

# Experimental and theoretical investigation on binary anionic clusters of $\text{Al}_m\text{Bi}_n^-$

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Received 10 April 2009; Revised 15 June 2009; Accepted 21 June 2009

$\text{Al}_m\text{Bi}_n^-$  ( $m = 1-12$ ;  $n = 1-4$ ) 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  $\text{Al}_m\text{Bi}_n^-$  ( $m + n \leq 7$ ) 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  $\text{Al}_2\text{Bi}_3^-$  cluster has a very stable structure, which agrees well with the experimental results. It is further established that  $\text{Al}_2\text{Bi}_3^-$  can be considered as a gas-phase Zintl analogue that follows Wade's rules and is the analogue of  $\text{Ga}_2\text{Bi}_3^-$  and  $\text{Sn}_5^{2-}$  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 experimental<sup>1–5</sup> and theoretical<sup>6–12</sup> 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 clusters<sup>1–3,6,13–20</sup> have been published. Neumark's group<sup>1</sup> studied size-selected  $\text{Al}_m\text{P}_m^-$  ( $m, n < 4$ ) clusters by photoelectron spectroscopy (PES). Taylor *et al.* reported the PES of

$\text{GaX}_2^-$ ,  $\text{Ga}_2\text{X}^-$ ,  $\text{Ga}_2\text{X}_2^-$ , and  $\text{Ga}_2\text{X}_3^-$  ( $X = \text{P}, \text{As}$ ).<sup>3</sup> Kamal *et al.*<sup>6</sup> studied  $\text{Ga}_n\text{P}_n$  ( $n = 2-5$ ) clusters by density functional theory (DFT) calculations. BelBruno<sup>7</sup> studied the electronic and geometric structures, and the bonding properties, of small  $\text{Ga}_n\text{As}_m$  clusters using DFT. Guo reported theoretical studies on  $\text{Al}_m\text{As}_n$  anions.<sup>8–10</sup> Quek *et al.*<sup>11</sup> reported tight binding molecular dynamics studies of  $\text{Ga}_m\text{As}_n$  and  $\text{Al}_m\text{As}_n$  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.*<sup>4</sup> reported a combined experimental and theoretical study of anionic and neutral  $\text{Bi}_m\text{Ga}_n$  clusters, and showed that  $\text{Bi}_3\text{Ga}_2^-$  can be considered as a Zintl ion. Jones *et al.*<sup>5</sup> reported an experimental and theoretical study of bismuth-doped aluminum clusters, and found two particularly stable clusters,  $\text{Al}_3\text{Bi}$  and  $\text{Al}_5\text{Bi}$ . However, there have been few studies of the multi-bismuth-doped aluminum clusters of  $\text{Al}_m\text{Bi}_n^-$ .

In this work, binary anionic clusters  $\text{Al}_m\text{Bi}_n^-$  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)

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Contract/grant sponsor: National Nature Science Foundation of China; contract/grant number: 20433080.

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.<sup>21</sup> 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, Chian), then stored on a PC. Typically, the final digitized mass spectra were averaged over 500 laser pulses. The mass resolution of the spectrometer ( $m/\Delta m$ ) 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,<sup>22,23</sup> 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<sup>24,25</sup> 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<sup>26</sup> 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,<sup>8,9,27</sup> so it should be adequate for studying Bi-containing clusters.

To search for the global minima of  $Al_mBi_n^-$  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

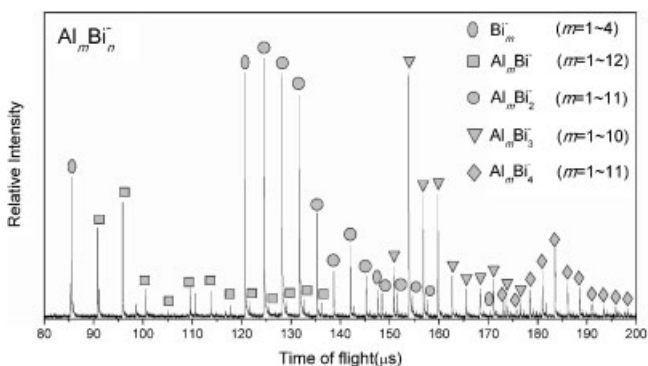
characterize the nature of the stationary points, harmonic vibrational frequencies were calculated. We found that the most stable structures for all these anionic species are presented as their lowest spin (singlet or doublet) electronic state. All the calculations were carried out with the Gaussian 03 program package.<sup>28</sup>

## 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:  $Bi_n^-$  ( $n = 1-4$ ),  $Al_mBi^-$  ( $m = 1-12$ ),  $Al_mBi_2^-$  ( $m = 1-11$ ),  $Al_mBi_3^-$  ( $m = 1-10$ ) and  $Al_mBi_4^-$  ( $m = 1-11$ ) appear. In the  $Al_mBi^-$  series ( $m = 1-12$ ), the relative intensity of the mass spectrum decreases with increasing of  $m$ , but the relative intensity of  $Al_4Bi^-$  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  $Al_mBi^-$  ( $m = 1-12$ ) clusters have a transition in stability. Jones *et al.*<sup>5</sup> reported that  $Al_3Bi$  and  $Al_5Bi$  are particularly stable clusters.  $Al_3Bi$  is an all-metal aromatic cluster, and  $Al_5Bi$  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  $Al_mBi_2^-$  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  $Al_6Bi_2^-$  is larger than that of its adjacent species, showing that the  $Al_6Bi_2^-$  cluster has a more stable structure. In the  $Al_mBi_3^-$  series ( $m = 1-10$ ), the intensity of  $Al_2Bi_3^-$  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  $Al_mBi_4^-$  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).

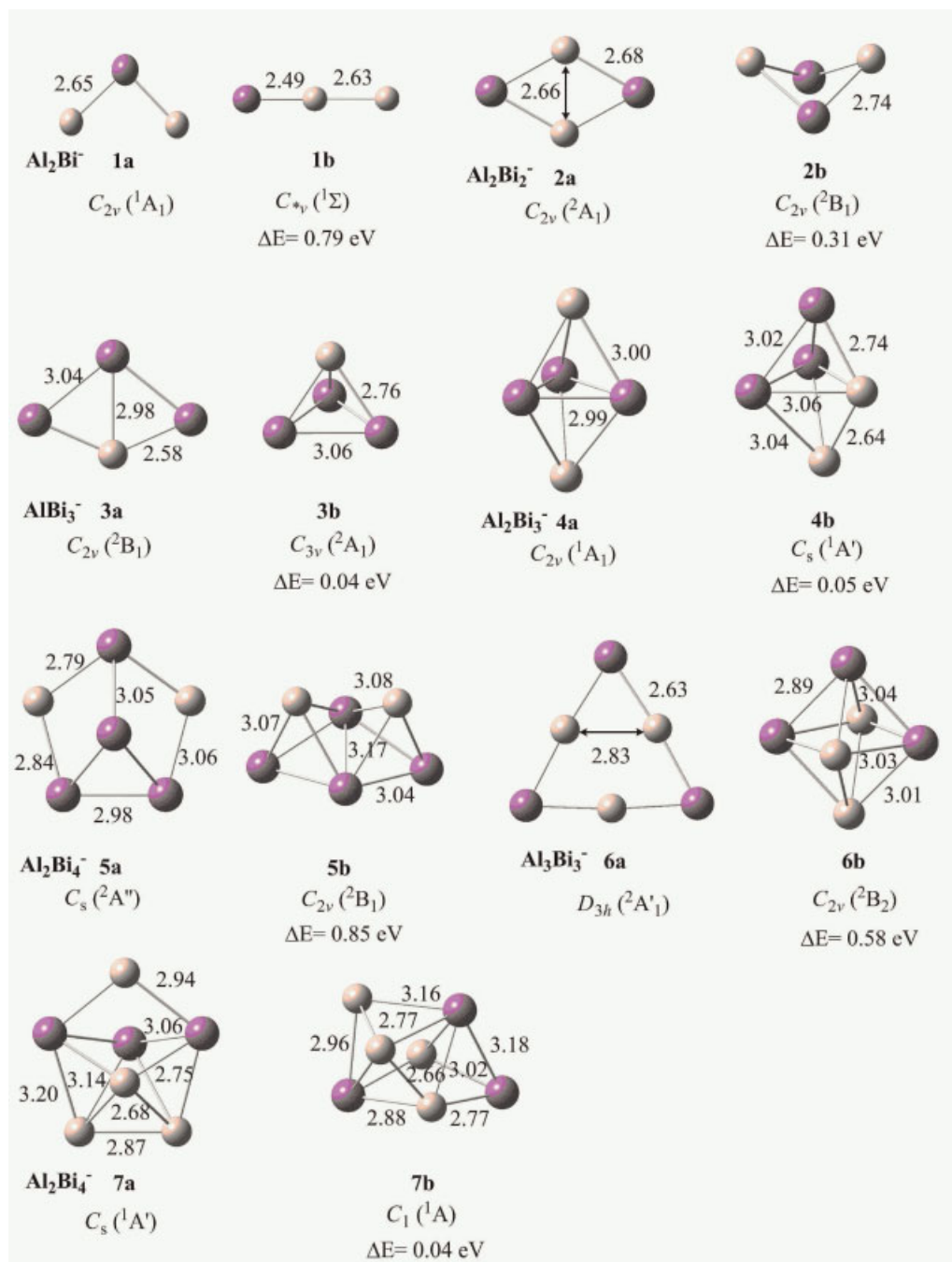
The  $\text{Al}_2\text{Bi}_3^-$  cluster has a particularly large intensity in the mass spectrum of the  $\text{Al}_m\text{Bi}_3^-$  ( $m=1-10$ ) clusters, which shows that the  $\text{Al}_2\text{Bi}_3^-$  cluster has a more stable structure than others in the series. It has been reported<sup>29</sup> that  $\text{Bi}_5$  has a planar  $D_{5h}$  structure and that it has aromatic character. Other reports<sup>8,9</sup> have shown that the  $\text{Al}_2\text{As}_3^-$  cluster has exceptional stability. Gupta *et al.*<sup>4</sup> reported that the  $\text{Ga}_2\text{As}_3^-$  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  $\text{Al}_2\text{Bi}_3^-$  cluster has a very stable structure.

### 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  $\text{Al}_m\text{Bi}_n^-$  clusters ( $m+n \leq 7$ ) are presented in Fig. 2.

For the  $\text{Al}_2\text{Bi}_1^-$  cluster, the ground state shows a  $C_{2v}$  structure (1a), which is in agreement with what was reported



**Figure 2.** Optimized geometries of the low-lying isomers of the  $\text{Al}_m\text{Bi}_n^-$  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.

by the Jones *et al.*<sup>5</sup> The Al–Bi bond length is 2.65 Å, in reasonable agreement with the reported result of 2.668 Å.<sup>5</sup> The line isomer (1b) is 0.79 eV higher in energy than the ground state (1a). The  $C_{2v}$  isomer with isosceles triangular geometry 'like a  $\Delta$  structure' has one imaginary frequency. For the  $Al_2Bi_2^-$  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<sup>12</sup> reported that the analogous  $Al_2As_2^-$  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  $Al_2Bi_3^-$  cluster, the ground state shows a  $C_{3v}$  trigonal bipyramidal structure (4a), and the  $C_s$  isomer (4b) is 0.05 eV higher in energy than the ground state. Gupta *et al.*<sup>4</sup> and Gao and Wu<sup>9</sup> reported that the analogous  $Ga_3Bi_2^-$  and  $Al_3As_2^-$  clusters have a trigonal bipyramidal structure in the ground state, and also that the  $Ga_3Bi_2^-$  cluster is a Zintl ion with special stability. For the  $Al_2Bi_4^-$  cluster, the ground state has a  $C_s$  structure (5a), which is similar to the structure of the  $Al_2As_4^-$  cluster.<sup>9</sup> The Al–Bi and Al–Al bond lengths are in accord with the reported result for the  $Al_mBi_n^-$  clusters.<sup>5</sup> The  $C_{2v}$  isomer (5b) is 0.85 eV higher in energy than the ground state (5a).

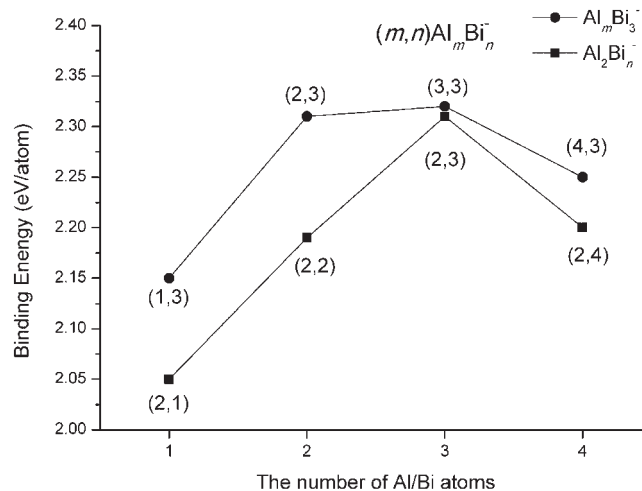
For the  $Al_3Bi^-$  cluster, the ground state is a  $C_{2v}$  planar structure, and the  $C_{3v}$  tetrahedron isomer (3b) is 0.04 eV higher in energy than the ground structure (3a). Jones *et al.*<sup>5</sup> reported that  $Al_3Bi^-$  has a  $C_{2v}$  planar structure with aromatic stability. For the  $Al_3Bi_3^-$  cluster, the ground state is a  $D_{3h}$  planar structure (6a), which is similar to the analogous  $Al_3As_3^-$  cluster in the ground state.<sup>12</sup> The Al–Bi and Al–Al bond lengths are in agreement with the reported results.<sup>12</sup> The 6b isomer has a higher energy than the 6a structure. For the  $Al_3Bi_4^-$  cluster, the ground state is a  $C_s$  structure (7a), which is similar to the structure of the analogous  $Ga_3Bi_4^-$  cluster<sup>4</sup> 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  $Al_mBi_n^-$  ( $m+n \leq 7$ ) further and to gain an understanding of the energy changes with the change of cluster size, we calculated the binding energy (BE), energy gain ( $\Delta$ ) and HOMO–LUMO gap of all the most stable structures obtained in our calculations.

The binding energy per atom (BE/atom) is defined as  $BE = [mE(Al) + nE(Bi) - E(Al_mBi_n^-)] / (m+n)$ . Figure 3 shows the binding energy (BE/atom, eV) of the  $Al_mBi_n^-$  clusters ( $m+n \leq 7$ ) 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  $Al_2Bi_3^-$  is the largest with the increase in the number of Bi atoms, and that both  $Al_3Bi_3^-$  and  $Al_2Bi_3^-$  have almost the same BE/atom with the increase in the number of Al atoms. This indicates that the  $Al_2Bi_3^-$  cluster has a more stable structure than the other clusters in the  $Al_mBi_n^-$  series ( $m+n \leq 7$ ).

The energy gain ( $\Delta$ ) is defined as  $\Delta_{Al} = E(Al_{m-1}Bi_n^-) + E(Al) - E(Al_mBi_n^-)$  and  $\Delta_{Bi} = E(Al_mBi_{n-1}^-) + E(Bi) - E(Al_mBi_n^-)$ . Figure 4 shows the  $\Delta_{Al}$  and  $\Delta_{Bi}$  of the  $Al_mBi_n^-$  clusters ( $m+n \leq 7$ ) 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

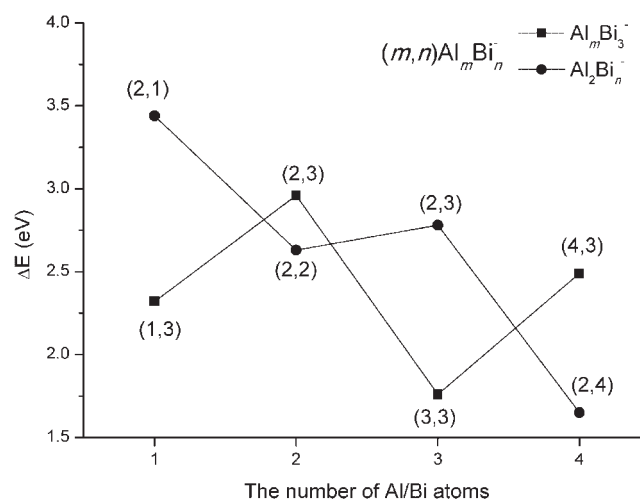


**Figure 3.** The binding energies per atom of  $Al_mBi_n^-$  clusters ( $m+n \leq 7$ ).

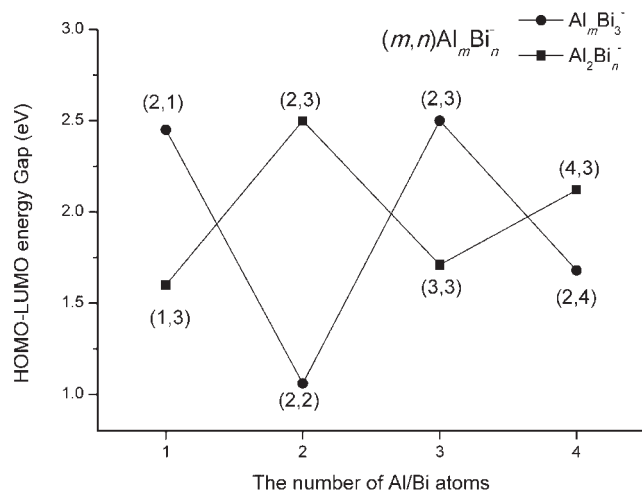
( $\Delta$ ) of  $Al_2Bi_3^-$  is much larger than that of its adjacent cluster anions, showing that the  $Al_2Bi_3^-$  cluster is much more stable than the other clusters.

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.<sup>30–32</sup> In Fig. 5, it can be seen that the HOMO–LUMO gap of  $Al_2Bi_3^-$  is the largest with the increase of  $m$  or  $n$ , which shows that the  $Al_2Bi_3^-$  cluster has relatively high stability.

The above analysis suggests that the  $Al_2Bi_3^-$  cluster has higher stability than the other clusters in the series of  $Al_mBi_n^-$  ( $m+n \leq 7$ ). 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, ...),<sup>33,34</sup> such as superatom  $Al_{13}^-$  (40 electrons).<sup>35</sup> For the  $Al_2Bi_3^-$  cluster, there are 22 valence electrons, which is not in accord with the Jellium model. The second model to explain electron stabilization is aromaticity, which has been mainly applied to organic systems,<sup>36</sup> where molecules, which are conjugated, cyclic and planar, and contain  $(4n+2)\pi$  electrons, are

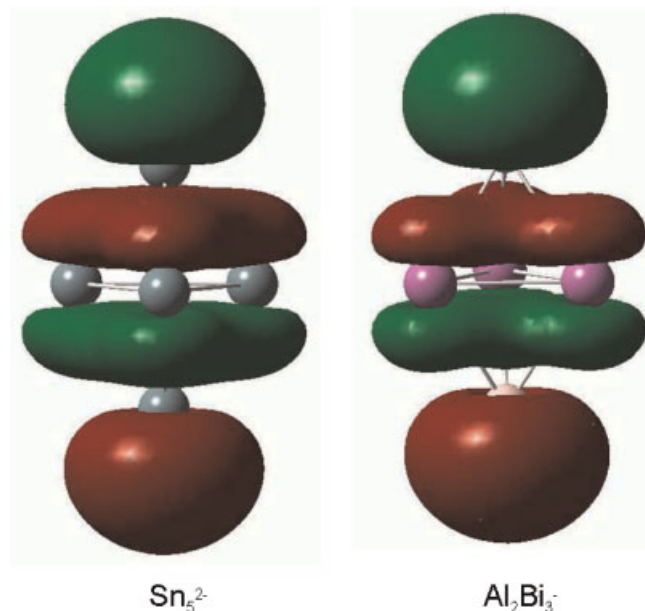


**Figure 4.** The energy gain of  $Al_mBi_n^-$  clusters ( $m+n \leq 7$ ).



**Figure 5.** The HOMO-LUMO gap of  $Al_mBi_n^-$  clusters ( $m+n \leq 7$ ).

traditionally classified as aromatic molecules. Recent studies by Li *et al.*<sup>37</sup> have extended the concept of aromaticity to all-metal anionic molecules, such as most notably the  $Al_4^{2-}$  dianion. The number of valence electrons of the  $Al_2Bi_3^-$  cluster ( $22 = 4 \times 5 + 2$ ) agrees with the number required for aromaticity, but the most stable structure is not planar but trigonal bipyramidal. Wang's group<sup>29</sup> reported that the  $Bi_5^-$  cluster with a planar pentagon structure has aromatic character. We have also calculated the planar pentagon structure of  $Al_2Bi_3^-$ , but obtained two imaginary frequencies. The third model to explain electron stabilization is the Zintl structure.<sup>38,39</sup> Gupta reported that the Zintl ion  $Ga_3Bi_2^-$  has special stability.<sup>4</sup> The  $Ga_3Bi_2^-$  and  $Al_2Bi_3^-$  clusters are analogous, and have similar structures, suggesting that the  $Al_2Bi_3^-$  cluster may be a Zintl ion. We therefore examined the applicability of Wade's rule<sup>40</sup> to the  $Al_2Bi_3^-$  cluster. The Bi atom has a total of two s ( $6s^2$ ) and three p valence electrons ( $6p^3$ ), and the Al atom has two s ( $3s^2$ ) and one p ( $3p^1$ ) valence electrons. There are 12 p-electrons in the  $Al_2Bi_3^-$  cluster. The calculations show that the ground state of the  $Al_2Bi_3^-$  cluster is a trigonal bipyramid 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  $Al_2Bi_3^-$  cluster is also a Zintl ion.



**Figure 6.** The molecular orbital pictures of HOMO for the  $Sn_5^{2-}$  and  $Al_2Bi_3^-$  clusters.

### Comparison of $Al_2Bi_3^-$ with $Sn_5^{2-}$ Zintl cluster

On considering Zintl ion chemistry, one notices that the  $Sn_5^{2-}$  cluster is one of the most stable Zintl clusters.<sup>38,41</sup> This cluster has five atoms, 12 p valence electrons and a trigonal bipyramidal geometry, quite similar to that of  $Al_2Bi_3^-$ . 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  $Sn_5^{2-}$  cluster was optimized with our theoretical model using the B3LYP/LANL2DZdp level. The electron energy levels and the molecular orbitals for  $Sn_5^{2-}$  are compared with the ones of  $Al_2Bi_3^-$  in Table 1. It is clear that the twelve most occupied levels of  $Sn_5^{2-}$  and  $Al_2Bi_3^-$  are very similar, although somewhat differently ordered. Finally, the calculated HOMO-LUMO gap of 2.85 eV for  $Sn_5^{2-}$  is very close to that of 2.50 eV for  $Al_2Bi_3^-$ . Figure 6 shows the molecular orbital pictures of the HOMO for the  $Sn_5^{2-}$  and  $Al_2Bi_3^-$  clusters, and both of them have the same HOMO molecular orbital. This analogy reinforces the conclusion that  $Al_2Bi_3^-$  is a gas-phase Zintl analogue of  $Sn_5^{2-}$ .

**Table 1.** The energies of molecular orbitals for the  $Sn_5^{2-}$  and  $Al_2Bi_3^-$  clusters

$Sn_5^{2-}$			$Al_2Bi_3^-$		
MO <sup>a</sup>	Configuration	Energy (eV)	MO	Configuration	Energy (eV)
LUMO <sup>b</sup>	e'	5.494	LUMO	e'	1.686
HOMO <sup>c</sup>	a2''	2.638	HOMO	a2''	-0.816
HOMO-1	e'	2.584	HOMO-1	e''	-1.550
HOMO-2	e''	2.219	HOMO-2	e'	-2.366
HOMO-3	a1'	1.795	HOMO-3	a1'	-2.883
HOMO-4	a1'	-1.088	HOMO-4	a1'	-4.162
HOMO-5	e'	-2.747	HOMO-5	e'	-10.635

<sup>a</sup>MO is molecular orbital.

<sup>b</sup>LUMO is the lowest unoccupied molecular orbital.

<sup>c</sup>HOMO is the highest occupied molecular orbital.

## CONCLUSIONS

$Al_mBi_n^-$  ( $m = 1-12$ ;  $n = 1-4$ ) 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  $Al_mBi_n^-$  ( $m + n \leq 7$ ) are obtained by DFT calculations. The calculations of binding energy (BE), energy gain ( $\Delta$ ) and HOMO-LUMO gaps confirm that the  $Al_2Bi_3^-$  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  $Al_2Bi_3^-$  cluster, the concept of Zintl ion chemistry can account for the geometry and stability of the gas-phase systems. Consequently,  $Al_2Bi_3^-$  can be considered as a gas-phase Zintl analogue that follows Wade's rules and is the analogue of  $Ga_2Bi_3^-$  and  $Sn_5^{2-}$  Zintl ions.

## Acknowledgements

We thank our colleagues in the State Key Laboratory of Molecular Reaction Dynamics for helpful discussions. This research was supported by the National Nature Science Foundation of China under Grant No. 20433080.

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