

# Aluminum–sulfur cluster ions: Formation and photolysis

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Aluminum–sulfur cluster ions were obtained by direct laser ablation (248 nm,  $\geq 10$  MW/cm<sup>2</sup>) and analyzed with a tandem time-of-flight mass spectrometer. The regular peaks of cluster ions having composition of  $\text{AlS}^+(\text{Al}_2\text{S}_3)_n$  ( $n=1,2,3,\dots,31$ ) were shown on the first time-of-flight mass spectrum (TOF-MS). The cluster ions of a certain mass number ( $m/e$ ) could be selected and photolyzed by an ArF laser (193 nm, 1 MW/cm<sup>2</sup>). The product ions were analyzed by a second TOF-MS. It was found that the cluster ions lost  $(\text{Al}_2\text{S}_3)_x$  ( $x=1, 3, \text{ or } 4$ ) and became smaller cluster ions of the same stable formula  $\text{AlS}^+(\text{Al}_2\text{S}_3)_{n-x}$ . Cagelike structures were proposed to be possible for these stable cluster ions. Semiempirical and *ab initio* quantum chemical calculations have also been performed for some of the clusters.

## I. INTRODUCTION

Geometrical cage structures are characteristic to carbon since the discovery of carbon fullerenes,<sup>1,2</sup> and also to metal carbon clusters (metcars,  $\text{M}_8\text{C}_{12}$ , M is V, Zr, Hf, or Ti).<sup>3</sup> The presence of metal in carbon clusters leads to enhancing the stability of the corresponding carbon clusters (e.g.,  $\text{Ti}_8\text{C}_{12}$  vs  $\text{C}_{20}$ ). The analogy between the layer structure of graphite and  $\text{MX}_2$  compounds (M is W or Mo, X is S or Se) suggests that closed polyhedra may also exist for the clusters of sulfur compounds. This point has been confirmed after the recent discovery of closed polyhedral and cylindrical structures of tungsten disulfide ( $\text{WS}_2$ ).<sup>4</sup>

Metal–sulfides are a class of compounds of many unique properties and thus important in many aspects. Besides the above layered characteristics, some metal–sulfides are known to have high melting points, great hardness, conductivity, lubrication, etc.<sup>5–7</sup>  $\text{Fe}_n\text{S}_n$  ( $n=2, 3, 4, \text{ and } 6$ ) clusters are known to be active centers of nitrogen fixation and other electron-transfer processes in many kinds of proteins.<sup>8</sup>

We have worked on a series of transition metal–sulfur binary cluster ions.<sup>9–11</sup> For example, a cagelike structure ( $T_d$  symmetry) has been suggested for  $\text{Ta}_4\text{S}_6$  cluster.<sup>9</sup> Also, for  $\text{Fe}_n\text{S}_n$  clusters, cagelike structures have been further considered in our experiments.<sup>10</sup> In this paper, we report our work on aluminum–sulfur cluster ions. Cagelike structures are suggested for these clusters based on the observed cluster distribution and their photodissociation upon UV laser irradiation. Photodissociation has been proved to be one of the useful tools in analysis of cluster structures.<sup>12,13</sup> The unique property of aluminum–sulfide suggests that it may form closed structures. The Al–S bond is more covalent in character, and aluminum has a valence 3 with  $sp^2$  hybridization or distorted  $sp^2$  hybridization.

## II. EXPERIMENT

Experiments were performed on a homemade tandem time-of-flight mass spectrometer (TOF-MS) which has been reported in detail previously.<sup>14,10</sup> In brief, the 532 nm output

from a pulsed YAG laser was focused on the sample to give an intensity of  $10^7$  W/cm<sup>2</sup> (at the focus). The repetition rate of laser pulses was kept at 10 pps. About 1000 pulses were used to give a satisfactory TOF-MS. The sample tablet was made of well-mixed Al fine powder (purity 99%) and precipitated sulfur (99%) with an atomic ratio Al:S=1:1, 1:5, or 1:10.

The cluster ions were measured by the first stage TOF-MS. The cluster ions produced by laser ablation were extracted and accelerated with a pulsed voltage of 0.1 and 1.1 kV, respectively, drifted in a flight path of 3.5 m. A dual microchannel plate (MCP) was used as detector. The mass resolution of this TOF-MS was  $\sim 300$ . Cluster ions of a certain mass number (e.g.,  $m/e=509$  for  $\text{Al}_7\text{S}_{10}^+$ ) could be selected out by a pulsed mass gate at the end of the first flight path. The selected ions, after deceleration to  $\sim 150$  eV, were photolyzed by an unfocussed excimer laser beam (193 nm, 1 MW/cm<sup>2</sup>; 248 nm, 5 MW/cm<sup>2</sup>). The product ions of photolysis and the remaining parent ions were then analyzed by the second stage TOF-MS, which is perpendicular to the first stage TOF-MS, and has a flight path of 1.5 m. The ions were detected with another dual microchannel plate. The signals were recorded with a transient recorder (10 MHz) and accumulated up to 1000 laser shots by an IBM-PC computer.

## III. RESULTS AND DISCUSSIONS

### A. The formation of aluminum–sulfur cluster ions

A typical TOF-MS of aluminum–sulfur cluster ions, formed by laser ablation on a sample of atomic ratio Al:S=1:5, is shown in Fig. 1. There are a series of strong peaks with equal mass difference  $\Delta m=150$  (for  $\text{Al}_2\text{S}_3$ ,  $m=150$ ), quite similar to the mass spectrum of carbon fullerenes. The general formula of the cluster ions for these peaks can be represented by  $\text{AlS}^+(\text{Al}_2\text{S}_3)_n$  or  $\text{Al}_{2n+1}\text{S}_{3n+1}^+$ , where  $n=1, 2, 3, \dots$ . This shows that Al has a valence of 3 and S has a valence of 2. The strong peaks are in the region of  $n=5-20$ , it means that these cluster ions are more stable. For sample Al:S=1:5, the largest cluster ion found is  $n=31$ , i.e.,  $\text{Al}_{63}\text{S}_{94}^+$ .

It should be pointed out that the atomic ratio of the

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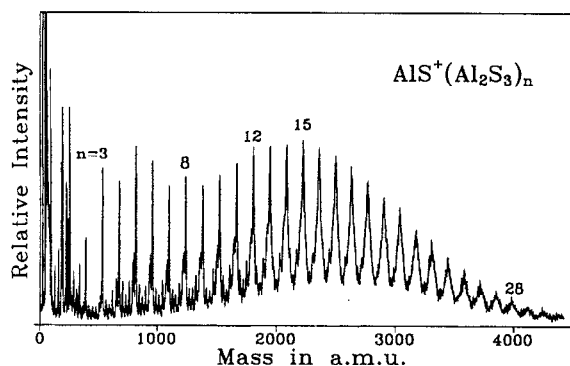


FIG. 1. The TOF-MS of aluminum-sulfur cluster ions at the first stage TOF-MS. It was obtained from a sample of Al:S=1:5 ablated with 532 nm laser at 10 mJ/pulse.

samples did not affect the mass distribution very much. The experimental results showed that when the sulfur content in the sample decreased to some extent, e.g., when Al:S=1:1, the largest cluster ion observed is only  $\text{Al}_{49}\text{S}_{73}^+$ . Thus, the higher sulfur content in the sample is helpful in formation of larger clusters.

In the low mass region, there are also some other strong peaks, such as  $\text{Al}^+$ ,  $\text{AlS}_4^+$ ,  $\text{AlS}_5^+$ ,  $\text{AlS}_6^+$ . These species might be formed via the reaction between  $\text{Al}^+$  and  $\text{S}_4$ ,  $\text{S}_5$ , and  $\text{S}_6$  rings. In our previous work on the pure sulfur clusters,<sup>15</sup> it was found that these sulfur cluster rings could be easily formed in the laser ablation of pure sulfur sample.

## B. The photolysis of aluminum-sulfur cluster ions

We have selected with the mass gate several kinds of aluminum-sulfur cluster ions for photolysis. It is surprising that, using KrF laser (248 nm), no photolysis product has been observed, while using ArF laser (193 nm), most cluster ions can be photolyzed. Some of the results are given in the following.

$\text{Al}_5\text{S}_7^+$  ( $n=2$ ) can hardly be photolyzed by 193 nm laser since no product ion was observed. So  $\text{Al}_5\text{S}_7^+$  is a species of very stable cluster ion. For  $\text{Al}_7\text{S}_{10}^+$ ,  $\text{Al}_9\text{S}_{13}^+$ ,  $\text{Al}_{11}\text{S}_{16}^+$ , and  $\text{Al}_{13}\text{S}_{19}^+$  ( $n=3, 4, 5, 6$ ), the photolysis results from the second stage TOF-MS are given in Fig. 2. The photodissociation channels are as follows:

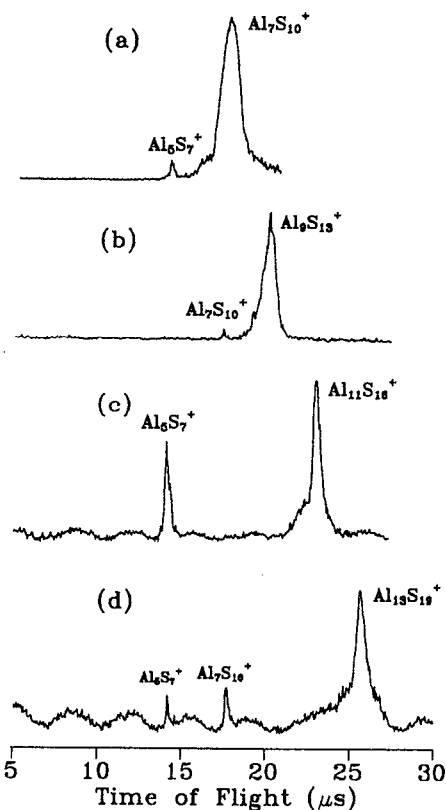
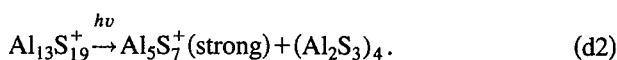
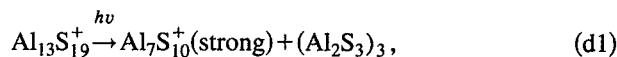
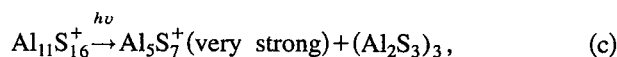
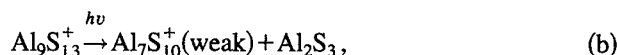
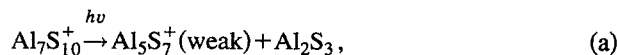


FIG. 2. The TOF-MS at the second stage TOF-MS showing UV photodissociation of mass-selected aluminum-sulfur cluster ions (a)  $\text{Al}_7\text{S}_{10}^+$ , (b)  $\text{Al}_9\text{S}_{13}^+$ , (c)  $\text{Al}_{11}\text{S}_{16}^+$ , and (d)  $\text{Al}_{13}\text{S}_{19}^+$ .

For analysis, we tabulate the results as follows.

$n =$	6	5	4	3	2	
	$\text{Al}_{13}\text{S}_{19}^+$	$\text{Al}_{11}\text{S}_{16}^+$	$\text{Al}_9\text{S}_{13}^+$	$\text{Al}_7\text{S}_{10}^+$	$\text{Al}_5\text{S}_7^+$	
(a)				----->		(weak)
(b)			----->			(weak)
(c)		=====>				(very strong)
(d1)	----->					(strong)
(d2)	----->					(strong)

By ArF laser, in reactions (a) and (b), both  $\text{Al}_7\text{S}_{10}^+$  and  $\text{Al}_9\text{S}_{13}^+$  can be photolyzed in low percentage (3.5% and 1.5%, respectively), being knocked out 1 unit of  $\text{Al}_2\text{S}_3$ . But in reaction (c),  $\text{Al}_{11}\text{S}_{16}^+$  can be photolyzed in high percentage (36%), being knocked out 3 units of  $\text{Al}_2\text{S}_3$ , producing  $\text{Al}_5\text{S}_7^+$  only. How are these 3 units of  $\text{Al}_2\text{S}_3$  knocked out? (1+1+1), (1+2), (2+1), or (3)? If 1  $\text{Al}_2\text{S}_3$  is knocked out and  $\text{Al}_9\text{S}_{13}^+$  is produced first, then  $\text{Al}_9\text{S}_{13}^+$  would not produce  $\text{Al}_5\text{S}_7^+$  [see reaction (b)]. If  $\text{Al}_4\text{S}_6$  is knocked out and  $\text{Al}_7\text{S}_{10}^+$  is produced first, then  $\text{Al}_7\text{S}_{10}^+$  could produce only a low  $\text{Al}_5\text{S}_7^+$  peak [see reaction (a)]. But now, we get a very high peak of  $\text{Al}_5\text{S}_7^+$  without  $\text{Al}_9\text{S}_{13}^+$  and  $\text{Al}_7\text{S}_{10}^+$  peaks. Therefore,  $\text{Al}_6\text{S}_9$  must be knocked out together.  $\text{Al}_6\text{S}_9$  can not be 3 individual  $\text{Al}_2\text{S}_3$  as too high an energy would be needed to break so many Al-S valence bonds. Therefore,  $\text{Al}_6\text{S}_9$  is knocked out as a stable cluster.

TABLE I. Structures of  $Al_nS_m$  clusters studied by MNDO calculation and *ab initio* calculation. Bond lengths  $d_{ij}$  (between atoms  $i$  and  $j$ ) in angstroms, bond angles  $\alpha_i$  (at atom  $i$ ) and dihedral angles  $\gamma$  in degrees.

Cluster	Structure	Point group	Coordinate	Geometry		Property from MNDO			
				Value		$\Delta H_f$ kcal/mol	I.P. eV		
				MNDO	<i>Ab initio</i>				
$Al_2S_3$	3(a)	$D_{3h}$	$d_{13}$	2.125	2.168	36.98	9.56		
			$\alpha_3$	65.5°	61.6°				
	3(a')	$C_2$	$d_{12}$	1.808	1.901	-6.08	10.40		
			$d_{23}$	2.016	2.083				
			$\alpha_2$	179.2°	179.9°				
			$\alpha_3$	110.6°	102.4°				
$Al_4S_6$	3(b)	$T_d$	$\gamma_{1234}$	117.2°	117.0°	-113.00	10.54		
			$d_{15}$	2.074	2.114				
			$d_{12}$	3.117	2.948				
			$\alpha_5$	97.4°	88.4°				
			$d_{15}$	2.053				-223.76	10.71
			$d_{78}$	3.494					
$Al_6S_9$	3(c)	$D_{3h}$	$d_{56}$	3.356		-223.76	10.71		
			$\alpha_1$	105.1°					
			$\alpha_7$	110.1°					
			$d_{12}$	3.500				-306.69	10.80
			$d_{89}$	2.038					
			$\alpha_9$	118.3°					
$Al_8S_{12}$	3(d)	$O_h$	$\gamma_{6789}$	22.9°		-394.39	10.87		
			$d_{12}$	3.568					
			$d_{1-18}$	2.027					
			$d_{10-11}$	2.033					
			$\alpha_{11}$	123.0°					
			$\alpha_{18}$	123.2°					
$Al_{10}S_{15}$	3(c)	$D_{5h}$	$\gamma_{8-9-10-11}$	28.5°		-394.39	10.87		
			$\gamma_{2-8-7-18}$	23.7°					
			$d_{14}$	2.183	2.200			132.21	14.79
			$d_{15}$	2.083	2.121				
			$d_{12}$	2.865	2.682				
			$\alpha_5$	86.9°	78.4°				
$\alpha_4$	82.1°	75.1°							
$\gamma_{3215}$	151.8°								
$Al_3S_4^+$	6(a)	$C_{3v}$	$d_{1-12}$	2.063		13.89	14.09		
			$d_{2-10}$	2.077					
			$d_{3-10}$	2.036					
			$d_{36}$	2.154					
			$d_{18}$	2.093					
			$d_{48}$	2.012					
			$d_{46}$	2.196					
			$d_{47}$	2.058					
			$\alpha_7$	90.1°					
			$\alpha_8$	103.0°					
			$\alpha_{10}$	96.9°					
			$\alpha_{12}$	117.3°					

In reaction (d),  $Al_{13}S_{19}^+$  can be photolyzed in relatively high percentage (13%), 3 or 4 units of  $Al_2S_3$  being knocked out, producing  $Al_7S_{10}^+$  and  $Al_5S_7^+$ , respectively. If  $Al_2S_3$  is knocked out and  $Al_{11}S_{16}^+$  is produced first, then  $Al_5S_7$  can be produced [see reaction (c)] but enough  $Al_{11}S_{16}^+$  should be left. If  $Al_4S_6$  is knocked out and  $Al_9S_{13}^+$  is produced first, then  $Al_7S_{10}^+$  can be produced [see reaction (b)], but most of  $Al_9S_{13}^+$  should be left. Now, we have strong peaks of  $Al_7S_{10}^+$  and  $Al_5S_7^+$ , without apparent peaks of  $Al_{11}S_{16}^+$  and  $Al_9S_{13}^+$ . Therefore,  $Al_7S_{10}^+$  must be produced directly by loss of  $Al_6S_9$ , and  $Al_5S_7^+$  must be produced directly by a loss of  $Al_8S_{12}$  (not 3+1, as  $Al_5S_7^+$  can be produced from  $Al_7S_{10}^+$  only in very low percentage; not 1+3 as no apparent  $Al_{11}S_{16}^+$  peak was ob-

served). We conclude that both  $Al_6S_9$  and  $Al_8S_{12}$  are stable clusters.

#### IV. THE STRUCTURES OF ALUMINUM-SULFUR CLUSTERS

The bond between Al and S is mainly covalent bond. For Al atom, the 3 electrons can be  $sp^2$  hybridized, therefore the bond angle is around 120°. For S atom, the typical (and thus stable) bond angle is 105°–110°. Generally speaking, sesquisulfides  $M_2S_3$  (M is a metal) have the following main structural aspects:<sup>16</sup> (i) Structures with 3 coordination of M,

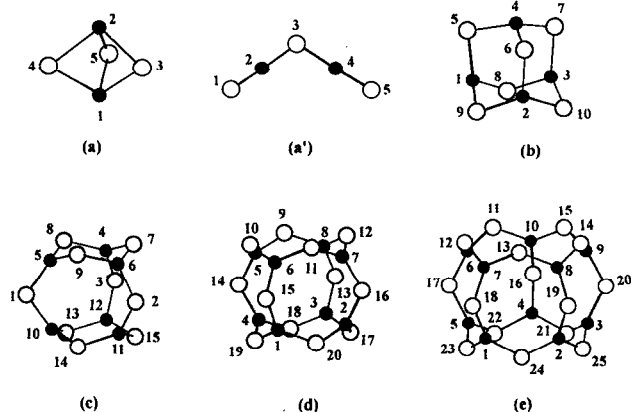


FIG. 3. Proposed structures for small neutral aluminum-sulfur clusters. Circles are for sulfur atoms, filled circles are for aluminum atoms (a), (a')  $\text{Al}_2\text{S}_3$ , (b)  $\text{Al}_4\text{S}_6$ , (c)  $\text{Al}_6\text{S}_9$ , (d)  $\text{Al}_8\text{S}_{12}$ , and (e)  $\text{Al}_{10}\text{S}_{15}$ .

for examples, layer structure ( $\text{As}_2\text{S}_3$ ) and chain structure ( $\text{Sb}_2\text{S}_3$ ,  $\text{Bi}_2\text{S}_3$ , etc.); (ii) Structures with close-packed S and 4 or 6 coordination of M.

In this section, we will propose some possible structures for the aluminum-sulfur clusters. Some of the structures will be discussed with the results of semiempirical [modified neglect of differential overlap (MNDO)] and *ab initio* quantum chemical calculations. Using a GAUSSIAN 86 program,<sup>17</sup> we have performed *ab initio* calculation at Hartree-Fock/STO-3G level for some small aluminum-sulfur clusters. This *ab initio* calculation is quite successful in predicting the geometry of a molecule.<sup>18</sup> Some calculations for larger clusters have been performed with MNDO.<sup>19</sup> Although it was not used in the literature for the calculation of metal sulfides, MNDO has been used for calculation of the structures of sulfur clusters<sup>20</sup> and sulfur-containing compounds,<sup>21</sup> and has been believed to be successful sometimes in predicting the structure of a molecule.<sup>22</sup> The accuracy of MNDO calculation on aluminum-sulfur clusters in this work is checked with the results of *ab initio* calculations. The results of our calculations are summarized in Table I.

### A. The structures of small neutral aluminum-sulfur clusters

For  $\text{Al}_2\text{S}_3$ , two possible structures are shown in Figs. 3(a) and 3(a'). Both MNDO and *ab initio* calculations have been performed for these isomers, and the geometries obtained do not differ very much as shown in Table I. In Fig. 3(a), there are 3 sulfur bridges between the two Al atoms. This structure is not stable as the bond angles at sulfur atoms are too small ( $65.5^\circ$  and  $61.6^\circ$  from MNDO and *ab initio* calculation, respectively). The second structure for  $\text{Al}_2\text{S}_3$  is its linear form shown in Fig. 3(a'), which is 12.1 kcal/mol lower than structure 3(a) in total energy, given by *ab initio* calculation. Both from MNDO calculation (lower formation heat) and from *ab initio* calculation (lower total energy), the

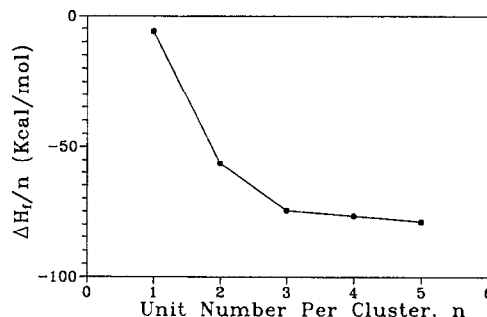


FIG. 4. The relationship between the heat of formation per  $\text{Al}_2\text{S}_3$  unit and the unit number in the cluster.

more stable structure for  $\text{Al}_2\text{S}_3$  is linear, as shown in Fig. 3(a'). The bond angle for central S atom is  $102.4^\circ$ , the bond lengths are 1.901 and 2.083 Å.

For  $\text{Al}_4\text{S}_6$  (i.e.,  $\text{Al}_2\text{S}_3$  dimer), the structure with highest symmetry is that the 4 Al atoms form a tetrahedron with six sulfur bridges near the six edges, as shown in Fig. 3(b). MNDO and *ab initio* calculation shows that the bond angle at sulfur is  $97.4^\circ$  and  $88.4^\circ$ , respectively. This structure for  $\text{Al}_4\text{S}_6$  is not very stable as the bond angles are still small. Since  $\text{Al}_4\text{S}_6$  can be regarded as a combination of two linear  $\text{Al}_2\text{S}_3$ , then the binding energy of  $\text{Al}_4\text{S}_6$  (the difference between the total energy of  $\text{Al}_4\text{S}_6$  and two linear  $\text{Al}_2\text{S}_3$ ) is calculated to be  $-265.9$  kcal/mol by *ab initio*.

For  $\text{Al}_6\text{S}_9$  (i.e.,  $\text{Al}_2\text{S}_3$  trimer), the 6 Al atoms form a triangular prism, with S bridges near all the edges, as shown in Fig. 3(c). The bond angles at sulfur atoms are  $105.1^\circ$  and  $110.1^\circ$ , and those at aluminum atoms are  $116.9^\circ$ ,  $119.2^\circ$  from MNDO calculation. This is a very stable structure as the bond angles are suitable compared with those in aluminum sulfide crystal [between  $104.5^\circ$  and  $113.9^\circ$  (Ref. 23)].

For  $\text{Al}_8\text{S}_{12}$  (i.e.,  $\text{Al}_2\text{S}_3$  tetramer), the 8 Al atoms form a cube, with S bridges near the edges, as shown in Fig. 3(d). MNDO calculation shows that the bond angle at sulfur atoms is  $118.3^\circ$ . This is a stable structure too, as the bond angles are suitable also.

The largest cluster studied with MNDO calculation is  $\text{Al}_{10}\text{S}_{15}$ , a pentagonal prism with a  $D_{5h}$  symmetry as shown in Fig. 3(e). It shows that the bond angle at sulfur atoms still increases up to  $123^\circ$ .

It should be pointed out that the results in Table I show that the bond length Al-S in the cage structures decreases steadily with the increase of the cluster size  $n$ , from 2.125 Å of  $\text{Al}_2\text{S}_3$  ( $D_{3h}$ ) to 2.03 Å of  $\text{Al}_{10}\text{S}_{15}$  ( $D_{5h}$ ), while the Al-S bond lengths in aluminum sulfide crystal are in the range between 2.164 and 2.302 Å.<sup>23</sup> This discrepancy is not surprising since the aluminum atom in crystal has valence more than 3, while that in our proposed structures only valence 3.

The heat of formation per atom is a quantity which shows the thermodynamic stability of clusters of different size.<sup>24</sup> In general, the smaller the heat of formation per atom is, the more stable the cluster would be. In Fig. 4, we have shown the relationship between the heat of formation per

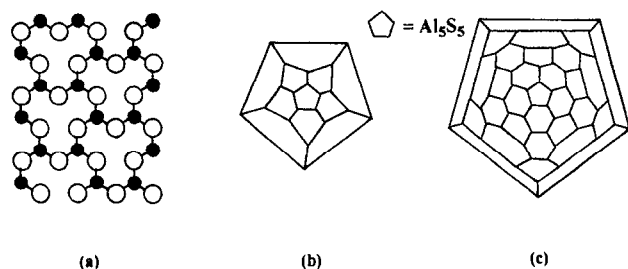


FIG. 5. Proposed structures for large neutral aluminum-sulfur clusters. (a) for crystal, (b) for  $\text{Al}_{20}\text{S}_{30}$ , and (c) for  $\text{Al}_{60}\text{S}_{90}$ .

$\text{Al}_2\text{S}_3$  unit,  $\Delta H_f/n$ , and the units of number for cluster,  $n$ . It shows that the curve drops sharply between  $n=1, 2$ , and  $3$ , and drops slowly between  $n=3, 4$ , and  $5$ . This implies that there might be a significant change in stability from  $\text{Al}_4\text{S}_6$  to  $\text{Al}_6\text{S}_9$ .

Therefore,  $\text{Al}_6\text{S}_9$  and  $\text{Al}_8\text{S}_{12}$  are proved to be stable clusters both from experimental results (Fig. 2) and from MNDO calculations (Fig. 4). Their structures are cage-like as discussed above and shown in Figs. 3(c) and 3(d).

## B. The structures of large neutral aluminum-sulfur clusters

In principle, the larger the cluster is, the more similar to crystal structures it would be. For the clusters  $(\text{Al}_2\text{S}_3)_n$  in the range  $n=5-30$ , there might be two possibilities for their structures. The first, the cluster structures are similar to  $\text{Al}_2\text{S}_3$  crystal structure,<sup>23,25</sup> i.e., the S atoms are in close packing (either face-centered cube or hexagonal prism), and the Al atoms sit in the holes with coordination number 4 or 6 as shown in Fig. 5(a). The second, the cluster structures are different from the  $\text{Al}_2\text{S}_3$  crystal structure. We propose the cage-like structures, e.g.,  $\text{Al}_{20}\text{S}_{30}$  ( $n=10$ ) might be of a cage-like structure of 12 pentagons with Al vertices and S-bridge edges, as shown in Fig. 5(b). For  $4 < n < 10$ , the cage structures are formed with squares, pentagons, and sometimes with hexagons. For  $n > 10$ , the cage structures may be formed with pentagons and hexagons, e.g.,  $\text{Al}_{60}\text{S}_{90}$  ( $n=30$ ) might have a structure of 12 pentagons and 20 hexagons, similar to Buckminsterfullerene  $\text{C}_{60}$ , but with 60 Al vertices and 90 S bridges as edges, as shown in Fig. 5(c).

## C. The structures of aluminum-sulfur cluster ions

The cluster ions have a formula  $\text{AlS}^+(\text{Al}_2\text{S}_3)_n$ . Their structures are similar to those of the neutral clusters. For example, the structure of  $\text{AlS}^+(\text{Al}_2\text{S}_3)$  is similar to  $(\text{Al}_2\text{S}_3)_2$ , only with a change of  $\text{S}^+$  for  $\text{AlS}_3$ , as shown in Fig. 6(a). Similar structures for  $\text{Al}_5\text{S}_7^+$  and  $\text{Al}_7\text{S}_{10}^+$  are given in Figs. 6(b) and 6(c).

The small aluminum-sulfur cluster ion  $\text{Al}_3\text{S}_4^+$ , with a  $C_{3v}$  symmetry as shown in Fig. 6(a), was studied by both MNDO and *ab initio* calculations. The bond lengths of Al-S are 2.200 and 2.121 Å from *ab initio* calculation, in agreement with MNDO calculation (2.183 and 2.083 Å). Bond

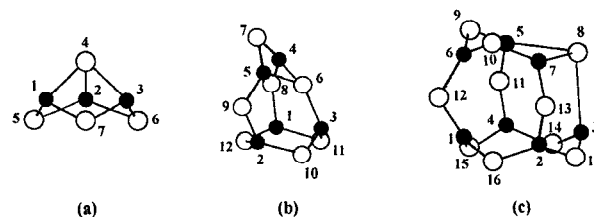


FIG. 6. Proposed structures for aluminum-sulfur cluster ions. Circles are for sulfur atoms, filled circles are for aluminum atoms (a)  $\text{Al}_3\text{S}_4^+$ , (b)  $\text{Al}_5\text{S}_7^+$ , and (c)  $\text{Al}_7\text{S}_{10}^+$ .

angles at sulfur atom are  $82.1^\circ$  and  $86.9^\circ$  from MNDO, and  $75.1^\circ$  and  $78.4^\circ$  from *ab initio*, which are small, indicating that this species is not very stable. This was also shown in the mass spectrum that the  $\text{Al}_3\text{S}_4^+$  ion has small intensity.

$\text{Al}_5\text{S}_7^+$  cluster ion was also studied by MNDO calculation for geometrical optimization. The only geometry considered is a structure with  $C_3$  symmetry [Fig. 6(b)], which is related with the structure of the corresponding neutral cluster  $\text{Al}_6\text{S}_9$ . The bond lengths and bond angles shown as in Table I are as follows. The bond lengths of Al-S vary slightly from 2.012 to 2.093 Å for the sulfur bridges, while those are around 2.2 Å for the sulfur atom having three bonds. The bond angles of the bridge sulfur atoms are  $90.1^\circ$ ,  $103.0^\circ$ ,  $96.9^\circ$ , and  $117.3^\circ$ . These comparatively larger angles indicate that this ion is more stable than  $\text{Al}_3\text{S}_4^+$  ion.

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- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* **318**, 162 (1985).
- Q. L. Zhang, S. C. O'Brien, J. R. Heath, Y. Liu, R. F. Curl, H. W. Kroto, and R. E. Smalley, *J. Phys. Chem.* **90**, 525 (1986).
- B. C. Guo, S. Wei, J. Purnell, S. Buzza, and A. W. Castleman, Jr., *Science* **256**, 515 (1992).
- R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature* **360**, 444 (1992).
- S. W. McElvany and C. J. Cassidy, *J. Phys. Chem.* **94**, 2057 (1990).
- R. Chevel, M. Hirrien, and M. Sergent, *Polyhedron* **5**, 87 (1986).
- P. C. H. Mitchell, *Wear* **100**, 281 (1984).
- S. Xiang, in *Introduction to New Fields of Inorganic Chemistry* (Peking University, Beijing, 1988), p. 321.
- N. Zhang, Z. Yu, X. Wu, Z. Gao, Q. Zhu, and F. Kong, *J. Chem. Soc. Faraday Trans.* **89**, 1779 (1993).
- Z. Yu, N. Zhang, Z. Gao, Q. Zhu, and F. Kong, *J. Chem. Phys.* **99**, 1765 (1993).
- Y. Shi, N. Zhang, Z. Gao, Q. Zhu, and F. Kong (to be published).
- S. C. O'Brien, J. R. Heath, R. F. Curl, and R. E. Smalley, *J. Chem. Phys.* **88**, 220 (1988).
- Q. L. Zhang, Y. Liu, R. F. Curl, F. K. Tittel, and R. E. Smalley, *J. Chem. Phys.* **88**, 1670 (1988).
- Z. Gao, F. Kong, X. Wu, N. Zhang, Q. Zhu, Z. Zhang, and Q. Lu, *Chin. J. Chem. Phys.* **5**, 343 (1992).
- N. Zhang, Z. Gao, F. Kong, Q. Zhu, and L. Zhen, *Prog. Natl. Sci.* **3**, 170 (1993).

- <sup>16</sup>A. F. Wells, in *Structural Inorganic Chemistry*, 4th ed. (Clarendon, Oxford, 1975), p. 617.
- <sup>17</sup>"GAUSSIAN 86," M. J. Frisch *et al.*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Carnegie-Mellon University, Pittsburgh, PA 15213.
- <sup>18</sup>G. Xu, L. Li, and D. Wang, in *Quantum Chemistry: Principles and Ab Initio Calculation Method* (Science, Beijing, 1985), p. 818.
- <sup>19</sup>"MNDO," M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4499 (1977).
- <sup>20</sup>N. C. Baird, *J. Comput. Chem.* **5**, 35 (1984).
- <sup>21</sup>M. J. S. Dewar and M. L. McKee, *J. Comput. Chem.* **4**, 84 (1983).
- <sup>22</sup>N. Chen, Z. Xu, H. Liu, H. Xu, and L. Wang, in *Computer Chemistry and Its Applications* (Shanghai Science and Technology, Shanghai, 1987), p. 347.
- <sup>23</sup>B. Eisenmann, *Z. Kristallogr.* **198**, 307 (1992).
- <sup>24</sup>D. Bakowies and W. Thiel, *J. Am. Chem. Soc.* **113**, 3704 (1991).
- <sup>25</sup>P. C. Donohue, *J. Solid State Chem.* **2**, 6 (1970).