Experimental and theoretical investigation on binary anionic clusters of Al$_m$Bi$_n$

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Al$_m$Bi$_n$ ($m = 1–12; n = 1–4$) binary cluster anions are generated by laser ablation of a sample composed of Al and Bi, and studied by reflectron time-of-flight mass spectrometry (RTOF-MS) in the gas phase. Some clusters with magic numbers are present in the mass spectrum. The structures of Al$_m$Bi$_n$ ($m + n \leq 7$) clusters are investigated with the density functional theory (DFT) method and the most likely structures are obtained. The calculations of the binding energy (BE), energy gain ($\Delta$) and HOMO-LUMO gaps confirm that the Al$_3$Bi$_3$ cluster has a very stable structure, which agrees well with the experimental results. It is further established that Al$_3$Bi$_3$ can be considered as a gas-phase Zintl analogue that follows Wade’s rules and is the analogue of Ga$_2$Bi$_5$ and Sn$_2$Zintl ions. Copyright © 2009 John Wiley & Sons, Ltd.

The study of atomic clusters has become an active area of research during the last three decades. The atomic clusters exhibit interesting size-dependent properties which can help to find the functional transition of molecules to solid-state regimes. Numerous experimental and theoretical investigations of atomic clusters have been carried out. These studies have shed light on the chemical binding, structures and reactivities of such clusters, and have given a better understanding of the change of geometric and electronic structures with size evolution from the clusters to the condensed matter. Among the atomic clusters, semiconductor clusters have been extensively investigated for both fundamental and technological interests.

Clusters consisted of III–V semiconductor elements have been the subject of experimental1–5 and theoretical6–12 studies. A primary driving force for such studies is that the materials with III–V elements are of great technological importance in the fabrication of fast microelectronic devices, small devices and light-emitting diodes. The detailed study of the properties of such clusters as a function of their size could provide significant insight into the evolution from the molecular level to the bulk. In the last few years, several studies of AlN, GaAs, InAs, InP, AlP and GaP binary clusters1–3,6,13–20 have been published. Neumark’s group3 studied size-selected Al$_m$P$_m$ ($m, n < 4$) clusters by photoelectron spectroscopy (PES). Taylor et al. reported the PES of GaX$_2$, Ga$_2$X$_2$ and Ga$_2$X$_3$ ($X = P, As$).3 Kamal et al.6 studied Ga$_m$P$_n$ ($n = 2–5$) clusters by density functional theory (DFT) calculations. BelBruno7 studied the electronic and geometric structures, and the bonding properties, of small Ga$_m$As$_m$ clusters using DFT. Guo reported theoretical studies on Al$_m$As$_n$, anions.8–10 Quek et al.11 reported tight binding molecular dynamics studies of Ga$_m$As$_n$ and Al$_m$As$_n$ clusters. Although there have been many studies on III–V semiconductor clusters, they have mainly been theoretical, and there have been few experimental studies of these binary clusters. Recently, Gupta et al.4 reported a combined experimental and theoretical study of anionic and neutral Bi$_m$Ga$_n$ clusters, and showed that Bi$_3$Ga$_2$ can be considered as a Zintl ion. Jones et al.5 reported an experimental and theoretical study of bismuth-doped aluminum clusters, and found two particularly stable clusters, Al$_4$Bi and Al$_5$Bi. However, there have been few studies of the multi-bismuth-doped aluminum clusters of Al$_m$Bi$_n$.

In this work, binary anionic clusters Al$_m$Bi$_n$ produced by laser ablation are studied both experimentally by reflectron time-of-flight mass spectrometry (RTOF-MS) and theoretically with density functional theory (DFT). Some clusters with especially stable structures have been found, which will provide the fundamental information for further studies of Al/Bi binary clusters.

**EXPERIMENTAL**

The binary metal cluster ions composed of Al and Bi were generated and analyzed under the following conditions. The samples were prepared with aluminum (purity: 99%; Beijing West Chemical Plant, Beijing, China) and bismuth (purity: 99%; Shanghai Chemical Reagent Station, Shanghai, China)
powders, mixed well in different atomic ratios and pressed into round tablets (diameter = 12 mm).

The experiments to produce and detect Al/Bi binary cluster ions were performed using a vaporization laser together with a home-made reflectron time-of-flight mass spectrometer. A detailed description of the RTOF-MS system has been given elsewhere. Briefly, the second harmonic of a Q-switched Nd:YAG laser (532 nm, ~10 mJ/pulse, 5 pulse/s) was focused on the surface of the tablet sample held in the source chamber (at 10^-4 Pa) of the spectrometer. The products were then extracted in the direction perpendicular to the cluster beam, and accelerated to about 1.2 keV. Two sets of deflectors and einzel electrostatic lenses were used to guide and focus the ion beam. The ions were reflected by a reflector and detected by a dual microchannel plate (MCP) detector installed at the space focus point. The output signal was amplified and recorded by a 100 MHz transient recorder (Fast Electronics Laboratory, University of Science and Technology of China, Hefei, China), then stored on a PC. Typically, the final digitized mass spectra were averaged over 500 laser pulses. The mass resolution of the spectrometer (m/Δm) is over 1000 under the present conditions, which enables us to clearly resolve all products even in the high-mass region. The timing of the laser vaporization, electric pulse acceleration and recording was optimized by a digital delay pulse generator (DG535, Stanford Research Systems Inc., Sunnyvale, CA, USA).

The high vacuum in the source chamber and the detecting region was maintained by differential pumping with turbomolecular pumps and mechanical pumps. The corresponding operating pressures were all 10^-4 Pa.

Theoretical method

In this study, geometric and electronic structure calculations of these binary clusters were performed using B3LYP functionals, which were widely used hybrid DFT-HF methods.

Two types of basis sets were used in both the geometry and the frequency calculations. In the first type of basis set, the relativistic effective core potentials (RECPs) given by Hay/Wadt and the corresponding LANL2DZ basis sets were used for the Bi element, and the LANL2DZ basis sets were extended by an additional set of diffuse and polarization functions appropriate for studying anions. RECPs are common and are an efficient way to reduce the complex calculations for molecules containing heavy atoms such as Bi, which replace the chemically inert core electrons with potentials and incorporate relativistic effects in the potentials.

For the Al element, we used the all-electron basis set 6-311+g(3df) in the second type of basis set. For the sake of brevity, the first type of basis sets is referred to as LANL2DZdp and the second is labeled as 6-311+g(3df) in the present paper. The theoretical method and basis sets have been successfully applied to systems containing Al and Bi, so it should be adequate for studying Bi-containing clusters.

To search for the global minima of Al\(_n\)Bi\(_m\) clusters, we first performed first-principle DFT calculations on a wide variety of singlet and triplet structures (or doublet and quadruplet) for these species at the level of B3LYP/LANL2DZdp. To characterize the nature of the stationary points, harmonic vibrational frequencies were calculated. We found that the most stable structures for all these anionic species are presented as their lowest spin (singlet or doublet) electronic state. All the calculations were carried out with the Gaussian 03 program package.

RESULTS AND DISCUSSION

Product analysis

Figure 1 presents the time-of-flight (TOF) mass spectrum of the cluster anions obtained by direct laser (the combined 1064 and 532 nm beams) ablation on the sample Al/Bi. The resolution of our RTOF-MS instrument allows the identification of the isotopic distribution in the mass spectrum.

In Fig. 1, the five different series of products: Bi\(_n\) (n = 1–4), Al\(_n\)Bi\(_m\) (m = 1–12), Al\(_{n-1}\)Bi\(_2\) (m = 1–11), Al\(_{n-2}\)Bi\(_3\) (m = 1–10) and Al\(_{n-3}\)Bi\(_4\) (m = 1–11) appear. In the Al\(_n\)Bi\(_m\) series (m = 1–12), the relative intensity of the mass spectrum decreases with increasing of m, but the relative intensity of Al\(_5\)Bi\(_4\) is the smallest in this series. From m = 5, the relative intensity also decreases with an increase in the number of Al atoms. This shows that the structures of Al\(_n\)Bi\(_m\) (m = 1–12) clusters have a transition in stability. Jones et al. reported that Al\(_3\)Bi and Al\(_4\)Bi are particularly stable clusters. Al\(_3\)Bi is an all-metal aromatic cluster, and Al\(_4\)Bi is a Jellium superatom candidate. This indicates that from m = 3 to m = 5 a transition of the structures occurs between aromatic and Jellium stability. In the Al\(_n\)Bi\(_2\) series (m = 1–11), the relative intensity of the mass spectrum decreases with an increase in the number of Al atoms. However, when m = 6, the intensity of Al\(_5\)Bi\(_3\) is larger than that of its adjacent species, showing that the Al\(_5\)Bi\(_3\) cluster has a more stable structure. In the Al\(_n\)Bi\(_3\) series (m = 1–10), the intensity of Al\(_4\)Bi\(_3\) is relatively the largest, and the relative intensity of the mass spectrum then decreases with an increase in the number of Al atoms. However, in the Al\(_n\)Bi\(_4\) series (m = 1–11), the relative intensity of the mass spectrum increases with the increased number of Al atoms until m = 5, which has the largest intensity, and then the relative intensity decreases with further increase in the number of Al atoms.

**Figure 1.** TOF mass spectrum of binary cluster anions produced by laser ablation on mixed samples of Al/Bi (atomic ratio 1:1).

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The Al\(_2\)Bi\(^{-}\) cluster has a particularly large intensity in the mass spectrum of the Al\(_m\)Bi\(_n\) \((m = 1\text{–}10)\) clusters, which shows that the Al\(_2\)Bi\(^{-}\) cluster has a more stable structure than others in the series. It has been reported\(^{29}\) that Bi\(_3\) has a planar \(D_{3h}\) structure and that it has an aromatic character. Other reports\(^{8,9}\) have shown that the Al\(_2\)As\(_3\) cluster has exceptional stability. Gupta \textit{et al.}\(^{4}\) reported that the Ga\(_2\)As\(_3\) cluster is a Zintl cluster and has exceptional stability. We know that the elements in the same group of the periodic table have the same number of valence electrons, and have similar physicochemical characteristics. Thus Al is expected to have the same character as Ga, and As to have the same as Bi. Therefore, it is reasonable to assume that the analogous Al\(_2\)Bi\(^{-}\) cluster has a very stable structure.

\textbf{The structures by DFT calculations}

We have optimized a number of initial structures with different spin states, and the normal vibrational frequencies at the optimized geometries were also checked to rule out imaginary frequencies at the same theoretical level. The optimized geometries of the low-lying isomers of the Al\(_m\)Bi\(_n\) clusters \((m + n \leq 7)\) are presented in Fig. 2.

For the Al\(_2\)Bi\(^{-}\) cluster, the ground state shows a \(C_{2v}\) structure (1a), which is in agreement with what was reported.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Optimized geometries of the low-lying isomers of the Al\(_m\)Bi\(_n\) clusters \((m + n \leq 7)\). Bond lengths are given in Angstroms, and the symmetry point group and electronic state (in parentheses) are given. The pink balls (lighter) correspond to Al atoms, while the purple balls (darker) represent Bi atoms.}
\end{figure}
by the Jones et al. The Al–Bi bond length is 2.65 Å, in reasonable agreement with the reported result of 2.668 Å. The line isomer (1b) is 0.79 eV higher in energy than the ground state (1a). The C_{2v} isomer with isoceles triangular geometry ‘like a Δ structure’ has one imaginary frequency. For the Al_{2}Bi_{3} cluster, the ground state has a C_{2v} rhombus structure (2a) in which the Al atoms occupy the shorter diagonal of the rhombus, and the isomer with a butterfly structure is 0.31 eV higher in energy than the ground state. Archibong and Marynick reported that the analogous Al_{2}As_{3} cluster has a planar rhombus structure and that the Al–Al bond length was 2.536 Å, in reasonable agreement with our result of 2.66 Å. For the Al_{2}Bi_{3} cluster, the ground state shows a C_{3v} trigonal bipyramidal structure (4a), and the C_{i} isomer (4b) is 0.05 eV higher in energy than the ground state. Gupta et al. and Gao and Wu reported that the analogous Ga_{3}Bi_{3} and Al_{2}As_{3} clusters have a trigonal bipyramidal structure in the ground state, and also that the Ga_{3}Bi_{3} cluster is a Zentl ion with special stability. For the Al_{3}Bi_{3} cluster, the ground state has a C_{3v} structure (5a), which is similar to the structure of the Al_{2}As_{3} cluster. The Al–Bi and Al–Al bond lengths are in accord with the reported result for the Al_{m}Bi_{n} clusters. The C_{2v} isomer (5b) is 0.85 eV higher in energy than the ground state (5a).

For the Al_{3}Bi_{3} cluster, the ground state is a C_{2v} planar structure, and the C_{3v} tetrahedron isomer (3b) is 0.04 eV higher in energy than the ground structure (3a). Jones et al. reported that Al_{3}Bi has a C_{2v} planar structure with aromatic stability. For the Al_{3}Bi_{3} cluster, the ground state is a D_{3h} planar structure (6a), which is similar to the analogous Al_{2}As_{3} cluster in the ground state. The Al–Bi and Al–Al bond lengths are in agreement with the reported results. The 6b isomer has a higher energy than the 6a structure. For the Al_{2}Bi_{4} cluster, the ground state is a C_{i} structure (7a), which is similar to the structure of the analogous Ga_{3}Bi_{3} cluster in the ground state. The 7b isomer has a higher energy than the ground state structure (7a).

**Stability**

In order to test the stability of Al_{m}Bi_{n} (m + n ≤ 7) further and to gain an understanding of the energy changes with the change of cluster size, we calculated the binding energy (BE), energy gain (Δ) and HOMO–LUMO gap of all the most stable structures obtained in our calculations.

The binding energy per atom (BE/atom) is defined as BE = mE(Al) + nE(Bi) – E(Al_{m}Bi_{n})/(m + n). Figure 3 shows the binding energy (BE/atom, eV) of the Al_{m}Bi_{n} clusters (m + n ≤ 7) as a function of the number of Al atoms m or Bi atoms n for the most stable structures. From Fig. 3 we can see that the BE/atom of Al_{2}Bi_{3} is the largest with the increase in the number of Bi atoms, and that both Al_{2}Bi_{3} and Al_{3}Bi_{3} have almost the same BE/atom with the increase in the number of Al atoms. This indicates that the Al_{2}Bi_{3} cluster has a more stable structure than the other clusters in the Al_{m}Bi_{n} series (m + n ≤ 7).

The energy gain (Δ) is defined as Δ_{Al} = E(Al_{m−1}Bi_{n}) + E(Al) – E(Al_{m}Bi_{n}) and Δ_{Bi} = E(Al_{m}Bi_{n−1}) + E(Bi) – E(Al_{m}Bi_{n}). Figure 4 shows the Δ_{Al} and Δ_{Bi} of the Al_{m}Bi_{n} clusters (m + n ≤ 7) as a function of the number of Al atoms m or Bi atoms n for the most stable structures. It is clear that the energy gain (Δ) of Al_{2}Bi_{3} is much larger than that of its adjacent cluster anions, showing that the Al_{2}Bi_{3} cluster is much more stable than the other clusters.

The HOMO–LUMO gap also is a very important criterion for cluster stability. It has been shown that clusters with a large HOMO–LUMO energy gap tend to be highly stable. In Fig. 5, it can be seen that the HOMO–LUMO gap of Al_{2}Bi_{3} is the largest with the increase of m or n, which shows that the Al_{2}Bi_{3} cluster has relatively high stability.

The above analysis suggests that the Al_{2}Bi_{3} cluster has higher stability than the other clusters in the series of Al_{m}Bi_{n} (m + n ≤ 7). There are several theories to explain the stability of clusters. One is the Jellium model, in which a Jellium electronic shell structure emerges with stable numbers in electron configurations (2, 8, 18, 20, 40, ...) such as superatom Al_{13} (40 electrons). For the Al_{2}Bi_{3} cluster, there are 22 valence electrons, which is not in accord with the Jullium model. The second model to explain electron stabilization is aromaticity, which has been mainly applied to organic systems, where molecules, which are conjugated, cyclic and planar, and contain (4n + 2) π electrons, are...
traditionally classified as aromatic molecules. Recent studies by Li et al.37 have extended the concept of aromaticity to all-metal anionic molecules, such as most notably the Al2Bi3 dianion. The number of valence electrons of the Al2Bi3/C04 dianion agrees with the number required for aromaticity, but the most stable structure is not planar but trigonal bipyramidal. Wang’s group29 reported that the Bi5/C05 cluster with a planar pentagon structure has aromatic character. We have also calculated the planar pentagon structure of Al2Bi3/C03, but obtained two imaginary frequencies. The third model to explain electron stabilization is the Zintl structure.38,39 Gupta reported that the Zintl ion Ga3Bi2/C02 has special stability. 4 The Ga3Bi2 and Al2Bi3 clusters are analogous, and have similar structures, suggesting that the Al2Bi3 cluster may be a Zintl ion. We therefore examined the applicability of Wade’s rule40 to the Al2Bi3 cluster. The Bi atom has a total of two s (6s2) and three p valence electrons (6p3), and the Al atom has two s (3s2) and one p (3p1) valence electrons. There are 12 p-electrons in the Al2Bi3 cluster. The calculations show that the ground state of Al2Bi3 cluster is a trigonal bipyramidal structure (Fig. 2). It has five vertices and also 12 p-electrons (2n + 2 = 12; n = 5 vertices) with a closo structure, and it thus follows Wade’s rule. Therefore, the Al2Bi3 cluster is also a Zintl ion.

Comparison of Al2Bi3 with Sn25 Zintl cluster
On considering Zintl ion chemistry, one notices that the Sn25 cluster is one of the most stable Zintl clusters.38,41 This cluster has five atoms, 12 p valence electrons and a trigonal bipyramidal geometry, quite similar to that of Al2Bi3. They both have five vertices and 12 p-electrons (2n + 2 = 12; n = 5 vertices) with a closo structure, and thus they follow Wade’s rule. To further investigate this similarity, the Sn25 cluster was optimized with our theoretical model using the B3LYP/LANL2DZdp level. The electron energy levels and the molecular orbitals for Sn25 are compared with the ones of Al2Bi3 in Table 1. It is clear that the twelve most occupied levels of Sn25 and Al2Bi3 are very similar, although somewhat differently ordered. Finally, the calculated HOMO-LUMO gap of 2.85 eV for Sn25 is very close to that of 2.50 eV for Al2Bi3. Figure 6 shows the molecular orbital pictures of the HOMO for the Sn25 and Al2Bi3 clusters. This analogy reinforces the conclusion that Al2Bi3 is a gas-phase Zintl analogue of Sn25.

Table 1. The energies of molecular orbitals for the Sn25 and Al2Bi3 clusters

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<tr>
<th>MOa</th>
<th>Configuration</th>
<th>Energy (eV)</th>
<th>MO</th>
<th>Configuration</th>
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a MO is molecular orbital.
b LUMO is the lowest unoccupied molecular orbital.
c HOMO is the highest occupied molecular orbital.

Figure 5. The HOMO-LUMO gap of AlmBi3n clusters (m + n ≤ 7).

Figure 6. The molecular orbital pictures of HOMO for the Sn25 and Al2Bi3 clusters.
CONCLUSIONS

Al_{m}Bi_{n} (m = 1–12; n = 1–4) cluster anions are produced by laser ablation and analyzed by reflectron time-of-flight mass spectrometry in the gas phase. The most stable structures of Al_{m}Bi_{n} (m + n ≤ 7) are obtained by DFT calculations. The calculations of binding energy (BE), energy gain (∆) and HOMO–LUMO gaps confirm that the Al_{2}Bi_{3} cluster is the most stable in these anion species, which agrees well with the experimental results. It is further established that while the Jellium model is insufficient to explain the stability of the gas-phase systems. Consequently, Al_{2}Bi_{3} can be considered as a gas-phase Zintl analogue that follows Wade’s rules and is the analogue of Ga_{3}Bi_{3} and Sn_{2}/C_{20}^{–} Zintl ions.

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