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## Equilibrium Geometries and Structural Stability of the $\text{Al}_m\text{Na}_n$ ( $m = 2-4$ ; $n = 1-8$ ) Clusters

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**Abstract:** The stable geometries and formation processes of the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ;  $n = 1-8$ ) clusters were investigated using the density functional theory (DFT). The  $\text{Al}_m$  ( $m = 2-4$ ) structures are maintained in the clusters. The Na atoms are attached to the Al–Al bond or Al plane for less than  $n = 4$  in the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ) clusters. The odd electron of the attached Na atom is transferred to the  $\text{Al}_m$  part for  $n \leq 4$  or 5 in the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ) clusters since the  $\text{Al}_m$  part becomes stable. The Na–Na bonding is formed by the attached Na atom after saturation of the Al–Al bonds or Al atoms. The  $\text{Al}_2\text{Na}_5$ ,  $\text{Al}_3\text{Na}_5$ ,  $\text{Al}_3\text{Na}_6$ ,  $\text{Al}_3\text{Na}_7$ , and  $\text{Al}_3\text{Na}_8$  clusters have a characteristic structure. The Na wing is formed in the  $\text{Al}_3\text{Na}_n$  ( $n = 5-8$ ) clusters. The 2S shell containing the 3s orbital of the Na atom and the 3p orbital of the Al atom becomes stable before the occupation of the 1D shell because the electrons are delocalized on the Na plane for  $n \geq 5$  in the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ) clusters. The stability of the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ;  $n = 1-8$ ) clusters was evaluated by comparison of the vertical ionization potential (IP), HOMO–LUMO gap, adsorption energy of the Na atom, and binding energy per atom.

### 1. Introduction

There have been many studies on the geometrical structures and physical properties of bimetallic clusters. Aluminum–sodium (Al–Na) bimetallic clusters have been produced by a molecular beam technique.<sup>1</sup> Recently, the geometries and physical properties of some Al–Na clusters have been examined by physical chemistry researchers. Kanhere and his co-workers reported the stable geometries of the Al–Na clusters,  $\text{AlNa}_n$  ( $n = 1-10$ ),<sup>2,3</sup>  $\text{Al}_m\text{Na}$  ( $n = 1-12$ ),<sup>4</sup>  $\text{Al}_n\text{Na}_2$  ( $n = 1-12$ ),<sup>4</sup>  $\text{Al}_2\text{Na}$ ,<sup>5</sup> and  $\text{Al}_4\text{Na}_4$ ,<sup>6</sup> using Car–Parrinello molecular dynamics (CPMD), the quadratic configuration interaction singles and doubles electron correlation (QCISD) method, the density-based molecular dynamics (DBMD) method, and local density approximation (LDA). They have

also reported the physical properties of these Al–Na clusters, for example, the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap, ionization potential, electron affinity, hardness, and polarizability using the B3LYP and the Vosko–Wilk–Nusair (SVWN) calculations. The geometry and stability of  $\text{Al}_{13}\text{Na}^{7,8}$  have been examined using the DFT and ab initio molecular dynamics. The stability of the Al–Na clusters has been discussed on the basis of the spherical jellium model for metallic clusters in these reports. An electronic shell closure effect known for simple metal clusters with 40 valence electrons is found in the  $\text{Al}_{13}\text{Na}$  cluster. We have also systematically studied the geometrical and electronic structures of the Al–Na cluster. The geometrical and electronic structures of the  $\text{Al}_n\text{Na}$  ( $n = 1-4$ ) clusters with the restricted open-shell Hartree–Fock (ROHF) calculations using the 6-31G\* basis set have been reported.<sup>9</sup> Some stable structures of the ground and excited states of both  $\text{Al}_n\text{Na}$  and  $\text{Al}_n\text{Na}^+$  ( $n = 1-4$ ) were described in our previous report. The stability, ionization

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potential, and formation processes of these clusters have also been discussed. It was found that the Al<sub>*n*</sub> cluster parts remain in the stable Al<sub>*n*</sub>Na cluster, and the charge transfer from the Na atom to the Al<sub>*n*</sub> part occurs.

In this study, the small size clusters, Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8), are examined, because we are interested in the early formation process, the geometrical feature, and the stability of the Al–Na cluster. The formation process of the Na cluster is expected in the large size Al–Na clusters, which have a high number of Na atoms. We considered the characteristics of the mixed cluster in the small size clusters. There are few experimental studies of the small size of the Al–Na cluster. It might be difficult to technically select the small size cluster. There are few studies of the formation process of the Al–Na cluster based on the geometric and electronic structures. The charge transfer from the Na atom to the Al atoms is expected due to the difference in the electron negativities between the Al and Na atoms. We are interested in the effect of the charge transfer on the geometry and stability of the Al–Na bimetallic cluster. It is suggested that the adsorption site of the added Na atom is determined on the basis of the electronic structure of the cluster before the addition of a Na atom. In this paper, the geometries and the electronic states of the stable Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) clusters using the DFT calculations are reported. We assumed that the Na atom is adsorbed into the Al<sub>*m*</sub>Na<sub>*n*–1</sub> clusters as the number of Na atoms increases in the Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) clusters. The calculated vertical ionization potentials, the HOMO–LUMO gap, the adsorption energy of the Na atom, and the binding energy per atom of the Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) clusters are used to discuss the stability of the clusters.

## 2. Calculation

The possible geometric and electronic structures of Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) were examined using the density functional theory (DFT) calculations. The initial geometries of the Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) clusters were assumed as follows. In the small Al<sub>2</sub>Na<sub>*n*</sub> clusters (*n* = 1–5), the Na atom was adsorbed by the Al–Al bond and Al atom. In addition, the Na atom was attached to the Al–Na–Al, Na–Al–Na, and Na–Na–Na plane in the large-sized clusters. Three types, i.e., on bond, on atom, and on plane, of the Na atom adsorption on the Al<sub>*m*</sub>Na<sub>*n*–1</sub> clusters were performed for the Al<sub>3</sub>Na<sub>*n*</sub> and Al<sub>4</sub>Na<sub>*n*</sub> clusters when the initial geometries were assumed as in the Al<sub>2</sub>Na<sub>*n*</sub> cluster. The addition of the Na atom was performed for all the Al<sub>*m*</sub>Na<sub>*n*–1</sub> isomers. The calculations were performed by Becke's three-parameter hybrid function using the Lee–Yang–Parr correlation functional (B3LYP)<sup>10–12</sup> method with the 6-311G\* basis set. The B3LYP method with the cc-pVTZ<sup>13</sup> basis set was used for the confirmation of the true minimum for some clusters. The geometries of Al<sub>*m*</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) were optimized using the energy gradient method. The stability of the optimized geometry was confirmed by a frequency analysis. The programs used were the GAUSSIAN 98<sup>14</sup> and GAUSSIAN 03<sup>15</sup> program packages on a COMPAQ Alpha 4100 at the Chiba Institute of Technology (CIT), an HP Exemplar V2500 at Hokkaido University, and a Fujitsu

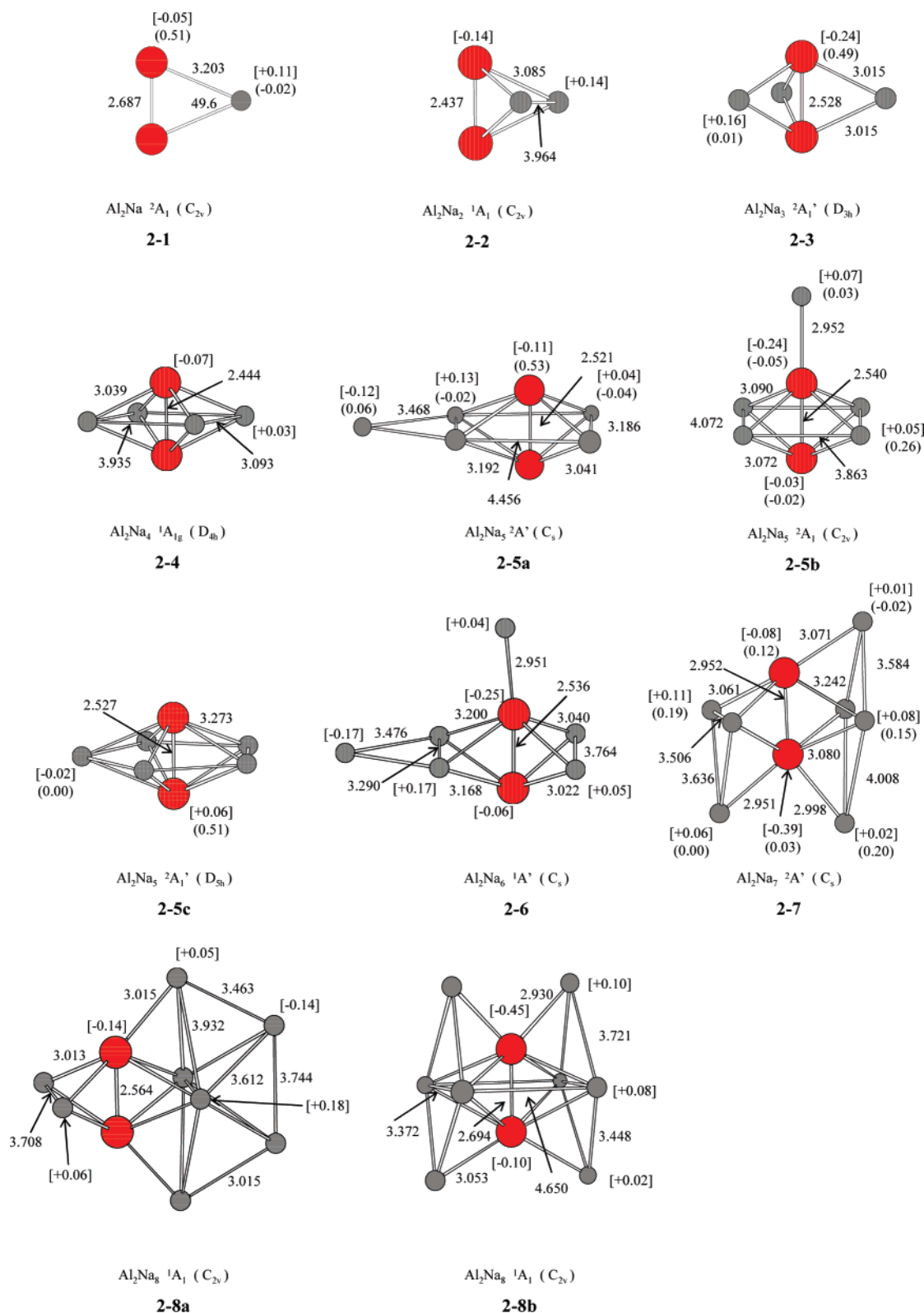
VPP5000/3 at the Tokyo University of Science (TUS). The symmetry was first assumed to be *C*<sub>1</sub>, and, then under the possible high-symmetry found in the preliminary calculations, the geometry of each cluster was reoptimized. Spin multiplicities of the singlet and triplet for an even electron system, and doublet and quartet for an odd electron system, were considered in the geometry optimization. The relative energy of each isomer for the ground state was obtained from the  $\Delta$ SCF method with the total energy after the zero-point correlation. The initial geometries of the examined clusters are determined on the basis of some precalculations. The vertical ionization potential was estimated by the difference in the total energy between the neutral and cationic clusters for the optimized geometry of a neutral cluster. We define the adsorption energy of the Na atom as  $E_{\text{Na}} = -[E(\text{Al}_m\text{Na}_n) - E(\text{Al}_m\text{Na}_{n-1}) - E(\text{Na})]$  and the binding energy per atom as  $E_b = -[E(\text{Al}_m\text{Na}_n) - mE(\text{Al}) - nE(\text{Na})]/(m+n)$ .

## 3. Results and Discussion

### 3-1. Stable Structures of the Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–8) Clusters.

The ground states of the Al<sub>2</sub>Na and Al<sub>2</sub>Na<sub>2</sub> clusters have been reported.<sup>4,5,9</sup> There has been no study on the geometric and electronic structures of the Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 3–8) clusters to the best of our knowledge. The stable geometries of the Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–8) cluster are shown in Figure 1. The electron configurations and some term energies of the Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–8) clusters are listed in Table 1. We assume that the Al<sub>2</sub>Na<sub>*n*</sub> cluster forms due to the adsorption of a Na atom on the Al<sub>2</sub>Na<sub>*n*–1</sub> cluster. In the small size clusters, a Na atom would directly adsorb on the Al<sub>2</sub> molecule, as the Al–Al bond is maintained in all of the obtained stable Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–8) clusters. The relationship between the formation process and geometric and electronic features is discussed on the basis of this assumption. Two stable structures with an isosceles triangular shape for the Al<sub>2</sub>Na cluster are found in our calculations. The <sup>2</sup>A<sub>1</sub> (*C*<sub>2v</sub>) (**2-1**) state is the ground state of the Al<sub>2</sub>Na cluster. The Al–Al bond length of 2.687 Å in **2-1** is slightly shorter than that of 2.765 Å for the <sup>3</sup>Π<sub>u</sub> (*D*<sub>∞h</sub>) state or the experimental result (2.701 Å)<sup>18</sup> of the Al<sub>2</sub> molecule. The Al–Al bond length (2.44 Å: BPW91/6-311G\*\*)<sup>17</sup> in the Al<sub>2</sub>Li cluster is also shorter than that of the Al<sub>2</sub> molecule. It is found that the Al–Al bond becomes shorter than that of the Al<sub>2</sub> molecule due to the adsorption of the alkali metal. The 2a<sub>1</sub> orbital of **2-1** contains the components of the Al–Al π-bonding and 3s orbital of the Na atom, and the paired electrons in this orbital are distributed in the Al–Na–Al plane. Therefore, the Al–Al bond becomes shorter because the odd electron of the Na atom is taken into the 1π<sub>u</sub> orbital of the Al<sub>2</sub> molecule. The spin density of 0.51 for the Al atom supports the electron transfer from the Na atom to the Al atoms. The linear Al–Al–Na cluster is the low-lying state based on our calculations. The stable structure of the linear Al–Na–Al cluster was not obtained.

The <sup>1</sup>A<sub>1</sub> (*C*<sub>2v</sub>) (**2-2**), <sup>2</sup>A<sub>1</sub>' (*D*<sub>3h</sub>) (**2-3**), and <sup>1</sup>A<sub>1g</sub> (*D*<sub>4h</sub>) (**2-4**) states of the Al<sub>2</sub>Na<sub>2</sub>, Al<sub>2</sub>Na<sub>3</sub>, and Al<sub>2</sub>Na<sub>4</sub>, respectively, are the most stable state of each cluster. It was found that the Na atom attaches to the Al–Al bond in the Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–4) clusters. In the Al<sub>2</sub>Na<sub>2</sub> (**2-2**) cluster, the dihedral angle



**Figure 1.** Optimized geometries of the  $\text{Al}_2\text{Na}_n$  ( $n = 1-8$ ) clusters with some bond lengths (Å) and angles (deg). Red and gray circles are Al and Na atoms, respectively. Mulliken charges in square brackets and the spin densities in parentheses are also given.

for Na–Al–Al–Na becomes  $88.7^\circ$  because the odd electron of the Na atom is taken into the  $1b_1$  orbital of the  $\text{Al}_2\text{Na}$  cluster, which has the out-of-plane Al–Al  $\pi$ -bonding character. It is required that the odd electron of the Na atom is transferred to the  $\text{Al}_2$  part in order to form the  $\text{Al}_2\text{Na}_3$  and  $\text{Al}_2\text{Na}_4$  clusters because both the SOMO of **2-3** and the

HOMO ( $2a_{1g}$ ) of **2-4** have a large Al–Al  $\sigma$ -bonding character. The spin density of 0.49 for the Al atom of **2-3** supports this electron transfer. The odd electron of a Na atom is transferred to the  $\text{Al}_2$  molecule because the electron negativity of an Al atom is greater than that of a Na atom.

The  $\text{Al}_2\text{Na}_4$  structure is maintained in the ground states

**Table 1.** Electronic States, Symmetries, Electron Configuration, and Term Energies of Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–8) Clusters

		electronic state	symmetry	electron configuration <sup>a</sup>	<i>T<sub>e</sub></i> /kJ·mol <sup>−1</sup>
Al <sub>2</sub> Na	<b>2-1</b>	<sup>2</sup> A <sub>1</sub>	<i>C</i> <sub>2<i>v</i></sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>1</sup>	0.0
Al <sub>2</sub> Na <sub>2</sub>	<b>2-2</b>	<sup>1</sup> A <sub>1</sub>	<i>C</i> <sub>2<i>v</i></sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup>	0.0
Al <sub>2</sub> Na <sub>3</sub>	<b>2-3</b>	<sup>2</sup> A <sub>1</sub> '	<i>D</i> <sub>3<i>h</i></sub>	(core)(1a <sub>1</sub> ') <sup>2</sup> (1a <sub>2</sub> '') <sup>2</sup> (1e <sub>+</sub> ') <sup>2</sup> (1e <sub>−</sub> ') <sup>2</sup> (1a <sub>1</sub> ') <sup>1</sup>	0.0
Al <sub>2</sub> Na <sub>4</sub>	<b>2-4</b>	<sup>2</sup> A <sub>1g</sub>	<i>D</i> <sub>4<i>h</i></sub>	(core)(1a <sub>1g</sub> ) <sup>2</sup> (1a <sub>2u</sub> ) <sup>2</sup> (1e <sub>u+</sub> ) <sup>2</sup> (1e <sub>u−</sub> ) <sup>2</sup> (2a <sub>1g</sub> ) <sup>2</sup>	0.0
Al <sub>2</sub> Na <sub>5</sub>	<b>2-5a</b>	<sup>2</sup> A'	<i>C</i> <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (3a') <sup>2</sup> (1a'') <sup>2</sup> (4a') <sup>2</sup> (5a') <sup>1</sup>	0.0
	<b>2-5b</b>	<sup>2</sup> A <sub>1</sub>	<i>C</i> <sub>2<i>v</i></sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>1</sup>	0.6
	<b>2-5c</b>	<sup>2</sup> A <sub>1</sub> '	<i>D</i> <sub>5<i>h</i></sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>1</sup>	10.4
Al <sub>2</sub> Na <sub>6</sub>	<b>2-6</b>	<sup>1</sup> A'	<i>C</i> <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (3a') <sup>2</sup> (1a'') <sup>2</sup> (4a') <sup>2</sup> (5a') <sup>2</sup>	0.0
Al <sub>2</sub> Na <sub>7</sub>	<b>2-7</b>	<sup>2</sup> A'	<i>C</i> <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (3a') <sup>2</sup> (1a'') <sup>2</sup> (4a') <sup>2</sup> (5a') <sup>2</sup> (6a') <sup>1</sup>	0.0
Al <sub>2</sub> Na <sub>8</sub>	<b>2-8a</b>	<sup>1</sup> A <sub>1</sub>	<i>C</i> <sub>2<i>v</i></sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>2</sup> (2b <sub>2</sub> ) <sup>2</sup>	0.0
	<b>2-8b</b>	<sup>1</sup> A <sub>1</sub>	<i>C</i> <sub>2<i>v</i></sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>2</sup> (2b <sub>2</sub> ) <sup>2</sup>	23.8

<sup>a</sup> The “core” in parentheses means the core electrons.

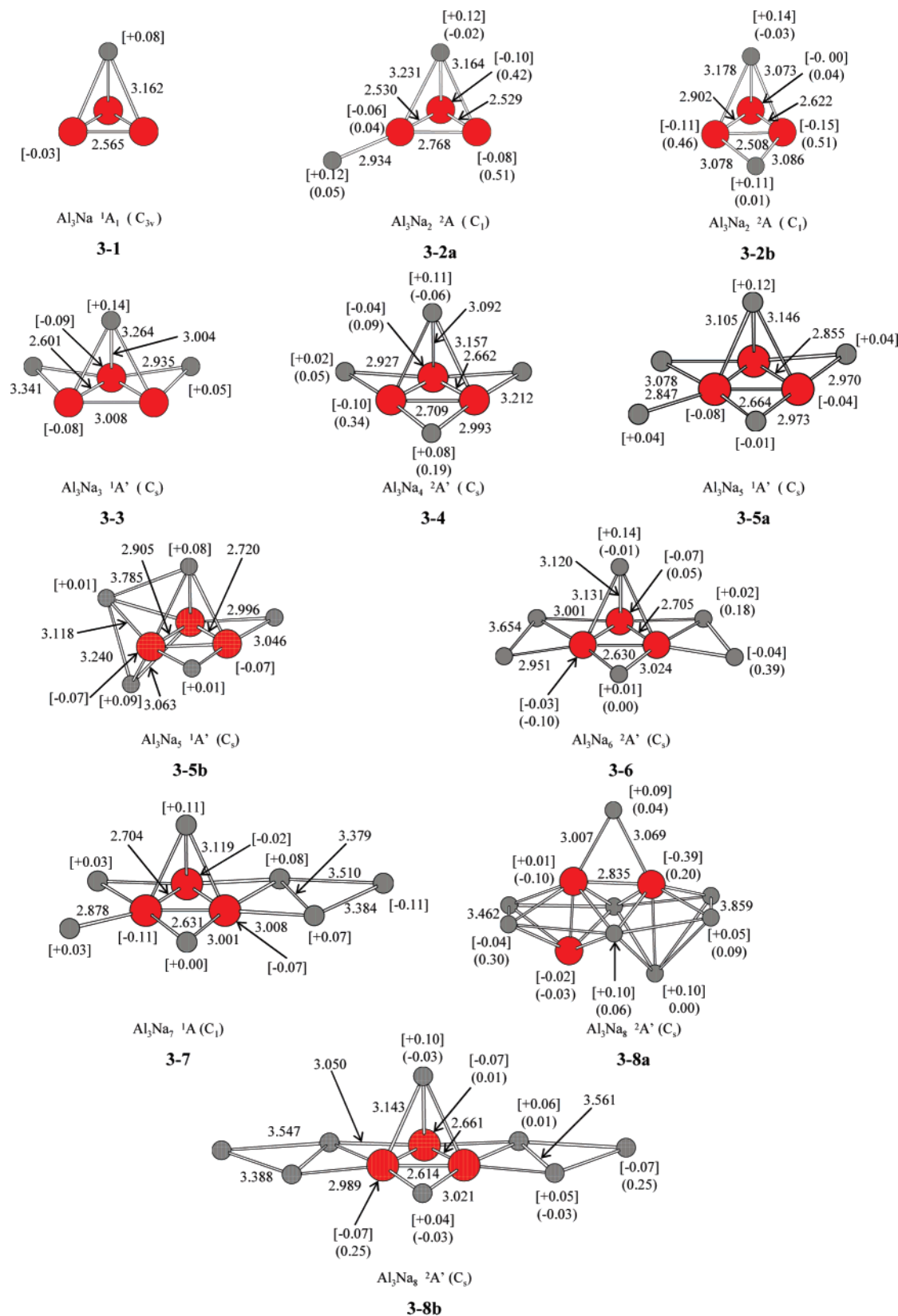
of the Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 5–8) clusters. It is suggested that the Al<sub>2</sub>Na<sub>4</sub> cluster is geometrically stable. Three stable structures of the Al<sub>2</sub>Na<sub>5</sub> cluster were obtained. The <sup>2</sup>A' (C<sub>s</sub>) (**2-5a**), <sup>2</sup>A<sub>1</sub> (C<sub>2v</sub>) (**2-5b**), and <sup>2</sup>A<sub>1</sub>' (D<sub>5h</sub>) (**2-5c**) states are formed by the attachment of the Na atom to the Na–Na bond, the Al atom, and the Al–Al bond of **2-4**, respectively. The <sup>2</sup>A' (C<sub>s</sub>) (**2-5a**) state is the most stable state. The <sup>2</sup>A<sub>1</sub> state (**2-5b**) was obtained when the Na atom approached the Na–Al–Na plane of **2-4** during the geometry optimization. The two geometries of **2-5a** and **2-5b** are shown to have essentially similar stabilities. The <sup>2</sup>A<sub>1</sub>' (D<sub>5h</sub>) state (**2-5c**) locates 10.4 kJ/mol higher than **2-5a** on the potential energy surface. The stability of the Al<sub>2</sub>Na<sub>5</sub> cluster will be discussed in a later section. The <sup>1</sup>A' (C<sub>s</sub>) (**2-6**) state is the most stable in the Al<sub>2</sub>Na<sub>6</sub> isomers. This geometry is formed by the attachment of a Na atom to the <sup>2</sup>A' (C<sub>s</sub>) state (**2-5a**) or <sup>2</sup>A<sub>1</sub> state (**2-5b**) of the Al<sub>2</sub>Na<sub>5</sub> cluster. This stable geometry supports the fact that the attachment of the Na atom to both the Al atom and the Na–Na bond produces a stable structure. The paired electrons of the HOMO containing the 3s character of the Na atoms are mainly distributed on the Na<sub>3</sub> plane. This means that the odd electron is transferred not to the Al–Al part but to the Na plane in the Al<sub>2</sub>Na<sub>6</sub> cluster. The attachment of the Na atom to the Na–Al–Na plane of **2-5b** produces the stable structure (no figure) located 11.7 kJ/mol higher than the ground state. The transition state of the Al<sub>2</sub>Na<sub>6</sub> cluster is obtained when two Na atoms add to each of the two Na–Al–Na planes of the Al<sub>2</sub>Na<sub>4</sub> cluster. In the <sup>2</sup>A' (C<sub>s</sub>) (**2-7**) state of the Al<sub>2</sub>Na<sub>7</sub> cluster, three Na atoms are attached to the Na–Al–Na planes of the Al<sub>2</sub>Na<sub>4</sub> structure. This state is formed due to the approach of the Na atom to one of the local minima of the Al<sub>2</sub>Na<sub>6</sub> cluster. A large deformation is required when the <sup>2</sup>A' (C<sub>s</sub>) (**2-7**) state is formed due to the attachment of the Na atom to the ground state of the Al<sub>2</sub>Na<sub>6</sub> cluster. The equilibrium structure of the pentagonal bipyramidal shape, i.e., the <sup>4</sup>A<sub>1</sub> (D<sub>5h</sub>) state, is the transition state because six imaginary frequencies are found. Therefore, it is considered that the approach of the Na atom to only the Al–Al bond or Na plane is impossible in the Al<sub>2</sub>Na<sub>7</sub> cluster. The most stable state of the Al<sub>2</sub>Na<sub>8</sub> cluster is the <sup>1</sup>A<sub>1</sub> (C<sub>2v</sub>) (**2-8a**) state. A large deformation of the Al<sub>2</sub>Na<sub>7</sub> attached to the Na atom is required for the formation of this state. Actually, the <sup>1</sup>A<sub>1</sub> (C<sub>2v</sub>) (**2-8a**) state is obtained for the Al<sub>2</sub>Na<sub>7</sub> cluster with the addition of a Na atom to the Na–Na bond. It is suggested that the stable part with the Na atoms

is formed in this cluster. The wave functions of the 2a<sub>1</sub> orbital (fifth HOMO) distribute in the hexagonal bipyramid part of four Na atoms and two Al atoms. This orbital is formed due to the mixture of the 3s orbital of six Na atoms and the π orbital of Al<sub>2</sub>. The paired electrons of this orbital are delocalized in the hexagonal bipyramid shape. The attachment of the Na atom to the leftover Na–Al–Na plane of the Al<sub>2</sub>Na<sub>7</sub> cluster produces the <sup>1</sup>A<sub>1</sub> state (**2-8b**) of the Al<sub>2</sub>Na<sub>8</sub> cluster, which is located 23.8 kJ/mol higher than the <sup>1</sup>A<sub>1</sub> (C<sub>2v</sub>) (**2-8a**) state.

The Al–Al bond is maintained in all of the stable Al<sub>2</sub>Na<sub>*n*</sub> (*n* = 1–8) clusters. The Na atom approaches the Al–Al bond of the Al<sub>2</sub>Na<sub>*n*–1</sub> cluster up to *n* = 4. It was found that the transfer of the odd electron from the attached Na atom plays an important role in the formation process of these clusters. The high spin densities of the Al atoms in the Al<sub>2</sub>Na (**2-1**) and Al<sub>2</sub>Na<sub>3</sub> (**2-3**) clusters mean that the odd electron is localized on the Al–Al bonding orbital. Up to *n* = 4, a small odd–even alternation of the Al–Al bond length is found. The Al–Al bond lengths of the even numbered system are slightly shorter than those of the odd numbered system because the Al–Al bonding orbital is doubly occupied in the even numbered system. The Al–Al bond becomes stable due to the electron transfer from the Na atom to the Al atoms in small-sized Al<sub>2</sub>Na<sub>*n*</sub> clusters. The Al<sub>2</sub>Na<sub>4</sub> cluster is expected to be geometrically stable because the molecular orbitals including the 3p characters of the Al atom are occupied. The valence electrons are delocalized on the Na plane for *n* ≥ 6 in the Al<sub>2</sub>Na<sub>*n*</sub> clusters.

**3-2. Structures of the Al<sub>3</sub>Na<sub>*n*</sub> (*n* = 1–8) Clusters.** Figure 2 shows the stable structures of the Al<sub>3</sub>Na<sub>*n*</sub> (*n* = 1–8) clusters. The most stable state of the Al<sub>3</sub>Na<sub>*n*</sub> cluster is the <sup>1</sup>A<sub>1</sub>(C<sub>3v</sub>) (**3-1**) state with the tetrahedral shape. The same structure was obtained as the ground state in the PW91 calculation using the LanL2DZ basis set<sup>4</sup> and in the ROHF calculation.<sup>9</sup> The Al–Al bond lengths have not changed from those of the Al<sub>3</sub> cluster (<sup>2</sup>A<sub>1</sub> state, 2.535 Å) after the adsorption of a Na atom. The Mulliken charges of the Na atom and Al atoms are small. This means that a small amount of charge is transferred from the Na atom to the Al<sub>3</sub> plane through the HOMO (2a<sub>1</sub>), in which the 3s orbital of the Na atom and the out-of-plane π orbital of the Al<sub>3</sub> cluster are mixed. The bonding of the Na atom in the <sup>2</sup>A(C<sub>1</sub>) (**3-2a**) state is the “on-atom” type. On the other hand, that in the <sup>2</sup>A(C<sub>1</sub>) (**3-2b**) state is the “on-bond” type. The odd electron



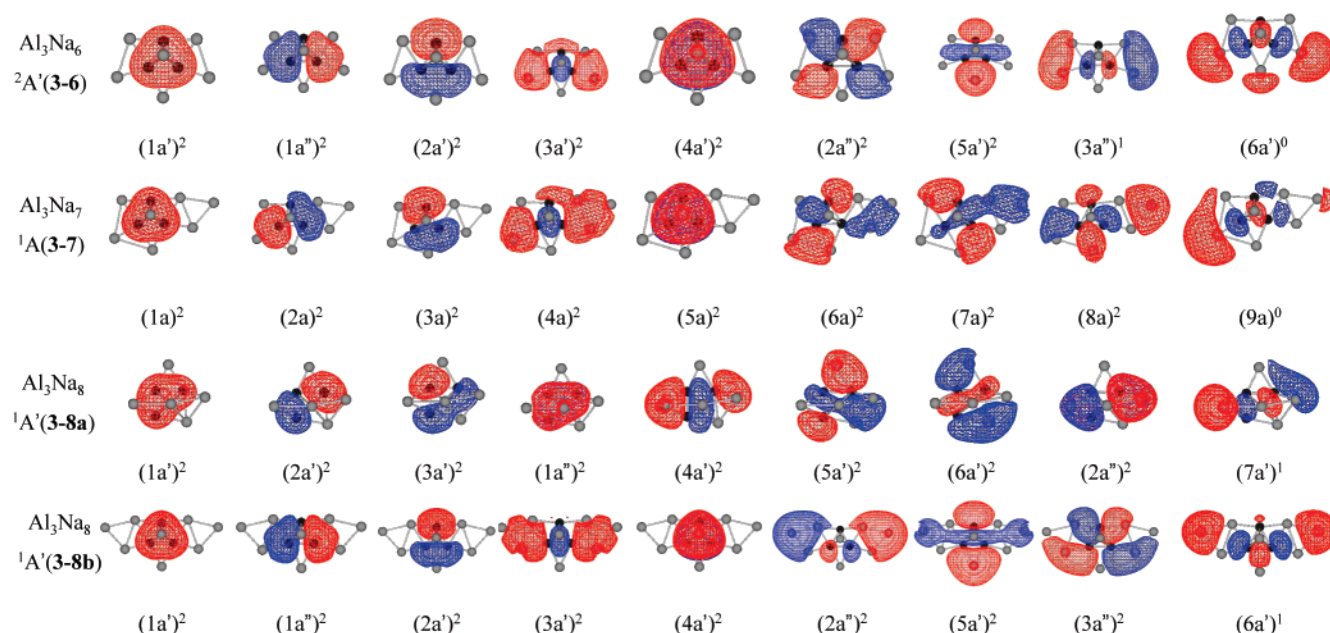


**Figure 2.** Optimized geometries of the  $\text{Al}_3\text{Na}_n$  ( $n = 1-8$ ) clusters.

of **3-2a** is localized on two Al atoms which are without the bonding of the Na atom, and that of **3-2b** is localized on two Al atoms which are bonded to the Na atom. There is essentially no energy difference between **3-2a** and **3-2b** though it is expected that the “on-bond” type is more stable

than the “on-atom” type based on the result of the  $\text{Al}_2\text{Na}_n$  cluster.

Two or three Na atoms are attached to the Al–Al bond of the  $\text{Al}_3$  plane in the ground states of the  $\text{Al}_3\text{Na}_3$  and  $\text{Al}_3\text{Na}_4$  clusters. The  $^1\text{A}'(\text{C}_s)$  (**3-3**) state is formed due to the



**Figure 3.** Valence molecular orbitals of the Al<sub>3</sub>Na<sub>6</sub>, Al<sub>3</sub>Na<sub>7</sub>, and Al<sub>3</sub>Na<sub>8</sub> clusters.

addition of a Na atom to the <sup>2</sup>A(C<sub>1</sub>) (3-2b) state of the Al<sub>3</sub>Na<sub>2</sub> cluster. Furthermore, the <sup>2</sup>A'(C<sub>s</sub>) (3-4) state is formed due to the addition of a Na atom to the <sup>1</sup>A'(C<sub>s</sub>) (3-3) state of the Al<sub>3</sub>Na<sub>3</sub> cluster. The spin densities of the corresponding Al and Na atoms of 3-4 are 0.34 and 0.19, respectively. Therefore, it is found that the odd electron is distributed to one of the Al–Na–Al planes. The Na atom is bonded to the Al atom of the Al<sub>3</sub>Na<sub>4</sub> in the ground state, i.e., <sup>1</sup>A'(C<sub>s</sub>) (3-5a), of the Al<sub>3</sub>Na<sub>5</sub> cluster. The two adsorption cases of the Na atom to the Al–Al bond [<sup>1</sup>A'(C<sub>s</sub>) (3-5b)] and the Al<sub>3</sub> plane [<sup>1</sup>A'(D<sub>3h</sub>) (3-5c)] are located 1.44 and 4.73 kJ/mol higher than the ground state, respectively. That is to say, three adsorption types of the Na atom to the Al<sub>3</sub> cluster, i.e., on-atom, on-bond, and on-plane, produce a similar stability for the cluster. In the Al<sub>2</sub>Na<sub>n</sub> clusters, the charge transfer from the added Na atom to the Al<sub>2</sub> molecule is important for producing a stable cluster, and the charge transfer occurs with the on-bond approach of the Na atom. In the Al<sub>3</sub>Na<sub>n</sub> (*n* = 1–5) clusters, it is suggested that the adsorption type is less important as there is a slight charge transfer from the Na atom to the Al<sub>3</sub> cluster.

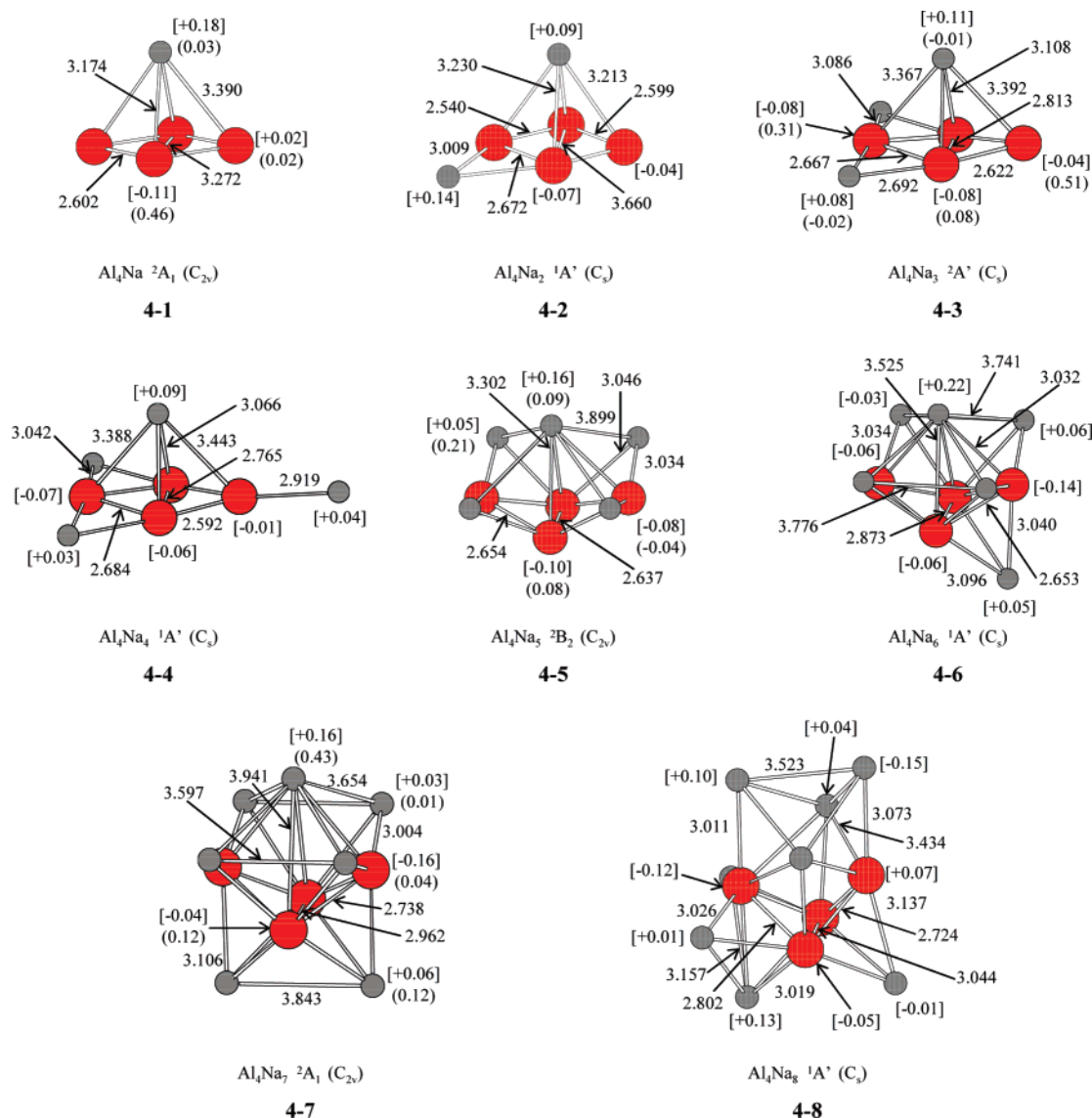
The most stable state of the Al<sub>3</sub>Na<sub>6</sub> cluster is the <sup>2</sup>A'(C<sub>s</sub>) (3-6), in which the Na atom is bonded to the Al atom of the Al<sub>3</sub>Na<sub>5</sub> (3-5a) cluster. The Na–Na bond begins to be formed in this state. The small negative charges (–0.04) of the Na atoms are also found. The spin densities of the four Na atoms (0.39 or 0.18) bonded to the Al atoms are greater than those of the other Na atoms. These high spin densities mean that the odd electron of the SOMO is distributed to the Na–Na bonds. In the <sup>1</sup>A(C<sub>1</sub>) (3-7) state of the Al<sub>3</sub>Na<sub>7</sub> cluster, the Na<sub>3</sub> plane is formed due to the addition of the Na atom to the Al<sub>3</sub>Na<sub>6</sub> (3-6) cluster. The <sup>1</sup>A'(C<sub>s</sub>) (3-8a) state locates 0.44 kJ/mol lower than the <sup>1</sup>A'(C<sub>s</sub>) (3-8b) state. A similar stability between the <sup>1</sup>A'(C<sub>s</sub>) (3-8a) and <sup>1</sup>A'(C<sub>s</sub>) (3-8b) states is found. The Al<sub>2</sub>Na<sub>4</sub> skeleton is included, and the Al<sub>3</sub> plane is broken in 3-8a. It seems that the origin of this cluster is 3-5b of the Al<sub>3</sub>Na<sub>5</sub> cluster. The <sup>1</sup>A'(C<sub>s</sub>) (3-8a) state is formed due to the adsorption of the Na atom on the Al<sub>3</sub>Na<sub>7</sub> isomer (17.3 kJ/

mol higher than the ground state) after the addition of a Na atom to one of the Al<sub>3</sub>Na<sub>6</sub> isomers, which is located 36.4 kJ/mol higher than the ground state. The <sup>1</sup>A'(C<sub>s</sub>) (3-8b) state is formed due to the addition of the Na atom to the Na–Na bond of the Al<sub>3</sub>Na<sub>7</sub> cluster. The Na atoms located on top of the Na wing have negative charges as in the Al<sub>3</sub>Na<sub>6</sub> (3-6) and Al<sub>3</sub>Na<sub>7</sub> (3-7) clusters. The spin densities of these Na atoms increase because the SOMO includes the 3s orbital characters of these Na atoms. In the Al<sub>3</sub>Na<sub>6</sub> (3-6), Al<sub>3</sub>Na<sub>7</sub> (3-7), and Al<sub>3</sub>Na<sub>8</sub> (3-8b) clusters, the Na wing grows together with the increasing number of Na atoms. The Al–Al bond lengths and Mulliken charges of the Al atoms are not changed with the number of Na atoms.

The ground states from the Al<sub>3</sub>Na<sub>6</sub> to Al<sub>3</sub>Na<sub>8</sub> clusters maintain the Na planes. The molecular orbitals of these ground states are shown in Figure 3. The 3a', 4a, and 3a' orbitals of 3-6, 3-7, and 3-8b, respectively, include the 3s orbital character of the Na atoms. It is suggested that these orbitals corresponding to the 2S shell of the shell model become stable because the electrons are delocalized on the Na plane. The spin densities of the Al<sub>3</sub>Na<sub>6</sub> and Al<sub>3</sub>Na<sub>8</sub> clusters show no charge transfer from the Na atoms. It is suggested that these clusters become stable due to the delocalization of the valence electrons to the wing Na atoms.

### 3-3. Stable Structures of the Al<sub>4</sub>Na<sub>n</sub> (*n* = 1–8) Clusters.

We assumed that the Al<sub>4</sub>Na<sub>n</sub> (*n* = 1–8) clusters are formed due to the adsorption of the Na atom on the Al<sub>4</sub>Na<sub>*n*–1</sub> (*n* = 1–8) clusters as in the other examined Al–Na clusters. Figure 4 shows the stable structures of the Al<sub>4</sub>Na<sub>n</sub> (*n* = 1–8) clusters with some bond lengths, angles, Mulliken charges, and spin densities. The electron configurations of the Al<sub>4</sub>Na<sub>n</sub> (*n* = 1–8) clusters are listed in Table 3. The most stable structure of the Al<sub>4</sub>Na is formed due to the addition of the Na atom on the rhombus Al<sub>4</sub> cluster from a direction perpendicular to the Al<sub>4</sub> plane. It has been reported that the ground state of the Al<sub>4</sub> cluster is the <sup>3</sup>B<sub>1u</sub> or <sup>3</sup>B<sub>1g</sub> state of the planar rhombus structure.<sup>9,19</sup> The ground state of Al<sub>4</sub>Na is the <sup>2</sup>A<sub>1</sub>(C<sub>2v</sub>) (4-1) state, though we have reported that the



**Figure 4.** Optimized geometries of the  $\text{Al}_4\text{Na}_n$  ( $n = 1-8$ ) clusters.

**Table 2.** Electronic States, Symmetries, Electron Configuration, and Term Energies of  $\text{Al}_3\text{Na}_n$  ( $n = 1-8$ ) Clusters

		electronic state	symmetry	electron configuration <sup>a</sup>	$T_e/\text{kJ}\cdot\text{mol}^{-1}$
$\text{Al}_3\text{Na}$	<b>3-1</b>	$1A_1$	$C_{3v}$	$(\text{core})(1a_1)^2(1e_+)^2(1e_-)^2(2a_1)^2(3a_1)^2$	0.0
$\text{Al}_3\text{Na}_2$	<b>3-2a</b>	$2A$	$C_1$	$(\text{core})(1a)^2(2a)^2(3a)^2(4a)^2(5a)^2(6a)^1$	0.0
	<b>3-2b</b>	$2A$	$C_1$	$(\text{core})(1a)^2(2a)^2(3a)^2(4a)^2(5a)^2(6a)^1$	0.9
$\text{Al}_3\text{Na}_3$	<b>3-3</b>	$1A'$	$C_s$	$(\text{core})(1a')^2(1a'')^2(2a')^2(3a')^2(4a')^2(2a'')^2$	0.0
$\text{Al}_3\text{Na}_4$	<b>3-4</b>	$2A'$	$C_s$	$(\text{core})(1a')^2(1a'')^2(2a')^2(3a')^2(4a')^2(2a'')^2(5a')^1$	0.0
$\text{Al}_3\text{Na}_5$	<b>3-5a</b>	$1A'$	$C_s$	$(\text{core})(1a')^2(1a'')^2(2a')^2(3a')^2(4a')^2(2a'')^2(5a')^2$	0.0
	<b>3-5b</b>	$1A_1'$	$D_{3h}$	$(\text{core})(1a_1')^2(1e_+')^2(1e_-')^2(1a_2'')^2(2a_1')^2(2e_+')^2(2e_-')^2$	4.7
$\text{Al}_3\text{Na}_6$	<b>3-6</b>	$2A'$	$C_s$	$(\text{core})(1a')^2(1a'')^2(2a')^2(3a')^2(4a')^2(2a'')^2(5a')^2(3a'')^1$	0.0
$\text{Al}_3\text{Na}_7$	<b>3-7</b>	$1A$	$C_1$	$(\text{core})(a)^2(a')^2(a'')^2(a'')^2(a'')^2(a'')^2(a'')^2$	0.0
$\text{Al}_3\text{Na}_8$	<b>3-8a</b>	$2A'$	$C_s$	$(\text{core})(1a')^2(2a')^2(3a')^2(1a'')^2(4a')^2(5a')^2(6a')^2(2a'')^2(7a')^1$	0.0
	<b>3-8b</b>	$2A'$	$C_s$	$(\text{core})(1a')^2(1a'')^2(2a')^2(3a')^2(4a')^2(2a'')^2(5a')^2(3a'')^2(6a')^1$	0.4

<sup>a</sup> The "core" in parentheses means the core electrons.

$^4B_2$  ( $C_{2v}$ ) state is the more stable structure using the ROHF level of calculations.<sup>9</sup> The  $^4B_2$  state is located 22.5 kJ/mol higher than the  $^2A_1$  ( $C_{2v}$ ) state using the B3LYP calculations. After the adsorption of the Na atom, the  $\text{Al}_4$  part is nearly planar, and the dihedral angle of the  $\text{Al}_4$  plane is  $179.4^\circ$ . The Al–Al bond length of 2.602 Å is slightly shorter than that of the  $\text{Al}_4$  (2.657 Å). The diagonal Al–Al distance of

3.272 Å is also shorter than that of the  $\text{Al}_4$  (3.417 Å) because the SOMO ( $4a_1$ ) of the  $\text{Al}_4\text{Na}$  cluster has the Al–Al  $\sigma$ -bonding character. The positive charge of the Na atom and high spin densities of the Al atoms suggest an electron transfer from the Na atom to the  $\text{Al}_4$  cluster. The Na atom is adsorbed on the Al–Al bond in the stable structures of the  $\text{Al}_4\text{Na}_2$  and  $\text{Al}_4\text{Na}_3$ . The  $^2A'$  ( $C_s$ ) (**4-2**) state of  $\text{Al}_4\text{Na}_2$

**Table 3.** Electronic States, Symmetries, Electron Configuration, and Term Energies of Al<sub>4</sub>Na<sub>*n*</sub> (*n* = 1–8) Clusters

		electronic state	symmetry	electron configuration <sup>a</sup>
Al <sub>4</sub> Na	<b>4-1</b>	<sup>2</sup> A <sub>1</sub>	C <sub>2v</sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (1a <sub>2</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>1</sup>
Al <sub>4</sub> Na <sub>2</sub>	<b>4-2</b>	<sup>2</sup> A'	C <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (1a'') <sup>2</sup> (2a'') <sup>2</sup> (3a') <sup>2</sup> (4a') <sup>2</sup> (5a') <sup>2</sup>
Al <sub>4</sub> Na <sub>3</sub>	<b>4-3</b>	<sup>2</sup> A'	C <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (1a'') <sup>2</sup> (3a') <sup>2</sup> (4a') <sup>2</sup> (2a'') <sup>2</sup> (5a') <sup>2</sup> (6a') <sup>1</sup>
Al <sub>4</sub> Na <sub>4</sub>	<b>4-4</b>	<sup>1</sup> A'	C <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (1a'') <sup>2</sup> (3a') <sup>2</sup> (4a') <sup>2</sup> (2a'') <sup>2</sup> (5a') <sup>2</sup> (6a') <sup>2</sup>
Al <sub>4</sub> Na <sub>5</sub>	<b>4-5</b>	<sup>2</sup> A <sub>2</sub>	C <sub>2v</sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (1a <sub>2</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>2</sup> (2b <sub>1</sub> ) <sup>2</sup> (2b <sub>2</sub> ) <sup>1</sup>
Al <sub>5</sub> Na <sub>6</sub>	<b>4-6</b>	<sup>1</sup> A'	C <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (1a'') <sup>2</sup> (3a') <sup>2</sup> (4a') <sup>2</sup> (5a') <sup>2</sup> (2a'') <sup>2</sup> (6a') <sup>2</sup> (3a'') <sup>2</sup>
Al <sub>4</sub> Na <sub>7</sub>	<b>4-7</b>	<sup>2</sup> A <sub>1</sub>	D <sub>2v</sub>	(core)(1a <sub>1</sub> ) <sup>2</sup> (1b <sub>2</sub> ) <sup>2</sup> (1b <sub>1</sub> ) <sup>2</sup> (2a <sub>1</sub> ) <sup>2</sup> (3a <sub>1</sub> ) <sup>2</sup> (4a <sub>1</sub> ) <sup>2</sup> (1a <sub>2</sub> ) <sup>2</sup> (2b <sub>2</sub> ) <sup>2</sup> (2b <sub>1</sub> ) <sup>2</sup> (5a <sub>1</sub> ) <sup>1</sup>
Al <sub>4</sub> Na <sub>8</sub>	<b>4-8</b>	<sup>1</sup> A'	C <sub>s</sub>	(core)(1a') <sup>2</sup> (2a') <sup>2</sup> (1a'') <sup>2</sup> (3a') <sup>2</sup> (4a') <sup>2</sup> (5a') <sup>2</sup> (2a'') <sup>2</sup> (6a') <sup>2</sup> (7a') <sup>2</sup> (3a'') <sup>2</sup>

<sup>a</sup> The "core" in parentheses means the core electrons.

has been reported in an earlier paper.<sup>20</sup> In the <sup>2</sup>A' (C<sub>s</sub>) (**4-2**) state, the molecular orbital character of the Al<sub>4</sub> part might be like that of the stable Al<sub>4</sub><sup>2-</sup> cluster.<sup>19</sup> This suggests that the odd electrons are transferred from two Na atoms to the Al<sub>4</sub> part though the small positive charges of two Na atoms remain. In the <sup>2</sup>A' (C<sub>s</sub>) (**4-3**) state of the Al<sub>4</sub>Na<sub>3</sub> cluster, two Na atoms are attached to the Al–Al bond of the Al<sub>4</sub> plane. The spin densities of 0.51 for the two Al atoms mean that an odd electron transfers from the Na atom to the Al atoms after the attachment of the Na atom to the Al–Al bond. The <sup>1</sup>A'(C<sub>s</sub>) (**4-4**) state is the ground state of the Al<sub>4</sub>Na<sub>4</sub> cluster though that is different from **4-4** with the CCD/6-31G(d, p) level of calculations.<sup>21</sup> In the <sup>1</sup>A'(C<sub>s</sub>) (**4-4**) state, the added Na atom is bonded to the Al atom (on-atom). A small positive charge of the Na atom bonded to the Al atom is found. Furthermore, there is no change in the Mulliken charges of the Al<sub>4</sub> plane from those of the Al<sub>4</sub>Na<sub>3</sub> cluster. These charge distributions suggest a small electron transfer in **4-4**. We obtained two isomers of the Al<sub>4</sub>Na<sub>4</sub> cluster. One is the <sup>1</sup>A (C<sub>1</sub>) state (no figure), in which the added Na atom is bonded to the Al–Al bond (on-bond). This isomer is 5.87 kJ/mol higher than **4-4**. It is suggested that the adsorption type of the Na atom to the Al<sub>4</sub>Na<sub>3</sub> cluster is less important when forming the stable Al<sub>4</sub>Na<sub>4</sub> cluster as in the Al<sub>3</sub>Na<sub>2</sub> and Al<sub>3</sub>Na<sub>5</sub> clusters. The others are located 28.0 kJ/mol higher than **4-4**. In this isomer, two Na atoms are attached to the Al–Na–Al plane in the octahedral shape of the Al<sub>4</sub>Na<sub>2</sub> cluster.

The most stable state of the Al<sub>4</sub>Na<sub>5</sub> cluster is the <sup>2</sup>B<sub>2</sub> (C<sub>2v</sub>) (**4-5**) state. The spin densities of 0.21 of each Na atom mean that the odd electron is localized on the Na atoms. The SOMO has the large 3s characters of the four Na atoms. The dihedral angle of the Al<sub>4</sub> frame becomes 142.8° from 172.0° for the Al<sub>4</sub>Na<sub>4</sub> (**4-4**) cluster. The distance of the central Na atom to each of the four Na atoms is 3.899 Å that means a weak Na–Na bond. Therefore, it is suggested that the formation of the Na–Na bond starts from this cluster. In the Al<sub>4</sub>Na<sub>6</sub> and Al<sub>4</sub>Na<sub>7</sub> clusters, the Na atoms are attached to the Al<sub>3</sub> plane in the Al<sub>4</sub>Na<sub>5</sub> frame. The <sup>1</sup>A' (C<sub>s</sub>) (**4-6**) state of the Al<sub>4</sub>Na<sub>6</sub> cluster is the most stable state. The wave function of the HOMO distributes to the tetrahedral Na atoms on the Al<sub>4</sub> frame. The Na–Na distance between the central Na atom and four apical Na atoms is shorter than that of the Al<sub>4</sub>Na<sub>5</sub> cluster. The Mulliken charges of the two Na atoms that formed the Al<sub>4</sub>Na<sub>5</sub> skeleton are slightly negative. On the other hand, the positive charge of the central Na atom of the Al<sub>4</sub>Na<sub>5</sub> skeleton is enhanced. By the addition of the Na atom to the Al<sub>3</sub> plane of **4-6**, the most stable state of the

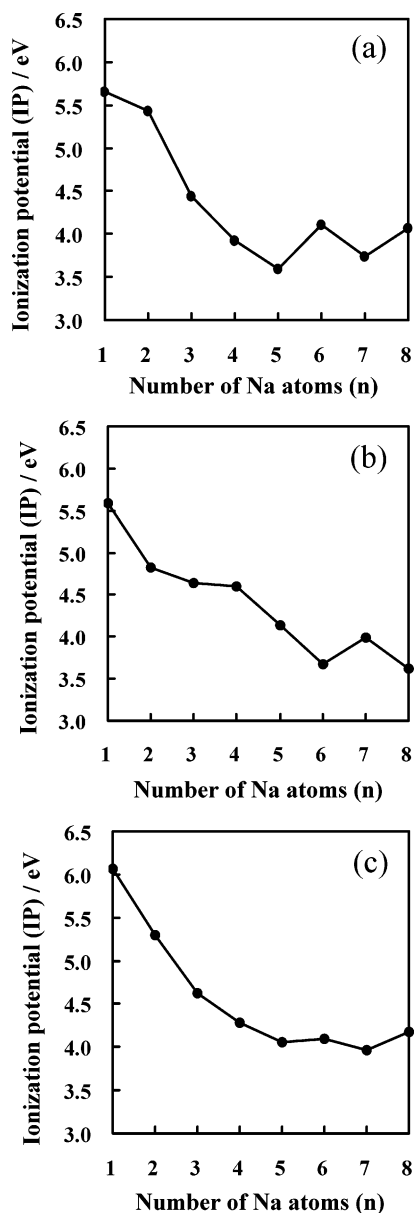
Al<sub>4</sub>Na<sub>7</sub> cluster, <sup>2</sup>A<sub>1</sub> (C<sub>2v</sub>) (**4-7**), is formed. The Na–Na distance between the central Na atom and four apical Na atoms is shorter than that of the Al<sub>4</sub>Na<sub>6</sub> cluster. The ground state of the Al<sub>4</sub>Na<sub>8</sub> is the <sup>1</sup>A' (C<sub>s</sub>) (**4-8**) state. The boat form of the Al<sub>4</sub> part is maintained in this state. It seems that the Na cluster part is distorted after the attachment of the Na atom to the Na–Na bond. The small negative charge of the Na atom is found as in the Al<sub>2</sub>Na<sub>8</sub> and Al<sub>3</sub>Na<sub>8</sub> clusters. The Al<sub>4</sub>Na<sub>8</sub> cluster is a 20-valence electrons system, which produces a stable structure.

In the Al<sub>4</sub>Na<sub>*n*</sub> (*n* = 1–8) clusters, the Na atom is first attached to the planar Al<sub>4</sub> cluster from the perpendicular plane. From the Al<sub>4</sub>Na<sub>2</sub> to the Al<sub>4</sub>Na<sub>5</sub> cluster, the Na atom essentially adsorbs on the Al–Al bond. The Na atom is added to the Al<sub>3</sub> plane from the opposite side of the Na<sub>5</sub> part in the Al<sub>4</sub>Na<sub>6</sub> and Al<sub>4</sub>Na<sub>7</sub> clusters. In the Al<sub>4</sub>Na<sub>8</sub> cluster, the Na atoms are attached to the Al–Al bond, Al atom, and Al<sub>3</sub> plane, and the Na<sub>4</sub> part is formed. From the view point of the cluster growth from Al<sub>4</sub>Na<sub>*n*-1</sub> to Al<sub>4</sub>Na<sub>*n*</sub>, after the formation of the Al<sub>4</sub>Na<sub>5</sub> cluster, the Na atom adsorbs on the Al<sub>4</sub>Na<sub>*n*-1</sub> cluster to maintain the Al<sub>4</sub>Na<sub>5</sub> structure. The Na–Na bond begins to be formed from the Al<sub>4</sub>Na<sub>5</sub> cluster. The negative charge of the Na atom is found in the Al<sub>4</sub>Na<sub>8</sub> cluster as in the Al<sub>2</sub>Na<sub>8</sub> and Al<sub>3</sub>Na<sub>8</sub> clusters.

**3-4. Stability of the Al<sub>m</sub>Na<sub>n</sub> (*m* = 1–4; *n* = 1–8) Clusters.** Figure 5 shows the vertical ionization potential (IP) of the Al<sub>m</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) clusters. The HOMO–LUMO gap, the adsorption energy of Na atom, and the binding energy per atom of the Al<sub>m</sub>Na<sub>*n*</sub> (*m* = 2–4; *n* = 1–8) clusters are shown in Figures 6–8, respectively. The stability of the clusters is discussed on the basis of the molecular orbital theory and shell model in this section. Three IP peaks (Al<sub>2</sub>Na<sub>2</sub>, Al<sub>2</sub>Na<sub>6</sub>, and Al<sub>2</sub>Na<sub>8</sub>) are found in Figure 5(a). The HOMO–LUMO gaps, the adsorption energy of Na atom, and the binding energy per atom of these clusters are also high in Figures 6(a), 7(a), and 8(a), respectively. The Al<sub>2</sub>Na<sub>2</sub> is an 8-valence electron system. The molecular orbitals that correspond to the 1S and 1P shell of the shell model are occupied in this cluster. In the Al<sub>2</sub>Na<sub>3</sub> and Al<sub>2</sub>Na<sub>4</sub> clusters, the electrons are taken into the 2S shell containing the Al–Al σ-bonding character before the occupation of the 1D shell.

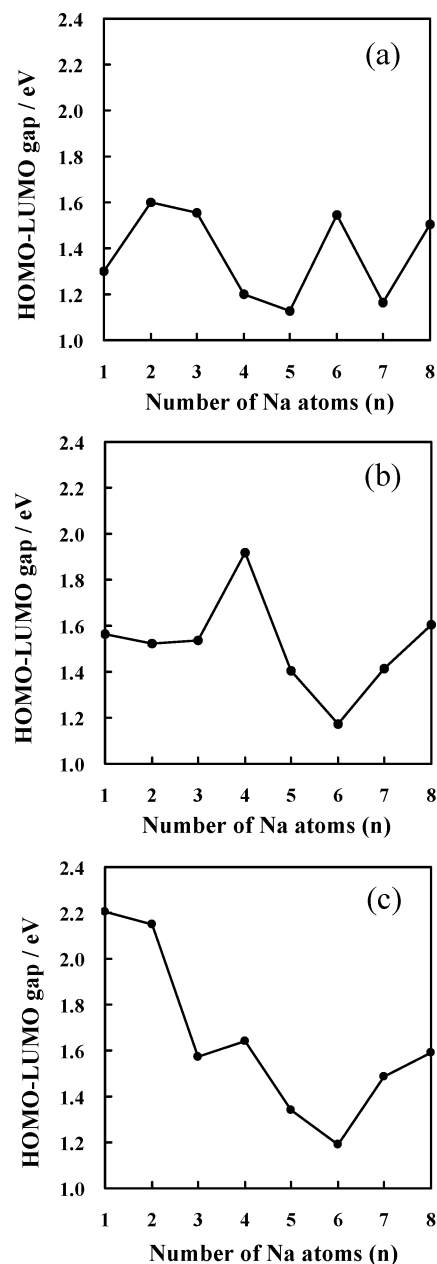
We tried to investigate the stability of the Al<sub>2</sub>Na<sub>5</sub> cluster before the discussion about the stability of the Al<sub>2</sub>Na<sub>6</sub> cluster. In the <sup>2</sup>A' state (**2-5a**), the 4a' and 5a' orbitals corresponded to the 2S shell and one of the 1D shells, respectively, contain the Al–Al σ-bonding and 3s orbital components of the plane Na atoms. The odd electron of the attached Na atom is





**Figure 5.** Vertical ionization potentials (IP) of the (a) Al<sub>2</sub>Na<sub>n</sub>, (b) Al<sub>3</sub>Na<sub>n</sub>, and (c) Al<sub>4</sub>Na<sub>n</sub> clusters with the number of Na atoms (*n*).

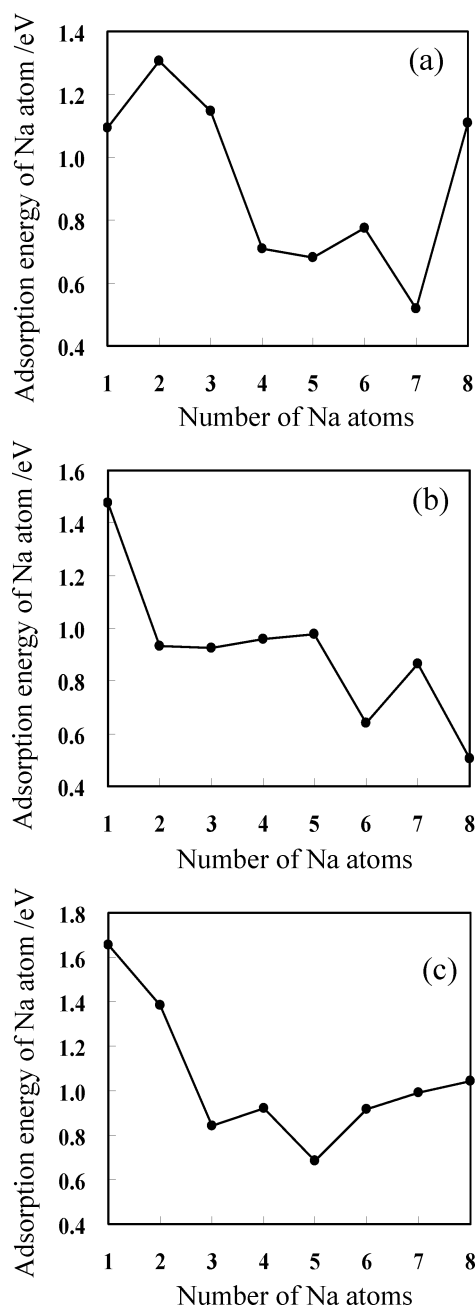
transferred to the Al–Al bond due to the addition of the Na atom perpendicular to the Al–Al bond (in plane of the Na atoms). The spin density (0.53) of the Al atom supports this electron transfer. The electron transfer might occur in order to form the stable Al–Al part. On the other hand, the paired electrons of the 3a<sub>1</sub> orbital (2S shell) of **2-5b** contribute to the stability of the Al–Al part due to the addition of the Na atom to the Al atom (on atom). The 4a<sub>1</sub> orbital (1D shell, SOMO) has the large 3s character of the four Na atoms. The spin density of 0.26 for the four Na atoms shows that the odd electron is distributed on the plane. It is suggested that this structure becomes stable due to the odd electron delocalized to the four Na atoms. A stable structure is not obtained due to the addition of the Na atom to the Na–Al–Na plane of the Al<sub>2</sub>Na<sub>4</sub> cluster. Therefore, two formation cases of the stable structure are found; one is the electron transfer to the Al–Al bond, and another is delocalization of the odd electron to the four Na atoms.



**Figure 6.** HOMO–LUMO gap of the (a) Al<sub>2</sub>Na<sub>n</sub>, (b) Al<sub>3</sub>Na<sub>n</sub>, and (c) Al<sub>4</sub>Na<sub>n</sub> clusters with the number of Na atoms (*n*).

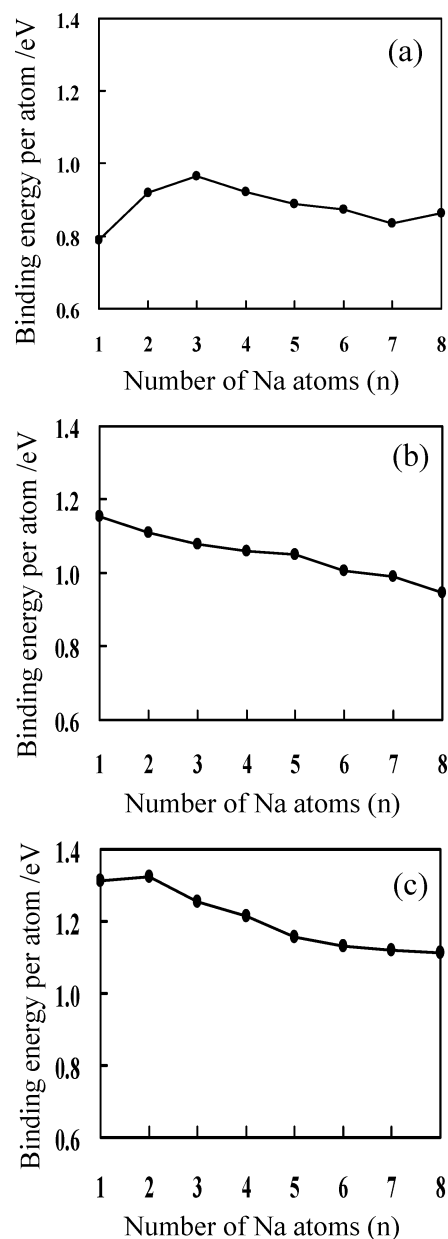
The Al<sub>2</sub>Na<sub>6</sub> cluster is more stable than the neighbor clusters. It is found that both the 4a' (2S shell) and 5a' (1D shell) are occupied. The 4a' orbital contains the Al–Al σ-bonding character, and the 5a' orbital contains the 3s orbital characters of the Na atoms and the Al–Na σ-bonding character of the added Na atom and the Al<sub>2</sub> molecule. That is, both the Al–Al part and the Na plane become stable. In the Al<sub>2</sub>Na<sub>8</sub> (**2-8a**) cluster, the 2a<sub>1</sub> (1P), 3a<sub>1</sub> (2S), and 2b<sub>2</sub>– (1D) orbitals have the 3s orbital character of the Na atoms in the hexagonal bipyramid shape. It suggested that this cluster becomes stable due to the valence electrons delocalized to the Na atoms. The addition of the Na atom to the Na–Al–Na plane, which forms the stable 1D shell, is found in the Al<sub>2</sub>Na<sub>7</sub> and Al<sub>2</sub>Na<sub>8</sub> (**2-8b**).

The IP of the Al<sub>3</sub>Na<sub>4</sub> in Figure 5(b) is larger than those of the Al<sub>3</sub>Na<sub>n</sub> (*n* = 5–8) cluster though it is an open shell system. The HOMO–LUMO gap of the Al<sub>3</sub>Na<sub>4</sub> cluster is



**Figure 7.** Adsorption energy of the Na atom ( $E_{\text{Na}}$ ) of the (a)  $\text{Al}_2\text{Na}_n$ , (b)  $\text{Al}_3\text{Na}_n$ , and (c)  $\text{Al}_4\text{Na}_n$  clusters with the number of Na atoms ( $n$ ).

also very large. These results suggest that the  $C_{3v}$  symmetry of the  $\text{Al}_3\text{Na}_4$  anion cluster is stable because the  $2a''$  and  $5a'$  of the neutral cluster are degenerated when the anion cluster is formed. The  $4a'$  orbital corresponding to the 2S shell contains the  $3s$  orbital characters of the Na atoms and  $\sigma$ -bonding of the Al atoms. The molecular orbitals containing the  $3s$  and  $3p$  characters of the Al atoms, from  $1a'$  to  $3a'$ , are already occupied. In the  $\text{Al}_3\text{Na}_n$  clusters of  $n = 6-8$ , the 2S shell is more stable than one of the 1P shells and 1D shells because the electrons are distributed to the Na wing. The explanation for the formation of the Na wing is difficult on the basis of the jellium. In the monometallic cluster, i.e.,  $\text{Na}_n$  and  $\text{Al}_n$ , the electron configuration of 1S, 1P, 1D, and 2S is found based on this model. In the Al–Na cluster, the 1S and 1P shells containing the  $3s$  or  $3p$  orbital character of



**Figure 8.** Binding energy per atom ( $E_b$ ) of the (a)  $\text{Al}_2\text{Na}_n$ , (b)  $\text{Al}_3\text{Na}_n$ , and (c)  $\text{Al}_4\text{Na}_n$  clusters with the number of Na atoms ( $n$ ).

the Al atom become stable due to the electron transfer from the Na atom. The 2S shell containing the  $3s$  orbital of the Na atom and one of the  $3p$  orbitals of the Al atom is also stable. It is considered that the formation of the sphere-shaped 2S shell is difficult due to the contribution of the  $3p$  orbital of the Al atom. The same tendency is found in the 2S shell of the  $\text{Al}_2\text{Na}_n$  ( $n = 1-8$ ) cluster. The shape of the 2S shell might be changed to spherical in the case of the large Al–Na cluster containing a large number of Na atoms. After the Na atoms attach to the Al–Al bond of the  $\text{Al}_3$  part, the addition of the Na atom on the Al–Na–Al plane, which forms the 1D shell or sphere-shaped 2S shell, does not occur because the odd electron of the Na atom added to the Na–Na bond is transferred to the Al–Al bond, for example, the  $^2A'$  state (**2-5a**) of the  $\text{Al}_2\text{Na}_5$  cluster.

There are two characteristics of the IP of the  $\text{Al}_4\text{Na}_n$  clusters in Figure 5(c). One is the monotonic decrease for  $n$

$< 5$ , and another is the small alternation for  $n \geq 5$ . The HOMO–LUMO gap of the  $\text{Al}_4\text{Na}_n$  clusters clearly shows the stability of the cluster. The  $\text{Al}_4\text{Na}_2$ ,  $\text{Al}_4\text{Na}_4$ , and  $\text{Al}_4\text{Na}_8$  clusters are relatively stable. In the  $\text{Al}_4\text{Na}_2$  cluster, the HOMO is the 2S shell. Recently, the stability of the  $\text{Al}_4\text{Na}_4$  cluster is described as a metalloaromatic compound. The character of the 2S shell is not clear in the  $\text{Al}_4\text{Na}_4$  cluster. The  $3a'$  and  $5a'$  orbitals include the 2S shell character. The  $\text{Al}_4\text{Na}_8$  cluster is stable because this cluster is a 20-valence electron system, which produces a stable structure based on the jellium model. In this cluster, the 2S shell ( $4a'$ ) becomes more stable than the 1D shell as in the  $\text{Al}_m\text{Na}_n$  ( $n = 2, 3$ ;  $n = 1-8$ ), and the five 1D shells are occupied. The contribution of the  $3p$  orbital of the Al atom in the  $\text{Al}_4\text{Na}_n$  cluster is different from those of the  $\text{Al}_2\text{Na}_n$  and  $\text{Al}_3\text{Na}_n$  clusters. It is suggested that the hybridized  $3p$  orbitals of the stereoscopic  $\text{Al}_4$  structure produce the spherical shape of the 2S shell.

The stability of the  $\text{Al}_2\text{Na}_6$ ,  $\text{Al}_3\text{Na}_4$  ( $\text{Al}_3\text{Na}_4^-$ ), and  $\text{Al}_4\text{Na}_4$  clusters is explained on the basis of the monovalence electron system as in the  $\text{AlNa}_7$  cluster.<sup>2,3</sup> On the other hand, an analysis of the stabilities for the  $\text{Al}_2\text{Na}_2$  and  $\text{Al}_4\text{Na}_8$  clusters are impossible because they have 4 and 12 electrons based on the monovalence system, respectively. They have 8- and 20-valence electrons based on the trivalence electron system per Al atom. Neither the monovalence system nor trivalence system explains the stability of the  $\text{Al}_2\text{Na}_8$ ,  $\text{Al}_3\text{Na}_7$ , and  $\text{Al}_4\text{Na}_2$  clusters. We will try to investigate the stability of the Al–Na clusters, especially the  $\text{Al}_m$  system, based on the stability and distribution of the 2S shell containing the  $3s$  orbital of the Na atom and the  $3p$  orbitals of the Al atom.

#### 4. Conclusion

The formation process of the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ;  $n = 1-8$ ) was investigated using the B3LYP method with the 6-311G\* basis sets. The stable structures of the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ;  $n = 1-8$ ) clusters were discussed on the basis of the assumption that the Na atoms adsorbed on the  $\text{Al}_m\text{Na}_{n-1}$  clusters because the  $\text{Al}_m\text{Na}_{n-1}$  part was remained in most of the stable structures of the  $\text{Al}_m\text{Na}_n$  cluster. The attachment of the Na atom first occurs for the Al–Al bond (or Al plane) in the formation of the  $\text{Al}_m\text{Na}_n$  cluster. The odd electron of the attached Na atom is transferred to the  $\text{Al}_m$  part for  $n \leq 4$  or 5 in the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ) clusters since the  $\text{Al}_m$  part becomes stable. The  $\text{Al}_2\text{Na}_4$  structure, in which the molecular orbitals formed by the component of the Al atoms are doubly occupied, is maintained for  $n \geq 5$ . The stable  $\text{Al}_3\text{Na}_4$  structure, in which the Al–Al bond is saturated by the Na atoms, is also maintained for  $n \geq 5$ . In the  $\text{Al}_4\text{Na}_n$  clusters, the Na atoms are attached to the Al–Al bond, and the  $\text{Al}_4$  plane maintained the planar  $\text{Al}_4$  structure for  $n \leq 4$ . The formation of the in-plane Na–Na bond started from  $n \geq 5$  or 6 for the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ) clusters. The  $\text{Al}_2\text{Na}_5$ ,  $\text{Al}_3\text{Na}_5$ ,  $\text{Al}_3\text{Na}_6$ ,  $\text{Al}_3\text{Na}_7$ , and  $\text{Al}_3\text{Na}_8$  clusters have a characteristic structure. The Na wing is formed in the  $\text{Al}_3\text{Na}_n$  ( $n = 5-8$ ) clusters. The stable 2S shell containing the  $3s$  orbital of the Na atom and  $3p$  orbital of the Al atom is formed in  $n \geq 5$  or 6 for the  $\text{Al}_m\text{Na}_n$  ( $m = 2-4$ ) clusters. It is considered

that the 2S shell becomes stable before the occupation of the 1D shell because the electrons are delocalized on the Na plane.

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