Density functional theory study of neutral $AlS_n(n = 2–9)$ clusters*

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This paper investigates the geometrical structures and relative stabilities of neutral AlS_n ($n = 2$–9) using the density functional theory. Structural optimisation and frequency analysis are performed at the B3LYP/6-311G(d) level. The ground state structures of the AlS_n show that the sulfur atoms prefer not only to evenly distribute on both sides of the aluminum atom but also to form stable structures in AlS_n clusters. The structures of pure S_n are fundamentally changed due to the doping of the Al atom. The fragmentation energies and the second-order energy differences are calculated and discussed. Among neutral AlS_n ($n = 2$–9) clusters, AlS_4 and AlS_6 are the most stable.

Keywords: aluminum sulfur clusters, density functional theory, structure and stability, energy
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1. Introduction

The group VIA elements, such as O, S and Se, show a range of structures unmatched in the periodic table.[1] Sulfur, in particular, has the largest number of allotropic forms. Therefore, there have been many studies on pure sulfur clusters, ranging from empirical to *ab initio* studies.[2−10] Based on these results, the structure, electronic state and stability of sulfur clusters have been relatively well understood.

With the gradual deepening of the studies for clusters, doped clusters have attracted more attention because of their variety of electronic and geometric characteristics. In recent years, several research efforts have been made to study the structures and the properties of some small X_mS_n clusters.[11−13] As is well known, aluminum is the most abundant metallic element in the Earth's crust. Thus in the past decades, extensive research on Al-doped clusters has been carried out.[14−20] However, there has been few works on Al-doped sulfur clusters. Zhang *et al.*[21] obtained aluminum–sulfur cluster ions by direct laser ablation and analysed the cluster ions with a tandem time-of-flight mass spectrometer. Liu *et al.*[22] concluded that $AlS_2^-(Al_2S_3)_k$ is more stable by studying the photo-electron spectra of $Al_mS_n^-$ cluster anions. Nakajima *et al.*[23] investigated the photo-electron spectra and time-of-flight mass spectrum of $Al_mS_n^-$ cluster anions ($0 \le n,\ m \le 10$) and concluded that the abundant aluminum–sulfur cluster anions are of three types (AlS^- $(Al_2S_3)_k$, AlS_2^- $(Al_2S_3)_k$ and $(Al_2S_3)_k^-$). Moreover, $Al_3S_3^-$ is exceptionally stable in $Al_mS_n^-$ cluster anions. However, the laboratory observations have not yet been well understood due to the lack of reliable information about their geometrical structures. Until now, no further study of geometrical structures and relative stabilities has been reported for Al-doped sulfur clusters. In this study, using a standard B3LYP/6-311G(d) method, we extend density functional calculations to neutral AlS_n ($n = 2$–9) in order to determine their ground state geometry and their relative stabilities.

The rest of the paper is organized as follows. In Section 2, we give a brief description of the computational methods used in this work. Results, discussion and stability are presented in Section 3 for aluminum–sulfur isomers. Finally, we summarize our conclusions in Section 4.

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2. Computational methods

Initial geometrical optimisations were performed at the B3LYP/6-31G(d) level. The lowest-energy and some low-lying AlS_n structures were further optimised by employing the B3LYP/6-311G(d) method. Geometrical optimisation of the neutral $AlS_n(n=2–9)$ was achieved by searching a symmetry-constrained multidimensional potential energy surface. Frequency analysis of the optimised structures were carried out at the same theoretical level in order to check whether the optimised structures were transition states or true minima on the potential energy surfaces of the corresponding clusters. All calculations were carried out using the GAUSSIAN 03 programme.[24]

3. Results and discussion

3.1. Geometry

Employing the computational scheme described in Section 2, we have explored a number of low-lying isomers and determined the lowest-energy structures for AlS_n clusters up to $n = 9$. The obtained geometric sketch figures of the ground state and some metastable states are shown in Figs. 1–8, respectively. The geometric parameters are listed in Table 1. Using the same computational scheme, we further optimised the pure S_{n+1} cluster for comparison, which have been investigated by different computational methods.[2–6] Only the ground state structures for S_{n+1} are shown in Figs. 1–8. In Figs. 1–8, the "bonds" for internuclear separations are less than 0.26 nm (Al–S) and 0.24 nm (S–S), respectively. The black and the white spheres denote Al and S atoms, respectively.

AlS_2 The lowest-energy structure for S_3 is the open C_{2v} form (Fig. 1(a)), this is in agreement with previous calculations.[2,4–6] For AlS_2, the linear structure (Fig. 1(b)) with $D_{\infty h}$ symmetry is predicted to be the most stable structure. The less favourable isosceles triangle C_{2v} isomer (Fig. 1(c)) with bond angle $\alpha_{SAlS} = 48.93°$ locates 43.32 $kJ \cdot mol^{-1}$ above the ground state. The next AlS_2 structure in order of energy possesses $C_{\infty v}$ linear geometry (Fig. 1(d)) with an imaginary mode frequency, which shows a tendency to form the Fig. 1(c) isomer. Furthermore, the structure in Fig. 1(d) is substantially higher in energy (143.35 $kJ \cdot mol^{-1}$ above the ground state), which indicates that the Al atom prefers to stay in a central position.

AlS_3 The most stable geometry of S_4 is a planar structure with C_{2v} symmetry (Fig. 2(a)) and this is in agreement with the result obtained by Chen *et al.*[6] The T-shaped planar C_{2v} form (Fig. 2(b)) gives the lowest energy for AlS_3, which can be obtained by capping the low-lying isomer (Fig. 1(c)) with a S atom. The next structure in in order of energy is the planar four-membered ring isomer (Fig. 2(c)) with C_{2v} symmetry, which lies 49.88 $kJ \cdot mol^{-1}$ above the ground state. The linear isomer (Fig. 2(d)) with an aluminum atom in a relatively central position is located 149.39 $kJ \cdot mol^{-1}$ above the ground state. Furthermore, it has an imaginary mode frequency

Table 1. Symmetry (S) and distances between two atoms (L) of $AlS_n(n=2–9)$ clusters for the ground state.

cluster	S	type	L/nm	cluster	S	type	L/nm
AlS_2	$D_{\infty h}$	1-2	0.2076	AlS_8	C_s	1-2	0.2333
AlS_3	C_{2v}	1-2	0.2135			1-4	0.2348
		1-3	0.2165			1-5	0.2234
		3-4	0.2261			2-3	0.2072
AlS_4	D_{2d}	1-2	0.2204			3-4	0.2059
		2-3	0.2169			5-6	0.2146
AlS_5	C_{2v}	1-2	0.2180			6-7	0.2105
		1-4	0.2307	AlS_9	C_s	1-2	0.2352
		2-3	0.2248			1-4	0.2347
		4-5	0.2071			1-5	0.2227
AlS_6	C_2	1-2	0.2296			2-3	0.2061
		1-4	0.2223			3-4	0.2067
		2-3	0.2074			5-6	0.2159
		4-5	0.2158			6-7	0.2022
		5-6	0.2082			7-8	0.2302
AlS_7	C_2	1-2	0.2351				
		1-5	0.2237				
		2-3	0.2062				
		5-6	0.2152				
		6-7	0.2083				

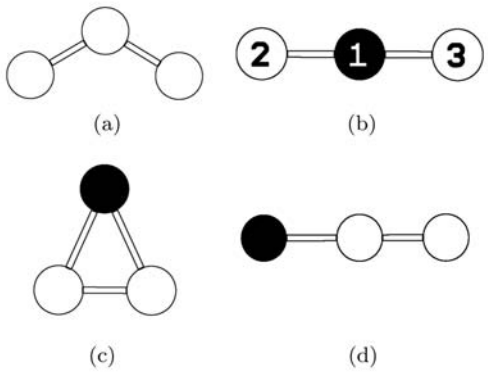


Fig. 1. The ground state and some metastable state structures of AlS_2 clusters and the ground state structure of the S_3 cluster.

which shows a tendency to form the Fig. 2(b) isomer. Another low-lying structure for AlS_3 is a trigonal pyramid with C_{3v} symmetry (Fig. 2(e)), lying 218.97 kJ · mol^{-1} above the ground state. It is a transition state because of two imaginary bending mode frequencies. The planar structure in Fig. 2(f) also has two imaginary bending mode frequencies and lies 304.30 kJ · mol^{-1} above the ground state. Their bending mode frequencies show a tendency to form the structure in Fig. 2(c). The features of the structures indicate that the cyclic isomers are more stable than the linear structures and the Al atom prefers to reside in a relatively central position. As the lowest-energy structures of AlS_n ($n = 4$–9) clusters are three-dimensional, $n = 3$ can be seen as the transitional point from a two-dimensional to a three-dimensional structure.

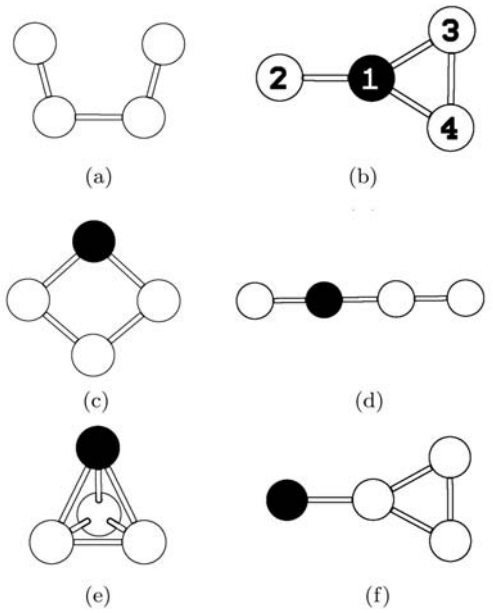


Fig. 2. The ground state and some metastable state structures of AlS_3 clusters and the ground state structure of a S_4 cluster.

AlS_4 Our calculations predict a D_{2d} ground state (Fig. 3(b)) for the AlS_4 molecule, which can be built by capping a S atom between atoms (1, 2, 3) and then deviating the AlS_3 ground state. One of the metastable states is the planar C_{2v} structure of Fig. 3(c), at 11.81 kJ · mol^{-1} is less stable, which can be derived from the isomer of Fig. 2(b) or Fig. 2(c) by capping an additional S atom. The next AlS_4 isomer (Fig. 3(d)) in order of energy (41.48 kJ · mol^{-1} above the ground state) possesses D_{2h} symmetry and has an imaginary axial mode frequency, which corresponds to a relative vibration of four S atoms in an axial direction and ultimately leads to the D_{2d} structure of Fig. 3(b) according to a vibrational frequency calculation. The spatial C_2 structure (Fig. 3(e)), which can be formed by the substitution of a S atom by an Al atom in the second-lowest energy structure of S_5,[2,4–6] lies 107.65 kJ · mol^{-1} above the ground state and 36.23 kJ · mol^{-1} below the planar C_{2v} pentagonal ring (Fig. 3(f)). The ground state of S_5 (Fig. 3(a)) also has a five-membered ring structure but with C_s symmetry. This structure agrees with previous theoretical predictions.[4–6] Therefore, we designed a configuration by substituting a S atom by an Al atom in the ground state structure of S_5 and performed geometric optimisation with it in the initial geometry. The result revealed that it finally became the isomer in Fig. 3(e).

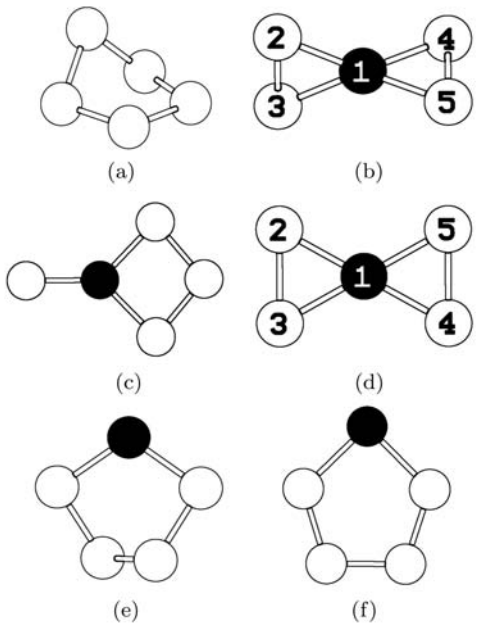


Fig. 3. The ground state and some metastable state structures of AlS_4 clusters and the ground state structure of S_5 cluster.

AlS_5 The ground state structure of S_6 is a spatial chair with D_{3d} symmetry (Fig. 4(a)), which is in agreement with Refs. [4]–[6]. For AlS_5, our result for the lowest-energy structure is the C_{2v} structure (Fig. 4(b)), which originates from capping a S atom on the side of the AlS_4 ground state. Two planar low-lying isomers with similar geometrical configurations (Figs. 4(c) and 4(e)) are 18.64 kJ · mol^{-1} and 22.05 kJ · mol^{-1} above the ground state, respectively. The C_{2v} isomer of Fig. 4(c) can also be obtained by adding a S atom between atoms (2, 3) in the structure of Fig. 3(d). Additionally, by using the vibrational frequency results, there exists an imaginary bending-mode frequency for the isomer of Fig. 4(c), which

shows a tendency to form the structure of Fig. 4(b). The third structure in the energetic ordering is the spatial C_2 isomer (Fig. 4(d)), which is derived from the structure of Fig. 3(e) by adding one more S atom above the Al atom. It is 19.95 kJ · mol^{-1} less stable in energy than the ground state. Another C_s isomer (Fig. 4(f)) containing a five-member ring, has energy 44.37 kJ · mol^{-1} higher than the structure of Fig. 4(b) and has an imaginary frequency that ultimately leads to forming the structure of Fig. 4(d). Furthermore, the five-member ring of the isomer of Fig. 4(f) can be obtained by the substitution of a S atom by an Al atom in the S_5 ground state.

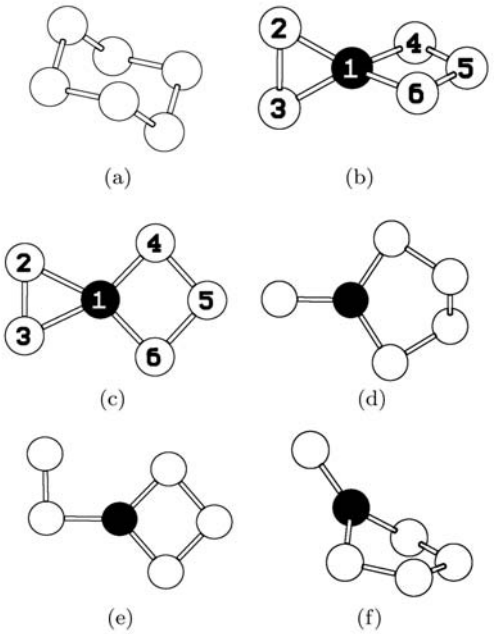


Fig. 4. The ground state and some metastable state structures of AlS_5 clusters and the ground state structure of S_6 cluster.

AlS_6 For S_7, we obtained a chair-form structure with C_s symmetry (Fig. 5(a)) for the ground state. Our result agrees with previous studies.[2,3] The ground state of AlS_6 (Fig. 5(b)) can be formed by capping a S atom among atoms (4, 5, 6) in the lowest-energy structure of Fig. 4(b) or above the Al atom in the structure of Fig. 4(d). It possesses C_2 symmetry because of its distorted five-member ring. If the atoms (4, 5, 6, 7) of the Fig. 5(b) structure became planar in form, a transition state with higher symmetry (C_{2v}) would be obtained (Fig. 5(d)), which is located 35.97 kJ · mol^{-1} above the structure and ultimately leads to the structure of Fig. 5(b). It can be obtained by adding a S atom on top of the isomer of Fig. 4(f) too. The isomer of Fig. 5(c) lies to only 6.56 kJ · mol^{-1} higher in energy, which can also be derived from the optimal structure of Fig. 4(b) by capping a S atom among atoms (1, 2, 3). It should be pointed out that the symmetry of the isomer in Fig. 5(c) is D_2 instead of D_{2d}. Fourth in the order of energy is a transition state with D_{2h} symmetry (Fig. 5(e)) and 38.33 kJ · mol^{-1} less stable than the ground state. It can be obtained by capping a S atom among atoms (1, 2, 3) in the configuration of Fig. 4(c) and the imaginary mode frequency gives a tendency to form the structure of Fig. 5(c). The total energy of the spatial C_s isomer of Fig. 5(f), which is formed by adding a S atom on the bottom of the AlS_5 cluster (Fig. 4(f)), is 76.14 kJ · mol^{-1} above the ground state structure. The chair form [atoms (1, 3, 4, 5, 6, and 7)] of Fig. 5(f) isomer can be obtained by substituting a S atom with an Al atom in the S_6 ground state.

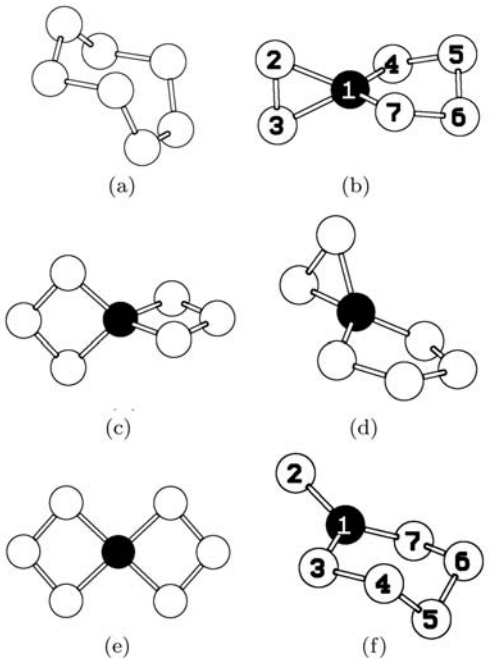


Fig. 5. The ground state and some metastable state structures of the AlS_6 clusters and the ground state structure of the S_7 cluster.

AlS_7 As is well known, D_{4d} crown-shaped geometry (Fig. 6(a)) is the most stable structure for S_8.[2,4–6] Our calculations also reach the same results. If one places an additional S atom between atoms (2, 3) in the ground state of AlS_6, then the lowest-energy structure for AlS_7 can be obtained with the C_2 symmetry (Fig. 6(b)). It can also be formed when the four-membered ring turns into a C_2 five-member ring with the structure given in Fig. 5(c). The spatial C_s form (Fig. 6(c)) originates from capping a S atom on the side of the structure of Fig. 5(d), which is 18.12 kJ · mol^{-1} less stable. There is an imaginary bending-mode frequency, which tends to form

the ground state. The third item in the energy order is a spatial C_s isomer (Fig. 6(d)), which is obtained by adding one S atom to the terminal of the AlS_6 structure of Fig. 5(d) or capping one S atom on the top of the Fig. 5(f) isomer. It is 19.69 $kJ \cdot mol^{-1}$ above the ground state. The next structure in the energy order, located 25.20 $kJ \cdot mol^{-1}$ above the structure of Fig. 6(b), is a C_2 isomer (Fig. 6(e)). It can be obtained by adding a S atom at the right side of the structure of Fig. 5(b). In fact, the distorted six-member ring in the Fig. 6(e) structure can be obtained by substituting a S atom with an Al atom in the S_6 low-lying isomer.[2,3−6] Another spatial C_s isomer (Fig. 6(f)) is considered and it can be formed by locating one more S atom at either side of the structure of Fig. 5(c), which is 77.45 $kJ \cdot mol^{-1}$ higher in energy. Furthermore, the isomers of Figs. 6(f) and 6(b) are similar.

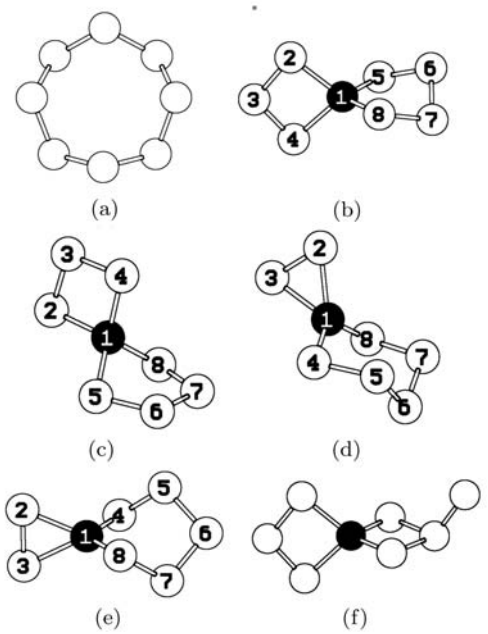


Fig. 6. The ground state and some metastable state structure of AlS_7 clusters and the ground state structure of S_8 cluster.

AlS_8 For S_9, the lowest-energy structure is the C_2 isomer (Fig. 7(a)), which in is agreement with the theoretical predictions made by Raghavachari *et al.*[4] and by Pan *et al.*[5] The isomer with C_s symmetry (Fig. 7(b)) is identified as the ground state structure for AlS_8, which originates from the structure of Fig. 6(c) by capping a S atom between atoms (6, 7) or the structure of Fig. 6(d) by capping a S atom between atoms (2, 3). The next structure in order of energy containing two distorted five-member rings with a Fig. 3(e) configuration is the isomer of Fig. 7(c), which is 9.19 $kJ \cdot mol^{-1}$ above the structure of Fig. 7(b). Similar to the structure of Fig. 5(c), it possesses D_2 symmetry instead of D_{2d} symmetry. If the distorted five-member rings of the structure of Fig. 7(c) became planar rings, a transition state with higher symmetry (D_{2d}) would be obtained (Fig. 7(f)), which is located 28.36 $kJ \cdot mol^{-1}$ above the isomer of Fig. 7(c) and ultimately leads to the structure of Fig. 7(c) according to a vibrational frequency calculation. The third isomer in order of energy is the C_2 isomer of Fig. 7(d), which can be obtained by capping a S atom between atoms (6, 7) in the structure of Fig. 6(b) or between atoms (2, 3) in the structure of Fig. 6(e) and is 9.45 $kJ \cdot mol^{-1}$ less stable than the ground state. The spatial isomer of Fig. 7(e) with C_2 symmetry lies to 28.36 $kJ \cdot mol^{-1}$ higher in energy, which is derived from the structure of Fig. 6(d) by adding a S atom among atoms (5, 6, 7). Moreover, the chair form [atoms (1 and 4–9)] of the isomer of Fig. 7(e) can be obtained by the substitution of a S atom by an Al atom in the minimum structure of S_7 (Fig. 6(a)).

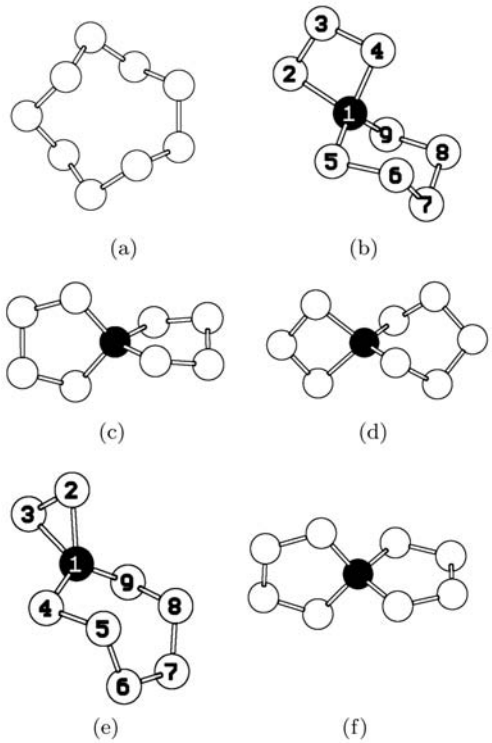


Fig. 7. The ground state and some metastable state structures of AlS_8 clusters and the ground state structure of a S_9 cluster.

AlS_9 For S_{10}, the ground state structure is a ten-member ring with D_{2d} symmetry (Fig. 8(a)). This structure agrees with the previous calculation results.[2,4−6] The ground state for AlS_9 (Fig. 8(b)) derives from the optimal structure of AlS_8 (Fig. 7(b)) by capping a S atom among atoms (6, 7, 8) or from

the structure of Fig. 7(e) by capping a S atom among atoms (1–3). The isomer of Fig. 8(c) with C_1 symmetry can be obtained by adding a S atom to make the four-member ring into a distorted five-member ring with the structure shown in Fig. 7(b). It lies only 3.68 kJ · mol^{-1} above the isomer of Fig. 8(b). The structure of Fig. 8(d) with higher symmetry (C_s) is similar to the isomer of Fig. 8(c) and is 16.28 kJ · mol^{-1} less stable than the ground state. It has two imaginary mode frequencies that, according to vibrational frequency calculations, ultimately lead to the C_1 isomer. The fourth structure in energy order is the C_2 isomer of Fig. 8(e), which is 25.47 kJ · mol^{-1} above the structure of Fig. 8(b). It originates from the structure of Fig. 7(d) by capping one more S atom at the right side. Another C_2 structure is shown in Fig. 8(f), which is located 40.96 kJ · mol^{-1} above the ground state. It can be obtained by capping a S atom at the left side of the isomer of Fig. 7(d) or at either side of the structure of Fig. 7(c).

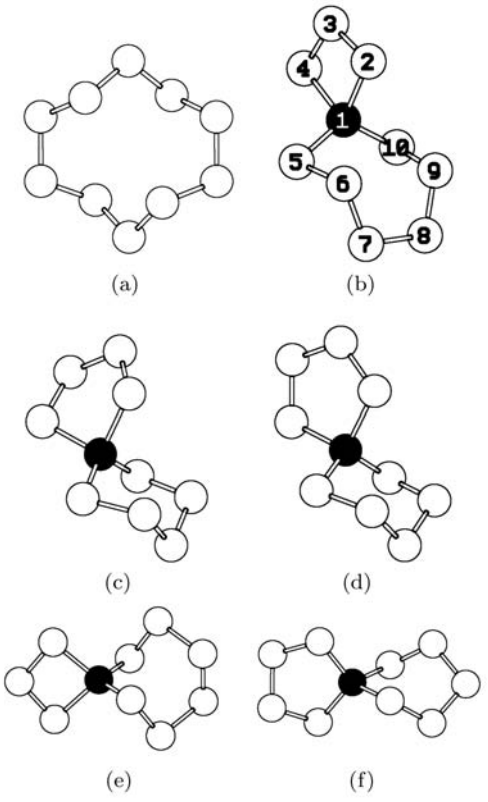


Fig. 8. The ground state and some metastable state structures of AlS_9 clusters and the ground state structure of S_{10} cluster.

From the above analysis, we can conclude that the Al atom prefers to reside at the central position in the ground state of AlS_n(n = 2–9) clusters, except for n = 6, 8 and 9. The S atoms of AlS_6, AlS_8 and AlS_9 are divided into 2–4, 3–5 and 3–6 groups by the Al atom, respectively. The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of S_2, S_5 and S_6 are 488.22 kJ · mol^{-1}, 302.00 kJ · mol^{-1} and 365.68 kJ · mol^{-1}, which are much greater than that of S_3 and S_4.[5] This may explain why the Al atom is not exactly at the centre in AlS_6, AlS_8 and AlS_9. The sulfur atoms prefer not only to evenly distribute on both sides of the aluminum atom, but also to form a stable structure in each side of the AlS_n clusters. The second rule can also explain why the majority of Al-sulfur rings for AlS_n clusters can be obtained by the substitution of a S atom by an Al atom in the ground state and in some low-lying metastable states of the pure sulfur clusters. These two rules determine the structure of AlS_n (n = 2–9) clusters. It is obvious that the structures of pure S_n are fundamentally changed due to the doping of the Al atom.

3.2. Stability

The fragmentation energy and the second-order difference energy of AlS_n(n = 2–9) clusters for the ground state are listed in Table 2. The relative stability of the clusters can be predicted by calculating the fragmentation energy. The fragmentation energy can be defined by following formula:

$$E_{\rm f}(n) = E_{\rm T}({\rm AlS}_{n-1}) + E_{\rm T}({\rm S}) - E_{\rm T}({\rm AlS}_n), \quad (1)$$

where $E_{\rm T}$(S) and $E_{\rm T}$ (AlS_n) represent the total energy of the most stable S and the most stable AlS_n clusters, respectively. As shown in Fig. 9, local maxima of fragmentation energies appear at n = 4, 6. This indicates that AlS_4 and AlS_6 clusters are more stable than their neighbours. Additionally, the $E_{\rm f}(n)$ values have a decreasing tendency with the increase in the size of these clusters.

Table 2. Fragmentation energy ($E_{\rm f}$/kJ · mol^{-1}) and second-order energy difference ($D_2(E)$/kJ · mol^{-1}) of AlS_n(n = 2–9) clusters for the ground state.

cluster	$E_{\rm f}$	$D_2(E)$	cluster	$E_{\rm f}$	$D_2(E)$
AlS_2			AlS_6	441.61	29.14
AlS_3	414.04	–61.96	AlS_7	412.47	14.44
AlS_4	476.00	67.21	AlS_8	398.03	10.24
AlS_5	408.79	–32.82	AlS_9	387.79	

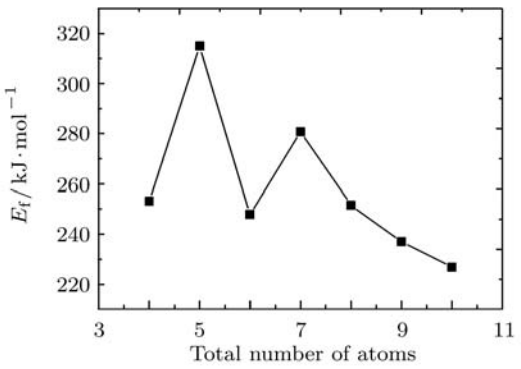


Fig. 9. Size dependence of the fragmention energy of AlS_n ($n = 2$–9) clusters.

To further test the stability of the AlS_n cluster, the following reaction energy variation is considered:

$$2(AlS_n) \rightarrow (AlS_{n+1}) + (AlS_{n-1}). \quad (2)$$

We define the energy variation in formula (2) as $D_2(E_n) = E_{n+1} + E_{n-1} - 2E_n$, the second-order difference in energy for the neutral AlS_n. Hence, we obtain the curve shown in Fig. 10 corresponding to the energy variation in formula (2) as the number of total atoms. The larger the $D_2(E_n)$ is, the more stable the cluster is. Therefore, it is clear that the AlS_4 and AlS_6 are most stable in the AlS_n clusters, which is consistent with the result of fragmentation energies shown in Fig. 9.

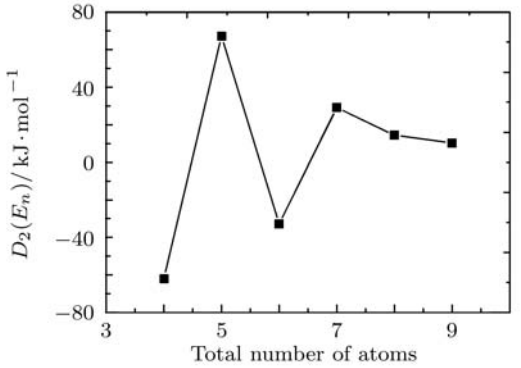


Fig. 10. Second-order energy differences of AlS_n ($n = 2$–9) clusters.

3.3. Vibrational frequency analysis

Calculation of the vibrational frequencies is important for predicting stability. To determine the ground state of the AlS_n clusters, we calculated the vibrational frequencies of the clusters. All the ground states reported are indeed equilibrium states without imaginary frequencies. They are not discussed in detail here due to the restriction on length.

4. Conclusions

A systematically theoretical investigation of the growth behaviours and stabilities of S_{n+1} and AlS_n (n up to 9) clusters have been performed at the B3LYP level by employing 6-311G(d) basis sets. The results of S_{n+1} clusters reveal that open forms are more stable up to S_4, whereas ring structures are favoured for larger clusters, which are in good agreement with previous conclusions.[2−6] The structures of pure S_n are fundamentally changed due to the doping of the Al atom. The ground state structures for AlS_n show that the sulfur atoms prefer not only to evenly distribute on both sides of the aluminum atom, but also to form a stable structure in AlS_n clusters. Moreover, almost all Al-sulfur rings in AlS_n clusters can be obtained by the substitution of a S atom by an Al atom in the ground state or some low-lying structures of pure sulfur clusters. The calculated fragmentation energies and the second-order energy differences show the AlS_4 and AlS_6 clusters to be extremely stable.

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