two NH_3 molecules bind further to $[Na(NH_3)_3]^+$ (c) from both above and below its molecular plane. It is also regarded as the structure whose three equatorial NH_3 molecules are rotated by 30° around their respective molecular axes from the neutral C_{3v} structure of $Na(NH_3)_5$ in Figure 1 (e). The equatorial Na−N distances (2.573 Å) are longer than the axial Na−N distances (2.533 Å). The other one is a C_s structure (f) where one NH_3 molecule is bound to $[Na(NH_3)_4]^+$ in the outer shell. This structure can be called "4 + 1" structure. The energy difference between the "5" structure (e) and the "4 + 1" structure (f) is less than 0.1 kcal/mol at both MP2 and HF levels.

Thus, we could find the structures where all NH_3 molecules are directly bound to the central Na^+ in one shell for all $n \leq 5$. In these structures, NH_3 molecules are bound to Na^+ avoiding the repulsive interaction among themselves. It should be worth emphasizing that the "one shell" ion structure resembles the neutral one with the same number of NH_3 molecules for $n = 1-5$. The major difference between the neutral and the ion structure is the N−Na−N bond angle for $n = 2$ and 3. Since there is an unpaired electron around Na in the neutral complex, the 3s−3p hybridization on Na would be more like sp^3, while it would be like sp^2 in the ion complex. This difference would result in a smaller N−Na−N bond angle in the neutral complex.



(a)n=1 C_{3v}
ΔE=29.3(30.2)

(b)n=2 D_3
ΔE=55.2(57.2)

(c)n=3 C_{3h}
ΔE=75.4(78.4)

(d)n=4 D_2
ΔE=91.1(95.6)

(e) n=5 C_{3h}
ΔE=99.2(106.1)

(f) n=5 C_s
ΔE=99.2(106.2)

(g) n=6 C_2
ΔE=107.0(116.0)

(h)n=6 D_3
ΔE=105.2(114.7)

Figure 2. Optimized structures of $[Na(NH_3)_n]^+$ ($n = 1-6$) calculated at the HF/6-31+G(d) level. Geometrical parameters are given in angstroms and degrees. 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.

The N−Na−N bond angles of neutral and cation complexes, however, become close to each other, as n becomes larger. In addition, looking at the bond distances, one sees that the Na−N distance increases almost linearly with the number of solvent molecules. It is also interesting to notice that Na−N distances are shorter in the ion complexes than in the neutral cluster for $n = 1-3$, and they become longer when n is 4 or 5. This trend has been found also for the interior complexes of $Na(H_2O)_n$.[22] It is related to the intrinsic strength of ion−neutral interaction over neutral−neutral interaction and the diffuse nature of the Na 3s orbital, which will be discussed in section IV.

For $[Na(NH_3)_6]^+$, we have also found two stable structures (g) and (h), both of which are interior structures. In the C_2 structure (g), Na^+ is surrounded by four first-shell NH_3 molecules and two additional NH_3 molecules are bound to the $[Na(NH_3)_4]^+$ in the second shell via two hydrogen bonds each. Thus this complex should be called a "4 + 2" structure. On the other hand, the D_3 structure (h) has six equivalent NH_3 molecules surrounding Na^+ and is a "6" structure. Although we have optimized geometries of "5 + 1"-type structures like Figure 1 (f), all of them have imaginary frequencies and are not minima on the potential surface.

Though no direct observation of the structure of $[Na(NH_3)_n]^+$ has been reported, two previous experimental studies[28,29] have provided the information on the ion structures. Castleman et al. have reported the thermochemical properties of the cluster ions obtained by a high-pressure mass spectrometry experiment and found a significant decrease in bond energy for the attachment of the fifth NH_3 molecules to $[Na(NH_3)_4]^+$.[28] They have concluded that Na^+ has a preferred first-solvation-shell coordination number of four. On the other hand, Selegue and Lisy have reported the vibrational predissociation spectra of $[Na(NH_3)_n]^+$ for $6 \leq n \leq 12$ and have concluded from the spectral dependence on cluster size that six ammonia molecules form the first solvation shell around the Na^+ ion.[29] The path integral Monte Carlo simulation predicted five[30] and six[31] for the number of ammonia molecules around Na^+ in the first shell in the liquid ammonia. In our calculation for $[Na(NH_3)_5]^+$, the energy of the "4 + 1" C_s structure (f) in Figure 2 is lower than that of the "5" C_{3h} structure (e) by only 0.1 kcal/mol at the MP2 level and the energy of (f) is higher than that of (e) by less than 0.1 kcal/mol at the HF level. On the other hand, the energy of (e) becomes lower than that of (f) of 0.7 (0.9) kcal/mol at the MP2 (HF) level by taking the zero point vibration correction (ZPC) into account with the HF harmonic frequencies scaled by 0.879. The Gibbs free energy of (e) of 1 atm, 298.15 K is only 0.3 (0.1) kcal/mol higher than that of (f). For $[Na(NH_3)_6]^+$, the

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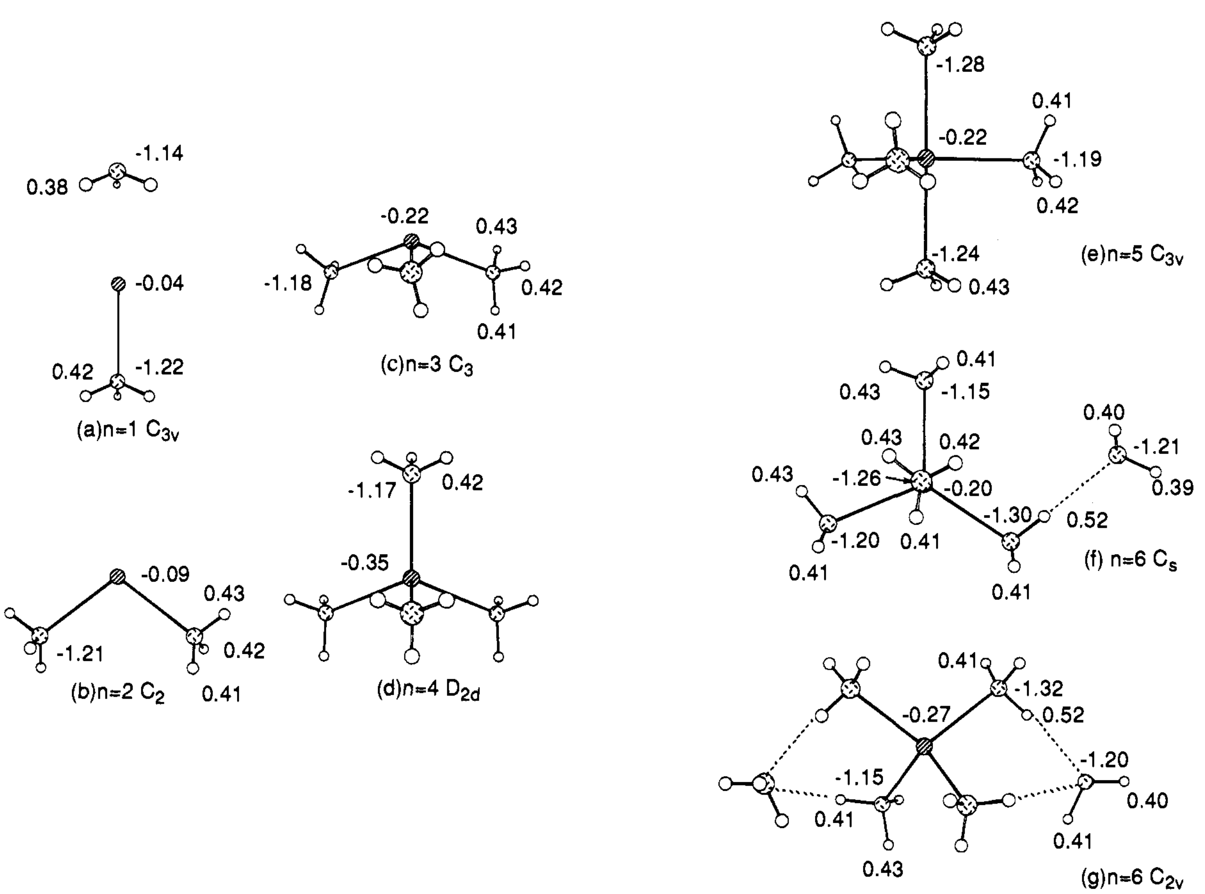

Figure 3. Mulliken atomic charge distribution of the Na(NH$_3$)$_n$ (n = 1−6) at the HF/6-31+G(d) level. The alphabetical labels correspond to the structures shown in Figure 1.

energy of the "4 + 2" structure (g) is lower than that of the "6" structure (h) by 1.3 (1.7) kcal/mol at the MP2 (HF) level. By using the zero point vibration correction with the scaled HF harmonic frequencies, (h) becomes more stable than (g) by 0.9 (0.5) kcal/mol at the MP2 (HF) level. The Gibbs free energy at 1 atm and 298.15 K calculated with the scaled frequencies is lower for (h) than (g) only by 0.4 kcal/mol at the MP2 level and is higher for (h) than (g) by 0.1 kcal/mol at the HF level. Thus, at this level of theory, we have to say that the energies of the structures with and without the inner shell of four NH$_3$ molecules are very close to each other and both structures are likely to coexist. The important conclusions here are that [Na(NH$_3$)$_5$]$^+$ and [Na(NH$_3$)$_6$]$^+$ have two kinds of most-stable structures in which four or all ammonia molecules are bound directly to the central Na$^+$ and that all the stable structures for [Na(NH$_3$)$_n$]$^+$ for $n \leq 6$ are interior structures.

For the ion complexes, we have thus found structural similarity rather than dissimilarity between the Na$^+$−NH$_3$ complex and Na$^+$−H$_2$O complex. For both complexes, the most stable structure is an interior structure having four solvent molecules in the first shell rather than the surface structure. This is because Na$^+$−solvent bond formation mainly due to electrostatic interaction is more important in dictating the molecular structure than the hydrogen bonds.

IV. Mulliken Electron Population Analysis and Bonding Nature of Na−N Bonds

Mulliken atomic charges[32] of Na(NH$_3$)$_n$ (n = 1−6) and their ions are shown in Figures 3 and 4, respectively. NH$_3$ molecules in the neutral complexes are slightly more polarized, nitrogen more negatively and hydrogens more positively charged, compared to the free state, and a similar trend has been found for H$_2$O molecules in hydrated Na complexes in our previous study.[22] Hydrogen atoms taking part in hydrogen bonding in Na(NH$_3$)$_6$ are more positively charged than those without hydrogen bonds. The amount of charge transfer to the Na atom is at most −0.35 *e* for Na(NH$_3$)$_4$, which is substantially larger than those (up to −0.15 *e*) seen in the Na(H$_2$O)$_n$ clusters.[22]

In the cation complexes, the positive charge on the central Na ranges from 0.98 *e* to 1.25 *e*. NH$_3$ molecules are more polarized, i.e., Ns are more negatively charged (up to −0.35 *e* for (f) in Figure 4) and Hs are generally more positively charged, than in neutral complexes of the same *n*, as expected from a large field due to Na$^+$. The amount of charge transfer from or to each NH$_3$ molecule differ at most only by 0.13 *e* (for "4 + 2"-type complexes) between neutral and cation complexes. This may provide some support to the model of small clusters in which the electron is trapped on the cation embedded in a polarizable medium, as is seen in the Na−H$_2$O clusters.

As we described above, we have found for the charge transfer from NH$_3$ to Na that the amount increases gradually up to n = 4 and decreases for $n \geq 5$ in the neutral system. In other words, the charge transfer from the negatively charged Na to NH$_3$ occurs for $n \geq 5$. It is instructive to see how the electron is distributed around Na. The total (i.e., all-electron) gross population on the Na valence s basis functions in the neutral clusters is summarized in Table 1, represented as the sum of contributions of the two valence-contracted basis functions and the diffuse-anion basis function. One can easily notice that the Na valence s atomic orbital totally holds about one to 1.6 *e*, of course qualitatively within the limitation of the Mulliken analysis method. The population in the "inner valence" basis function is about 0.2 and is almost constant for $n \geq 4$ while that in the "outer valence" basis function gradually increases as the number of NH$_3$ molecules increases up to 3 and then decreases for *n*

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[32] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

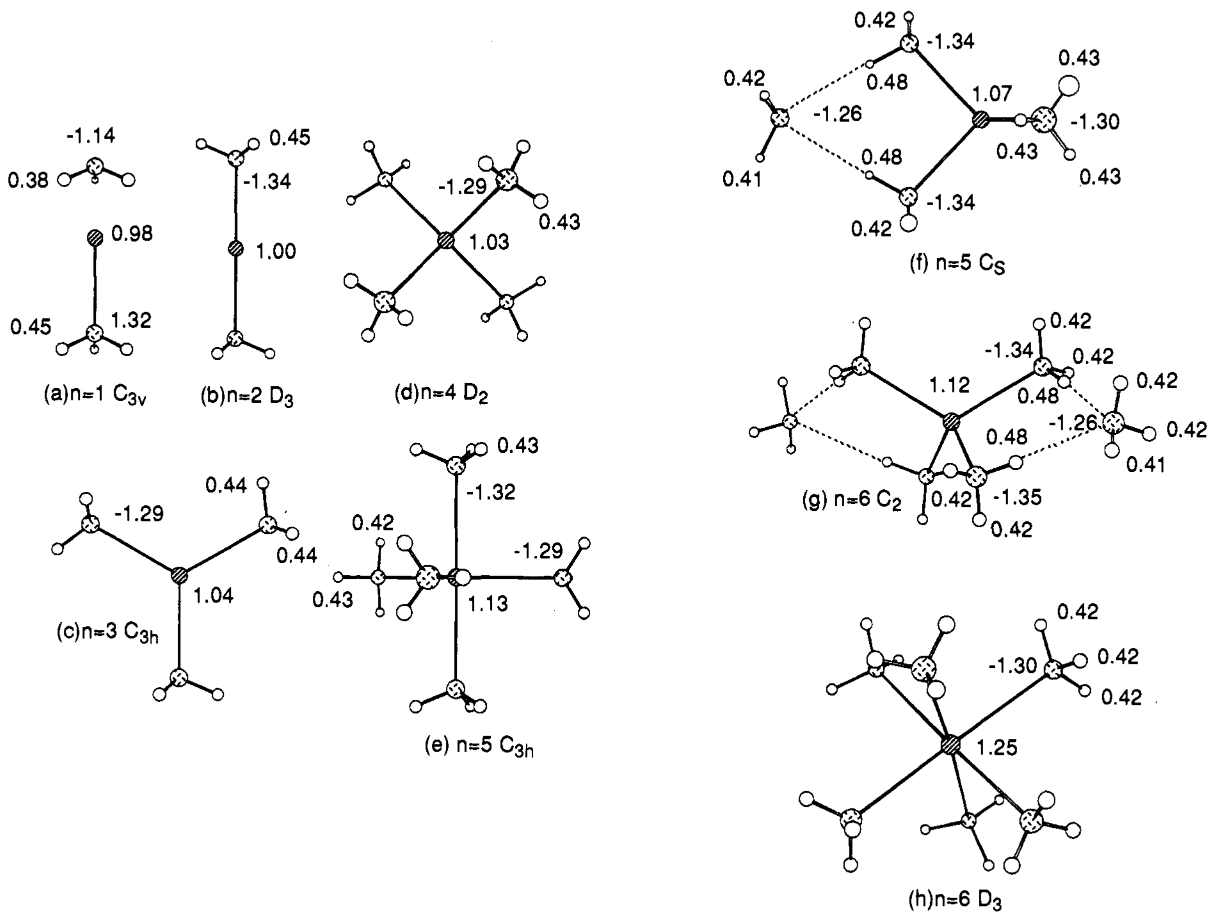

Figure 4. Mulliken atomic charge distribution of $[Na(NH_3)_n]^+$ ($n = 1-6$) at the HF/6-31+G(d) level. The alphabetical labels correspond to the structures shown in Figure 2.

Table 1. Mulliken Total Gross Population on Na Valence s Basis Functions in $Na(NH_3)_n$ Clusters by the HF/6-31+G(d) Method

		Na s basis function			
n	structure	inner	outer	diffuse	total
0		0.49	0.51	0.01	1.01
1	(a)	0.32	0.66	0.05	1.03
2	(b)	0.19	0.76	0.14	1.09
3	(c)	0.14	0.79	0.35	1.29
4	(d)	0.22	0.63	0.73	1.59
5	(e)	0.21	0.50	0.84	1.55
6	(f) "5 + 1"	0.20	0.40	0.80	1.40
6	(g) "4 + 2"	0.19	0.39	0.71	1.30
6	(h) "3 + 3"	0.13	0.57	0.35	1.04

larger than 3. On the other hand, the population in the "diffuse" basis function increases very rapidly up to $n = 5$ and shows a saturation. A close examination of the table indicates the relative basis function contributions are essentially determined by the number of first-shell ligands. For instance, for $Na(NH_3)_6$, the "5 + 1" structure (f) (cf. Figure 1), the "4 + 2" structure (g), and the "3 + 3" structure (h) have similar basis function contributions to those of $Na(NH_3)_5$ (e), $Na(NH_3)_4$ (d), and $Na(NH_3)_3$ (c), respectively. In the structure (f), 57% of the population of Na s valence basis functions is in the diffuse function. The present analysis clearly shows that for a bare Na atom ($n = 0$) and $Na(NH_3)$ ($n = 1$), the odd electron is in the normal Na 3s valence orbital. In the interior complexes $Na(NH_3)_5$ and $Na(NH_3)_6$, the odd electron is now in a very diffuse orbital, stabilized by five first-shell NH_3 molecules. The character of the extra electron in this series of interior complexes changes very gradually, with $n = 2$, 3, and 4 falling between the normal valence electron and the diffuse "solvated" electron. Since the first solvation shell for the neutral cluster appears to be completed as $n = 5$, as discussed in the preceding section, the "diffusification" of the orbital should be saturated at $n = 5$. If one compares the $Na(NH_3)_6$ "5 + 1" structure (f) and the $Na(NH_3)_5$ "5" structure (e), one notices that the second-shell solvent molecule further increases the size of the odd electron, with the weight of the "diffuse" basis function increased from 54 to 57%, and at the same time it decreases the total number of electrons by about 10% from 1.55 to 1.40, presumably sending some population to ligand molecules. The same trend is found for (d) and (g) and for (c) and (h). It is interesting to notice that the outer valence orbital plays an important role in transferring the charge from the negatively charged Na to the ligands. Extrapolation of the present analysis to larger clusters and liquid will require further theoretical studies.

As was discussed in the previous section, Na−N bond distances gradually decrease in $Na(NH_3)_n$ up to $n = 4$ and these bonds in $Na(NH_3)_4$ are unexpectedly shorter than those in $[Na(NH_3)_4]^+$. The singly occupied molecular orbitals (SOMO) in neutral complexes are drawn in Figure 5, in order to investigate these structural features in connection with its nature. In small clusters with three or less NH_3 molecules, SOMO looks like a valence orbital. In the clusters $Na(NH_3)_n$ of $n \geq 4$, SOMO is spread out widely all over or even beyond the cluster, consistent with the above population analysis. One notices clearly in the figure that SOMO has a bonding character between Na and the surrounding NH_3 molecules. This bonding character of SOMO in neutral $Na(NH_3)_n$, especially for $n = 4$, can be considered to be the origin of shortening of the Na−N bond lengths in the neutral cluster compared to its cation counterpart.

V. Energetics

In $Na(H_2O)_n$ complexes and their cations, we were able to investigate the clarify the origin of difference in the character of their surface and interior structures by dividing the total

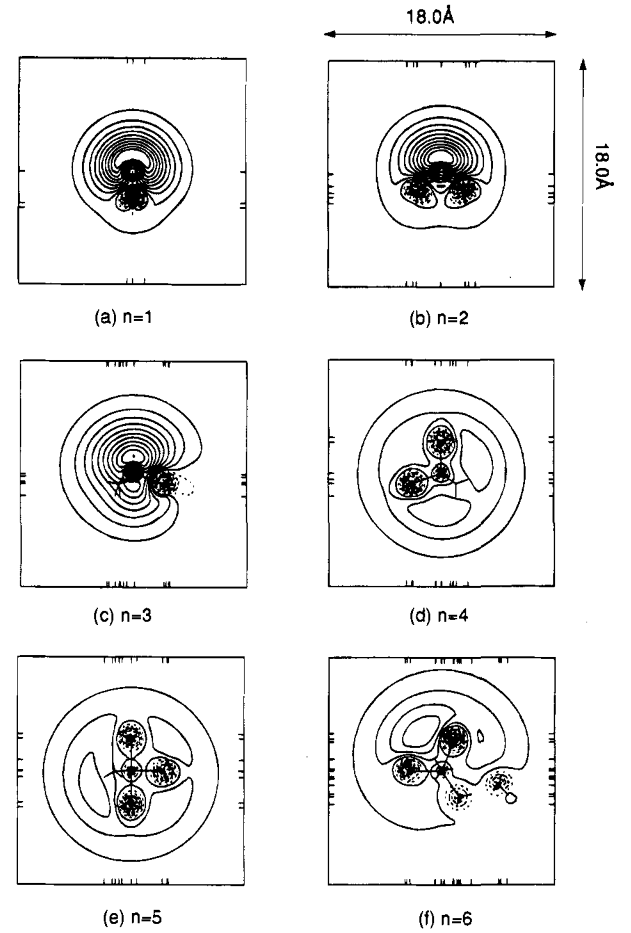

Figure 5. Contour maps of SOMO for $Na(NH_3)_n$ ($n = 1-6$) at the HF/6-31+G(d) level. The alphabetical labels correspond to the structures shown in Figure 1. The spacing of the contour is 0.005 $bohr^{-3/2}$, with solid and broken lines for positive and negative values, respectively, and with those of over ±0.05 omitted. The Na atom is placed at the origin of each figure. Plots for (a), (b), and (f) are in the molecular plane, for (c) and (e) in the plane containing the C_3 axis and one of the first shell N atoms, and for (d) in the plane containing Na and two N atoms.

binding energy into the solute–solvent contribution and the solvent–solvent contribution.[22] We will apply the same analysis for the present $Na(NH_3)_n$ complexes and their cations. Total binding energies $\Delta E(n)$ of both neutral $Na(NH_3)_n$ and ion $[Na(NH_3)_n]^+$ ($n = 1-6$) complexes are given in Figures 1 and 2, respectively. They are defined by

$$-\Delta E(n) = E[M(NH_3)_n] - E[M] - n\,E[NH_3]\ (M = Na\ and\ Na^+) \quad (1)$$

The solvent–solvent contribution, $\Delta E_S(n)$, and the solute–solvent contribution, $\Delta E_M(n)$, are evaluated by eqs 2 and 3, respectively.

$$-\Delta E_S(n) = E[(NH_3)_n^{\#}] - n\,E[NH_3] \quad (2)$$

$$-\Delta E_M(n) = E[M(NH_3)_n] - E(M) - E[(NH_3)_n^{\#}]\ (M = Na\ and\ Na^+) \quad (3)$$

$E[(NH_3)_n^{\#}]$ is the energy of complex of n NH_3 molecules whose structure is fixed at that in the $Na(NH_3)_n$ or $[Na(NH_3)_n]^+$ complex in question. $\Delta E_S(n)$ in eq 2 gives the interaction energy among the NH_3 molecules in the Na complex. The $\Delta E_M(n)$ is the interaction energy between the prepared NH_3 cluster and the Na atom or ion, and the sum of the two components gives the total binding energy:

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

$\Delta E(n)$, $\Delta E_S(n)$, and $\Delta E_M(n)$ as functions of the number of NH_3 molecules are shown for both neutral and ion complexes in Table 2.

The total stabilization energy $\Delta E(n)$ changes almost linearly with n with a partial saturation at $n = 5-6$ in neutral and ion complexes, though the absolute value is much larger for the ion complexes for each n. The effect of the electron correlation is larger for the neutral complexes than the ion complexes, reflecting the more covalent nature of Na–N bonds in neutrals. For the ion complexes, the solvent–solvent interaction $\Delta E_S(n)$ is always negative for all n examined. For the neutral complexes, it is also negative except for the "3 + 3" structure (h) of $Na(NH_3)_6$ in Figure 1 at the MP2/6-31+G(d)//HF/6-31+G(d) level. The negative $\Delta E_S(n)$ means that the interaction among the solvent NH_3 molecules is repulsive. In the structures with the second solvation shell, for both neutral and ion complexes, the second-shell NH_3 molecule does not contribute to $\Delta E_S(n)$ as much as the first-shell NH_3 molecules but plays a role in reducing the repulsive energy among the solvent molecules by hydrogen bond(s). The negative $\Delta E_S(n)$ values for small n and the reduction of the repulsion energy by the second-shell molecule(s) have been found for the interior complex of $Na(H_2O)_n$ clusters and its cation in the previous study.[22] It is worth noting that $\Delta E_S(n)$ for the neutral $Na(NH_3)_n$ is as large as that for the ion complex with the same symbol in Figure 2 except for (f) and (h). In other words, $\Delta E_S(n)$ for the neutral $Na(NH_3)_n$ is almost the same as that for the ion complex with the same number of NH_3 molecules and the same type of structure.

The larger n dependency of $\Delta E(n)$ in the ion complex than in the neutral complex thus comes from the larger n dependency of $\Delta E_M(n)$, which in turn is due to a stronger electrostatic interaction between Na^+ and NH_3 molecules. It is also interesting to notice that $\Delta E_M(n)$ for the structure (g) is larger than that of structure (d) for the neutral, though the former has two additional NH_3 molecules in the second shell and its first-shell structure resembles (d). This situation is found for the ion complex as well. $\Delta E_M(n)$ increases almost linearly for (d), (f), and (g) in this order, all of which have the "4" structure as the first shell. By decomposing the total interaction energy, as was done in the previous study,[22] we have found that the three-body interaction energy among Na, the first-shell $Na(NH_3)_4$ part, and the second-shell NH_3 molecule is 3.0 (3.5) kcal/mol at the MP2 (HF) level for each second-shell NH_3 molecule and is a main contributor of the increase in $\Delta E_M(n)$ from (d) to (g). We have found that the increase of $\Delta E_M(n)$ from $Na(NH_3)_5$ (e) to $Na(NH_3)_6$ (f) with the "5" structure in the first shell results also from the three-body interaction among Na, the first-shell molecules, and the second-shell molecules. This type of three-body interaction has been found for the interior $Na(H_2O)_n$ complexes as well in the previous study.[22] On the other hand, the increase in $\Delta E_M(n)$ from $[Na(NH_3)_4]^+$ (d) to $[Na(NH_3)_5]^+$ (f) and $[Na(NH_3)_6]^+$ (g) (with the alphabetical symbols corresponding to the structures in Figure 2) comes mainly from the interaction energy between Na^+ and the NH_3 molecules in the second shell in (f) and (g). This interaction energy, and thus the increase in $\Delta E_M(n)$ for (f) and (g), is almost additive against the number of molecules in the second shell. The three-body term was −0.6 (MP2) kcal/mol at most for these two ion complexes. It is instructive to compare the total binding energy and its components between the interior structure of $Na(NH_3)_n$ and that of $Na(H_2O)_n$. For $1 \le n \le 4$, the total binding energy of $Na(H_2O)_n$ is slightly smaller than that of $Na(NH_3)_n$ for each n. And ΔE, ΔE_S, and ΔE_M of the interior $Na(H_2O)_4$ were 37.5 (29.0), −3.8 (−7.3), and 41.3 (36.3) kcal/mol, respectively, at

Table 2. Total Binding Energy, $\Delta E(n)$,[a] Solvent–Solvent Contribution $\Delta E_S(n)$,[a] and Solute–Solvent Contribution, $\Delta E_M(n)$[a] for Neutral $Na(NH_3)_n$ and $[Na(NH_3)_n]^+$ Ion Complexes ($n = 1-6$) Calculated at the MP2/6-31+G(d)//HF/6-31+G(d) Level. The Values in Parentheses Are by the HF/6-31+G(d) method. The Unit of the Values is kcal/mol

	neutral $Na(NH_3)_n$				$[Na(NH_3)_n]^+$ ion			
n	symbol in Figure 1	$\Delta E(n)$	$\Delta E_S(n)$	$\Delta E_M(n)$	symbol in Figure 2	$\Delta E(n)$	$\Delta E_S(n)$	$\Delta E_M(n)$
1	a	8.9 (7.0)	0.0 (0.0)	8.9 (7.0)	a	30.2 (29.3)	0.3 (0.0)	30.4 (29.6)
2	b	17.7 (13.6)	−2.7 (−3.1)	20.4 (16.7)	b	57.2 (55.2)	−2.1 (−2.4)	59.3 (52.8)
3	c	28.1 (20.9)	−7.0 (−8.1)	35.0 (29.0)	c	78.4 (75.4)	−6.5 (−7.7)	84.9 (83.1)
4	d	41.0 (30.7)	−13.2 (−15.2)	54.2 (45.9)	d	95.6 (91.1)	−13.4 (−15.3)	109.0 (106.4)
5	e ("5")	48.6 (35.5)	−21.7 (−25.9)	70.3 (61.4)	e ("5")	106.1 (99.2)	−21.5 (−25.5)	127.6 (124.7)
5					f ("4 + 1")	106.2 (99.2)	−9.9 (−14.1)	116.1 (113.3)
6	f ("5 + 1")	54.5 (39.8)	−19.1 (−25.2)	73.6 (65.0)				
6	g ("4 + 2")	53.8 (39.8)	−8.1 (−14.0)	61.9 (53.8)	g ("4 + 2")	116.0 (107.0)	−6.5 (−13.1)	122.5 (120.1)
6	h ("3 + 3")	48.2 (35.2)	2.2 (−4.2)	46.0 (39.4)	h ("6")	114.7 (105.2)	−29.4 (−35.9)	144.1 (141.1)

[a] $\Delta E(n)$, $\Delta E_S(n)$, and $\Delta E_M(n)$ are defined by eqs 1–3. See text.

Table 3. Calculated Successive Enthalpy Change, $\Delta H_{n-1,n}$[a] (1 atm, 298.15 K) of $[Na(NH_3)_n]^+$, in kcal/mol, Compared with the Experiment

n	symbol in Figure 2	HF/6-31+G(d)	MP2/6-31+G(d)// HF/6-31+G(d)	expt (ref 28)
1	a	29.6	30.5	29.1
2	b	24.9	26.1	22.9
3	c	22.4	23.3	17.1
4	d	16.4	17.9	14.7
5	e	9.1	11.4	10.7
5	f	8.6	4.5	10.7
6	g	7.9[b]	10.1[b]	9.7
6	h	7.1[b]	9.7[b]	9.7

[a] $-\Delta H_{n-1,n} = H([Na(NH_3)_{n-}]^+) - H(NH_3)$. Calculated using the scaled HF/6-31+G(d) harmonic vibrational frequencies. [b] The $H([Na(NH_3)_5]^+$ value for (e) in Figure 2 was used in the calculation.

the MP2 (HF) level. Thus, the solute–solvent contribution, ΔE_M, of $Na(NH_3)_4$ is larger than that of $Na(H_2O)_4$ by about 10 kcal/mol, showing the importance of Na–N bond formation in the $Na-NH_3$ complex. On the other hand, at $n = 6$, ΔE, ΔE_S, and ΔE_M of the interior $Na(H_2O)_6$ with the "4" structure in the first shell were 60.7 (47.2), 6.3 (−2.6), and 41.3 (49.8) kcal/mol, respectively, at the MP2 (HF) level. The stabilization of $Na(H_2O)_6$ from $Na(H_2O)_4$ by the additional two solvent molecules is larger than that of $Na(NH_3)_6$ from $Na(NH_3)_4$. Since the changes in $\Delta E_S(n)$ and ΔE_M from $n = 4$ to $n = 6$ for the interior $Na-H_2O$ complex are 10.1 (4.7) and 13.1 (13.5) kcal/mol and those for the $Na-NH_3$ complex with "4" first shell are 5.1 (1.2) and 7.7 (7.9) kcal/mol, the larger stabilization of the $Na-H_2O$ complex than that of the $Na-NH_3$ complex by the second shell can be attributed to both the hydrogen bonding and many-body interaction due to the shell structure formation mentioned above.

The calculated incremental solvation enthalpy changes $\Delta H_{n-1,n}$ of the ion complex and the experimental values by Castleman et al.[28] are compared in Table 3. Our calculated results are in good agreement with the experiment and reproduce well the trend of the experiment n dependency. The enthalpy change decreases monotonically and saturates partially at $n = 5$ in both experimental and calculated results, though the deviation of the computed values from the experiment at $n = 3$ seems a little too large.

VI. Ionization Potentials of $Na(NH_3)_n$ ($n = 1-6$) Clusters and SOMO Electron Distribution

The vertical ionization potentials (IPs) of $Na(NH_3)_n$ ($n = 1-6$) clusters by the ΔMP2 method as functions of n are shown in Figure 6. The calculated IPs are improved from the previous HF/3-21G study and are in good quantitative agreement with the experimental values for all n examined. It changes almost in parallel with the experimental values. It decreases monotonically and gradually with n, and its slope becomes smaller for $n \geq 4$ than for $n \leq 4$, which has been seen for the interior complexes of $Na(H_2O)_n$.[22]

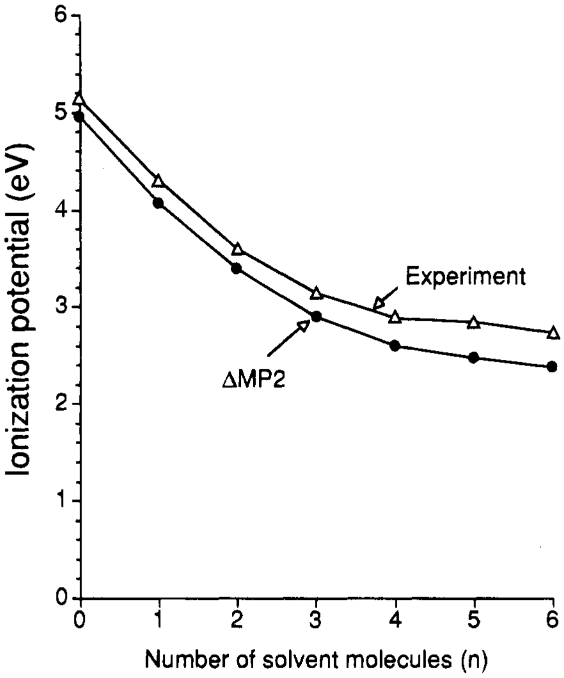

Figure 6. Calculated vertical ionization potentials, in eV, of $Na(NH_3)_n$ ($n = 1-6$) as a function of n by the ΔMP2 method at HF/6-31+G(d)-optimized geometries together with the experimental values.

The electron density distribution of SOMO in the $Na(NH_3)_n$ cluster should give, in the spirit of Koopmans' theorem, qualitative information about the electron being ionized in a photoionization experiment. In a previous study on $Na(H_2O)_n$,[22] we have found that the SOMO electron density is very different between surface complexes and interior complexes. In surface complexes, it is concentrated in the vicinity of Na opposite hydrating H_2O molecules, while in interior complexes it is mainly distributed on Na and O atoms and in the space between hydrating water molecules. This difference has been found to be responsible for the different behavior of their IPs as functions of n.

Contour maps of SOMO for the most stable isomer of $Na(NH_3)_n$ for each n have been given in Figure 5. For small $Na(NH_3)_n$ clusters of $n \leq 3$, SOMO is mainly distributed in the vicinity of the Na atom and extends in space in the directions where NH_3 molecules do not exist. SOMO has a character of a normal Na valence 3s orbital polarized, or forced to mix the 3p orbitals, by the solvent molecules. The total electron density distribution (not shown for brevity) around the Na almost coincides with that of SOMO for $n \leq 3$. The surface ionization must occur in these small clusters. This feature has also been found in $Na(H_2O)_n$ for small ($n \leq 3$) complexes as well as for surface complexes for $n \geq 4$.[22] On the other hand, for $Na(NH_3)_n$ of $n \geq 4$, the SOMO distribution is heavily concentrated around Na and N atoms and also spread in the space between coordinating NH_3 molecules, but is essentially well inside the total electron cloud. This situation is similar to that for interior complexes of $Na(H_2O)_n$ for $n \geq 4$.[22] These analyses indicate that the ionization of a $Na(NH_3)_n$ cluster changes from the surface ionization for incompletely solvated $n \leq 3$ complexes to the interior ionization for complexes of $n \geq 4$, where Na is surrounded completely by the first-shell solvent molecules. Once the cluster becomes the interior complex for $n \geq 4$, i.e., once the interior ionization starts, the slope of the IP as a function of n decreases. The IP is expected to decrease further until the electronic structure of the inner shell becomes unaffected by NH_3 molecules in outer shells.

VII. Concluding Remarks

In the present paper, we have investigated the $Na(NH_3)_n$ ($n = 1-6$) complexes as well as their ions with the *ab initio* MO method and systematically compared with the $Na(H_2O)_n$ ($n = 1-6$) complexes. The neutral $Na(NH_3)_n$ complex for $n \geq 4$ prefers the interior structure where Na is surrounded in a tetrahedral or trigonal bipyramidal fashion by NH_3 molecules in the first shell. On the other hand, the neutral $Na(H_2O)_n$ complex for $n \geq 3$ prefers the surface structure, though the interior structure can exist and is competitive in energy for $n = 3$, 4, and 5. Both $[Na(NH_3)_n]^+$ and $[Na(H_2O)_n]^+$ ion complexes are interior complexes.

For the neutral $Na(NH_3)_n$ complex, the first shell seems to be completed by four or five ammonia molecules, as seen in "5 + 1" and "4 + 2" structures found to have a similar energy for $Na(NH_3)_6$. On the other hand, the cation complex seems to accept four, five, or six ammonia molecules in the first shell, as seen in "4 + 1" and "5" structure for $[Na(NH_3)_5]^+$ and "4 + 2" and "6" structures for $[Na(NH_3)_6]^+$, where the "5 + 1" structure is mysteriously missing. The larger number of the first-shell solvent molecules in the cation complex, compared to the neutral complex, may be attributed to the stronger metal−N interaction which can overcome the steric and electrostatic repulsion among solvent molecules. For the neutral $Na(H_2O)_n$ complex, the "4" structure is the first-shell structure of the interior complex. In the neutral surface structures, three or four H_2O molecules are bound directly to Na and the additional H_2O molecules are bound to H_2O molecules in the first shell through hydrogen bonds from the opposite site of Na. $[Na(H_2O)_n]^+$ ion complex prefers the interior structure with "4" structure in the first shell. Up to $n = 4$, H_2O molecules are bound to the central Na^+, minimizing the repulsion energy among the H_2O molecules without hydrogen bonds. The hydrogen bonding starts stabilizing from $n = 5$ and $[Na(H_2O)_6]^+$ having a "4 + 2" structure is more stable than that with the surface "3 + 3" and the interior "6" structures.

The binding energy in both neutral and ion ammonia complexes comes solely from the stabilization due to Na−N bonds until the first solvation shell completed. The interior structure is preferred to allow formation of a maximum number of Na−N bonds. In the interior structure, the total ammonia−ammonia interaction is actually repulsive, but ammonia molecules are so arranged to make the repulsion among them as small as possible without destroying Na−N bonds. The hydrogen bonds among solvent NH_3 molecules start playing a role in stabilizing the system after the first shell is completed. The second-shell ammonia molecules are arranged to maximize the hydrogen bond energy, which is the source of incremental stabilization after the first solvation shell is completed. The three-body interaction energy among Na and $(NH_3)_4$ in the first shell and an NH_3 molecule in the second shell is as well important in stabilizing the interior $Na(NH_3)_n$ complex. The binding energy in ion water complexes is also dominated by the strong Na^+-O bonds, and a similar argument can be made. For neutral $Na(H_2O)_n$ complex, however, the balance between the Na−O bond and the water−water hydrogen bond is critical. The surface structure is the structure where the hydrogen-bond energy is maximized, and Na is attached to the neutral water cluster at the position where the net Na−cluster attraction is the largest. On the other hand, the interior structure is the structure where the Na−O interaction is maximized, as in the case of $Na(NH_3)_n$ and cation complexes.

In comparison of the present theoretical results with experiments, one finds that the calculated incremental enthalpy changes of $[Na(NH_3)_n]^+$ are in good agreement with the experimental values. The computed vertical ionization potential by the ΔMP2 method as a function of the number of NH_3 molecules, n, is also in good quantitative agreement with experiment. It decreases monotonically with n though its slope becomes smaller for $n \geq 4$. For small $Na(NH_3)_n$ clusters of $n \leq 3$, SOMO is mainly distributed in the vicinity of the Na atom and extends in space in the directions where NH_3 molecules do not exist. For $n \geq 4$, the SOMO of $Na(NH_3)_n$ is a diffuse s-type orbital, mainly localized on Na and N atoms, spread in part in the space between NH_3 molecules, and bonding between Na and NH_3 molecules. This bonding character of SOMO in neutral $Na(NH_3)_4$ complexes results in shortening of Na−N bonds compared to those in ion complexes. From the comparison of the spatial distribution of total and SOMO electron density, we have found that the ionization of $Na(NH_3)_n$ changes from the "surface ionization" for $n \leq 3$ to the "interior ionization" for $4 \leq n$ and the IP is considered to decrease until the electronic state around Na becomes unchanged by the additional solvent molecules in the outer shell. The SOMO and therefore the behavior of IPs against n of the interior structure of $Na(H_2O)_n$ are very similar to those of $Na(NH_3)_n$. On the other hand, the SOMO of the neutral surface structure of $Na(H_2O)_n$ complex is a normal valence 3s + 3p hybridized orbital extended to the open direction of the surface, away from the solvent molecules. The surface ionization of the surface $Na(H_2O)_n$ complexes is considered to be responsible for the behavior of the IPs becoming constant for $n \geq 4$.

From the present systematic comparison between $Na(NH_3)_n$ and $Na(H_2O)_n$, the recent experimental studies are considered to have observed the surface ionization for $Na(H_2O)_n$ and the interior ionization for $Na(NH_3)_n$. Different n dependency of ionization potential between the two complexes results from the different SOMO electron distribution of the most stable structures. The role of hydrogen bonds in Na complexes is important and responsible in determining their most stable structures.

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