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Probing the electronic structures and properties of neutral and charged arsenic sulfides (As$_n$S$^{(-1,0,+1)}$, n =1–7) using Gaussian-3 theory

Jucai Yang · Yali Kang · Xi Wang · Xue Bai

Abstract The structures and energies of neutral and charged arsenic sulfides As$_n$S$^{(-1,0,+1)}$ (n =1–7) were systematically investigated using the G3 method. The bonding properties and the stabilities of As$_n$S and their ions were discussed. The adiabatic electron affinities (AEAs) and adiabatic ionization potentials (AIPs) were presented. The ground-state structures of As$_n$S can be considered as the lowest-energy structure of neutral As$_{n+1}$ by replacing an As atom with a S atom, that is, "substitutional structure", in which the feature of sulfur bonding is edge-bridging. The ground-state structures of As$_n$S$^+$ tend to be derived from the lowest-energy structure of cation As$_n^+$ by attaching to a S atom, that is, "attaching structure", in which the sulfur can be three-fold coordinated. There is no rule to be found for the ground-state structure of anion As$_n$S$^-$, in which the sulfur can be a terminal atom. There are odd-even alternations in both AEAs and AIPs as a function of size of As$_n$S. The dissociation energies of S, S$^-$, and/or S$^+$ from neutral As$_n$S and their ions were calculated to examine their stabilities.

Keywords Arsenic sulfides · Dissociation energy · Electron affinity · Ionization potential

J. Yang (✉) · Y. Kang · X. Wang
School of Energy and Power Engineering, Inner Mongolia University of Technology, Hohhot 010051,
People's Republic of China
e-mail: yangjc_zhao@aliyun.com

J. Yang
e-mail: yangjc@imut.edu.cn

X. Bai
School of Chemical Engineering, Inner Mongolia University of Technology, Hohhot 010051, People's Republic of China

Introduction

For many years arsenic species have received a great amount of attention from both experimental and theoretical fields [1–6]. In addition to other reasons, this is because arsenic is widely used in such fields as semiconductors, optoelectronics, and bio-pharmaceutics, and because arsenic is one of the most toxic and carcinogenic species, raising a very important environmental issue [7–12]. For example, arsenic contamination of groundwater has led to massive epidemics of arsenic poisoning in such areas as South and South East Asia [13]. The ground-state structures of small arsenic clusters confirmed by theoretical schemes [2, 3, 7, 8] and experimental methods, such as photoelectron spectroscopy [4, 5, 14–16], Raman spectra [17], or gas–phase electron diffraction analysis [18], are *isosceles triangle* for As$_3$, *tetrahedron* for As$_4$, and *distorted trigonal bipyramid* for As$_5$. For n ≥6, the calculated ground-state structures of As$_n$ clusters were found to be dependent on the adopted functional and basis set. Many theoretical studies [2, 3, 7–9, 19, 20] revealed that the type of benzvalene form and type of trigonal prism compete with each other for the ground state structure of As$_6$ and As$_7$, respectively.

The various arsenic sulfides have also attracted a lot of attention during the past two decades due to their distinctive characteristics as broad transparency in the near and far infrared spectra region, high refractive indices, and excellent photochemical sensitivity [21–23]. It has been known that they are used as infrared sensors, wave-guide materials, p-n junctions, and photoresists in optical and ultraviolet lithography, optical memory devices, switches, modulators and optical computing [24–26]. Arsenic sulfide films have recently been considered as materials for optical fibers [27, 28]. Extensive experimental and theoretical studies on arsenic sulfides have been reported in the literature. For instance, a large number of arsenic sulfide clusters of various sizes and compositions such as AsS$_n$ (n=1–8), As$_2$S$_n$ (n=1–7), As$_3$S$_n$ (n=1–7), As$_4$S$_n$ (n=3,4), As$_3$S$_n^+$ (n=1–4), and AsS$_n^+$ (n=1–7) clusters

obtained by pulsed laser ablation were identified by time-of-flight mass spectrometry [21, 25, 26]. The photoinduced transformation of arsenic-sulfur clusters in the realgar form to pararealgar was monitored by X-ray diffraction, Raman, and/or infrared spectroscopy [22, 29, 30]. The vibrational properties of As_2S_3, As_2S_5, As_4S_6, As_6S_9, As_4S_4, and As_8S_9 were obtained by infrared, Raman, and/or UV-visible spectroscopy, and compared with theoretical calculated spectra [31–33]. The nature of sublimation processes of As_2S_3 and As_4S_4 was investigated by mass spectrometric and vapor pressure techniques, and their second-law enthalpy for sublimation was reported [34–36]. From the theoretical aspect, Banerjee et al. [24] examined the structure, bonding, electron distribution, and normal mode frequencies of As_4S_4 using the HF, MP2 and B3LYP methods and 6-311G(d) basis set. Babić et al. [37, 38] performed local-density pseudopotential calculation for As_4S_4, As_4S_5, and As_4S_6, and found that the As–As bond is the main reason for the stability of arsenic sulfides and the As–S bond charge density has excellent transferability.

The objective of the present study is to perform a detailed investigation of the neutral and charged arsenic sulfide species using the higher level of the Gaussian-3 (G3) theory [39, 40], intending to provide the first theoretical description of the structures and properties including electron affinities (EAs), ionization potentials (IPs), and dissociation energies (DEs). The knowledge of these properties and structures may provide required theoretical guidance for the design and synthesis of novel functional materials of arsenic sulfides. In addition, the EA and IP are both a key spectroscopic value and vitally important for use in the chemical cycle to determine bond dissociation energy. The knowledge of the thermochemical properties, the ground and low-lying electronic states of the neutral and charged species is indispensable for understanding chemical reactivity and predicting reaction mechanism.

The G3 scheme provides accurate energies of molecular systems for calculation of atomization energies (AEs), IPs and EAs because it is really an approximation to a full calculation at the level QCISD(T)/G3large. The mean absolute error between experimental and theoretical values for 188 (23 for AEs, 63 for EAs, and 102 for IPs) reactions are 1.05 kcal mol^{-1} [39, 40]. Recently, we calculated the EAs, IPs, and DEs of As_n and Si_n clusters by means of the G3 method. The mean absolute error for 19 reactions is only 0.05 eV [3, 41].

Computational methods

All calculations at the extension of G3 theory [39, 40] have been performed by means of the Gaussian 09 package [42]. In addition to the HF/6-31G(d) vibrational frequencies, scaled by 0.893 [39, 40], were applied for the zero-point vibrational energy (ZPVE) correction at 0 K. The MP2(full)/6-31G(d) harmonic frequency analyses for all of species reported in this

paper were carried out to guarantee that the optimized structures are local minima.

A large number of isomers need to be studied to obtain the global minimum energy structure. In particular, no experimental values are available for comparison. Hence, in the optimization process of cluster geometries, we considered a large number of isomers generated from the following four types. One is the "substitutional structure", which can be viewed as being derived from the ground state structure of As_{n+1} (As_{n+1}^- and/or As_{n+1}^+) by replacing an As atom with a S atom. The second is the "attaching structure", in which the S atom is bound to different positions on surface or edge or apex of the lowest energetic structure of As_n (As_n^- and/or As_n^+). The third type is also "attaching structure", in which the As atom is bound to different positions on surface or edge or apex of the lowest energetic structure of As_nS (As_nS^- and/or As_nS^+). Several structures designed by us are named the "fourth type". Starting with these structures, we obtained as many of the refined low-lying structures as possible at the B3LYP/6-31+G* level. Then, we refined the energies of the selected low-energy isomers by the G3 method. We found that the finally local minima isomers of the third type are very close to those of the "substitutional structures" (one type), and the structures of the fourth type are not the ground state. Hence, we only reported the first two types. In addition, the spin multiplicities of singlet, doublet, triplet, and quartet state were taken into account for $n \leq 3$ species.

Results and discussion

AsS and its charged molecules

The optimized geometries of the neutral AsS and its charged species are displayed in Fig. 1. The bond length for $^2\Pi$ ground state structure, **1(a),** is predicted to be 2.045 Å, which is 0.023 Å longer than the experimental value of 2.0216 Å measured by emission spectrum [43]. A quartet state isomer (not shown in Fig. 1) was also obtained. However, it is higher in energy than that of doublet ground state by 0.58 eV.

For negatively charged ion AsS$^-$, the ground state is triplet analogous to AsSi$^+$ [44], HAs [45], AsF [46], AsCl [47], and CH$_3$As [11] species. The $^3\Sigma$ ground-state structure, **1(b)**, is more stable in energy than the isomer **1(c)** of singlet $^1\Pi$ state by 0.66 eV at the G3 level. The As–S bond lengths of the ground-state structure of AsS$^-$ are 0.076 Å longer than its neutral counterpart.

For positively charged ion AsS$^+$, the As–S bond distances of $^1\Sigma^+$ ground state structure **1(d)** are evaluated to be 1.980 Å. Which are 0.035 Å longer than the experimental value of 1.9447 Å obtained by emission spectrum [48]. At HF/6-311G(d) and B3LYP/6-311G(d) level, the As–S bond distances are respectively 1.91 and 1.96 Å [21].
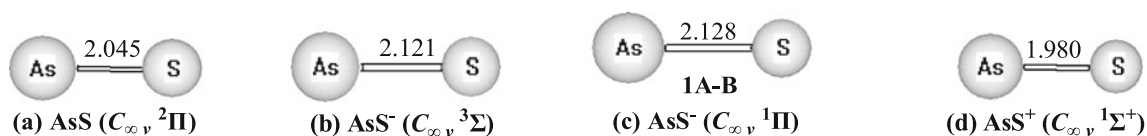
Fig. 1 Geometries of neutral AsS and its charged species optimized at MP2(full)/6-31G(d) level. The bond lengths are in angstrom

As$_2$S and its charged molecules

Five minimal structures for neutral As$_2$S, four for anionic As$_2$S$^-$, and four for cationic As$_2$S$^+$ are shown in Fig. 2. For neutral As$_2$S, the global minimum is predicted to be *isosceles* *triangle* **2(a)** with C_{2v} symmetry and $^1A_1$ ground state. The isomer **2(d)** is also C_{2v} symmetry and $^1A_1$ state. Energetically, it is higher 1.10 eV than the structure **2(a)**. Two *linear* isomers of **2(c)** and **2(e)** possess $C_{\infty v}$ symmetry with $^1\Sigma$ and $C_{\infty h}$ symmetry with $^1\Sigma_g$ state, respectively. They are less
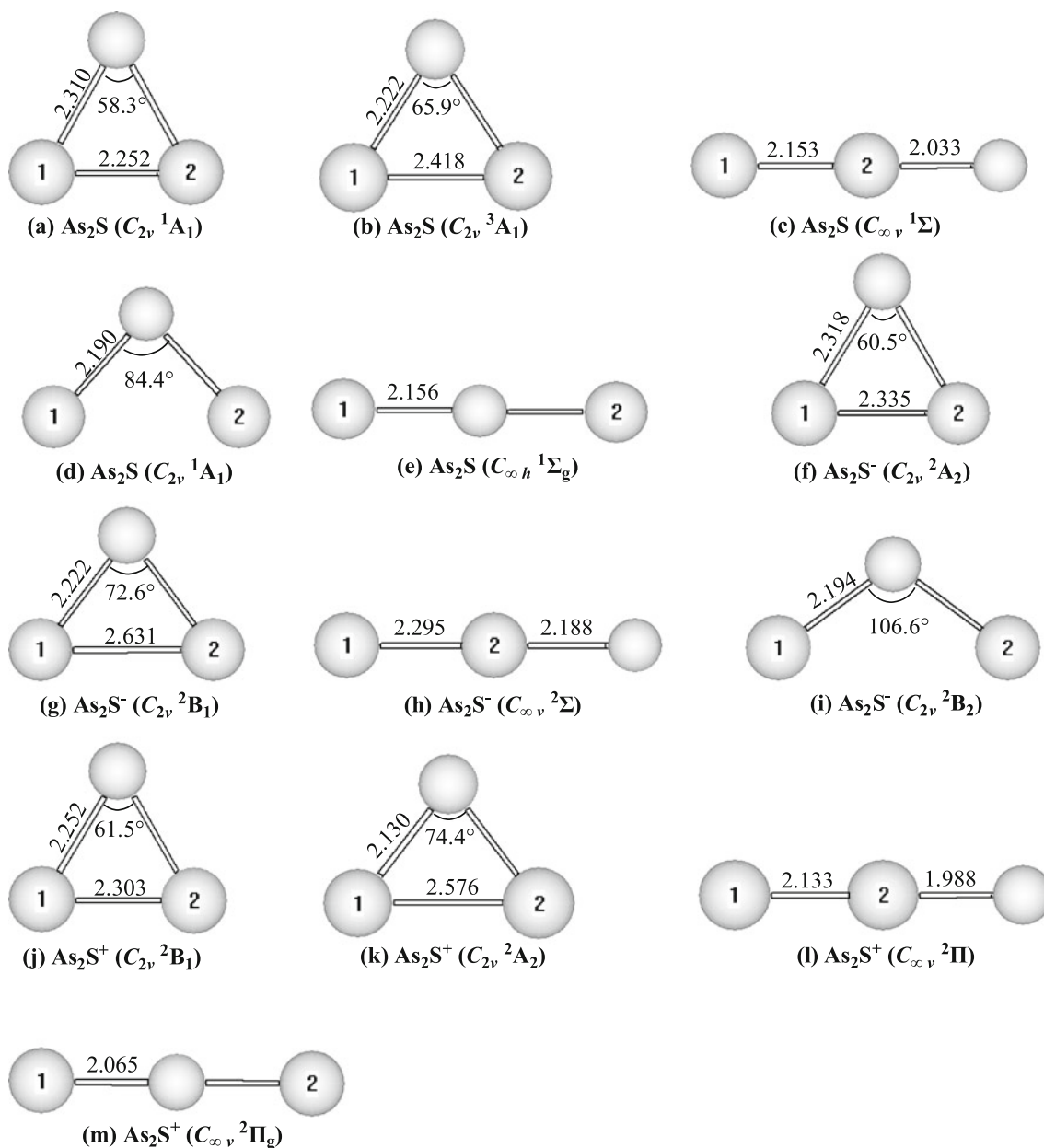

Fig. 2 Geometries of neutral As$_2$S and its charged species optimized at MP2(full)/6-31G(d) level. Only arsenic atoms are numbered. The bond lengths and bond angles are respectively in angstrom and degree

stable than the ground-state structure **2(a)** by 0.79 and 1.96 eV in energy, respectively. The lowest lying triple state is predicted to be *isosceles triangle* **2(b)** with C_{2v} symmetry and $^3A_1$ electronic state, which is evaluated to lie 0.33 eV above the ground-state **2(a)**. The As–As and S–As bond distances of the **2(a)** are calculated to be 2.252 and 2.310 Å, respectively. Compared with the ground-state structure of As_2, the As–As bond distances of the ground-state structure of As_2S increase by 0.102 Å [3].

For negatively charged ion As_2S^-, three *isosceles triangle* structures (**2(f)**, **2(g)**, and **2(i)**) are C_{2v} symmetry with $^2A_2$, $^2B_1$, and $^2B_2$ electronic state, respectively. Energetically, the lowest-energy $^2A_2$ structures are more stable than those of $^2B_1$ and $^2B_2$ by 0.75 and 1.23 eV, respectively. The $C_{\infty v}$-symmetry *linear* isomer of $^2\Sigma$ electronic state is higher 0.97 eV in energy than the lowest-energy structure. The $C_{\infty h}$-symmetry *linear* isomer (not shown in Fig. 1), corresponding to neutral **2(e)**, is a saddle point due to having an imaginary π frequency of $326i$ cm^{-1} at the MP2(full)/6-31G(d) level. Following the mode π, it collapses to the *isosceles triangle* **2(i)**. The lowest lying quartet state is predicted to be *isosceles triangle* isomer (not shown in Fig. 2) with C_{2v} symmetry and $^4A_1$ electronic state. Energetically, it is 1.22 eV higher than the ground $^2A_2$ state. The As–As and S–As bond distances of the lowest-energy **2(f)** are calculated to be 2.335 and 2.318 Å, which are 0.083 and 0.008 Å longer than their neutral counterparts, respectively.

For positively charged ion As_2S^+, two *isosceles triangle* structures of **2(j)** and **2(k)** have respectively $^2B_1$ and $^2A_2$ electronic state, and two *linear* isomers of **2(l)** and **2(m)** display respectively $C_{\infty v}$ symmetry with $^2\Pi$ state and $C_{\infty h}$ symmetry with $^2\Pi_g$ state. Energetically, the ground-state $^2B_1$ structure is more stable than those of $^2A_2$, $^2\Pi$, and $^2\Pi_g$ by 0.51, 1.80, and 1.85 eV, respectively. The lowest lying quartet state is predicted to be *isosceles triangle* isomer (not shown in Fig. 2) with C_{2v} symmetry and $^4B_2$ electronic state. Energetically, it is 1.71 eV higher than the ground $^2B_1$ state. The S–As bond distances of the lowest-energy **2(j)** are shorter by 0.058 Å than their neutral counterparts, while the As–As bond distances are longer by 0.051 Å. The reason is that the orbital occupied by removing electron has bonding character along the As–As bond.

As_3S and its charged molecules

The equilibrium geometries of the As_3S and its charged species are shown in Fig. 3. For neutral As_3S, four isomers are presented. Both C_{2v}-symmetry structure **3(b)** of $^2A_2$ state and **3(e)** of $^2B_1$ state can be viewed as being derived from *isosceles triangle* As_3 by edge-bridging with a S atom. The isomer **3(e)** of $^2B_1$ state is a saddle point due to having an imaginary b_1 frequency of $301i$ cm^{-1} at the MP2(full)/6-31G(d) level. Following the mode b_1, the isomer **3(e)** collapses to the C_s-symmetry structure **3(a)** of $^2A'$ state, which is the ground state. The C_{3v}-symmetry isomer **3(c)** of $^2A_1$ state can be

viewed as being derived from the ground-state *tetrahedral* structure of As_4 [1–4] by replacing an As atom with a S atom. The C_s-symmetry **3(d)** isomer of $^2A''$ state can be regarded as tilted attaching one S atom to the vertex of the *isosceles triangle* of the As_3 ground-state structure. Energetically, the **3(a)** structures are more stable than the **3(b)**, **3(c)**, and **3(d)** isomers by 0.33, 0.64 and 0.84 eV, respectively. The lowest lying quartet state is predicted to be C_s-symmetry structure (similarly to **3(a)**, not shown in Fig. 2) of $^4A''$ electronic state, which is higher in energy than the ground-state structure **3(a)** by 1.45 eV. The two equivalent S–As bond distances of the ground-state **3(a)** are 2.294 Å, and the As–As bond lengths are 2.398 and 2.436 Å, respectively.

The polyline structures of neutral As_nS and their charged ions are higher in energy. Therefore, the polyline structures of neutral As_nS and charged ions with $n \geq 3$ are not considered.

For anion As_3S^-, four isomers are reported. The global minimum is predicted to be C_{2v}-symmetry *planar rhombus* structure **3(f)** with $^1A'$ ground state. Both isomers **3(g)** and **3(h)** display C_s symmetry with $^1A'$ state. The form **3(i)** possesses C_{3v} symmetry with $^1A'$ state. Energetically, the **3(g)**, **3(h)**, and **3(i)** isomers are less stable than the ground-state structure **3(f)** by 0.22, 0.29, and 1.47 eV, respectively. The lowest lying triple state is predicted to be the structure (similarly to **3(g)**, not shown in Fig. 3) with C_s symmetry and $^3A''$ electronic state. Energetically, it is higher 1.14 eV than the ground $^1A'$ state. The As–As and S–As bond distances of the lowest-energy **3(f)** are calculated to be 2.359 and 2.239 Å, respectively.

For cation As_3S^+, three isomers are presented. The global minimal C_{3v}-symmetry **3(j)** of $^1A'$ ground state can be viewed as being derived from the ground state *equilateral triangle* structure of As_3 [3, 7] by face-capping with a S atom. Removing an electron from the neutral **3(b)** results in a cationic As_3S^+ with C_{2v} symmetry and $^1A'$ electronic state, which is a saddle point on the potential surface due to having two imaginary frequencies with b_2 ($294i$ cm^{-1}) and b' ($238i$ cm^{-1}) modes at the MP2(full)/6-31G(d) level. Following the mode b_2, it undergoes Jahn-Teller distortion to give a C_s-symmetry structure of $^1A'$ state, which is also a saddle point on the potential surface on account of having an imaginary a'' frequency of $23i$ cm^{-1}. It undergoes again Jahn-Teller distortion to actually give a C_s-symmetry isomer **3(k)** of $^1A'$ state. Of course, the **3(k)** structure can be regarded as being derived from the neutral **3(d)** by removing an electron. Removing an electron from the neutral **3(e)** results in a cationic As_3S^+ with C_{2v} symmetry and $^1A_1$ state, which is also a saddle point on the potential surface due to an imaginary b_1 frequency of 224 cm^{-1}. Following the mode b_1, it collapses to structure **3(l)** with C_s-symmetry and $^1A'$ state. Energetically, the ground-state **3(j)** is more stable than the **3(k)** and the **3(l)** isomer by 2.25 and 2.43 eV, respectively. The lowest lying triple state is predicted to be C_s-symmetry structure of $^3A'$
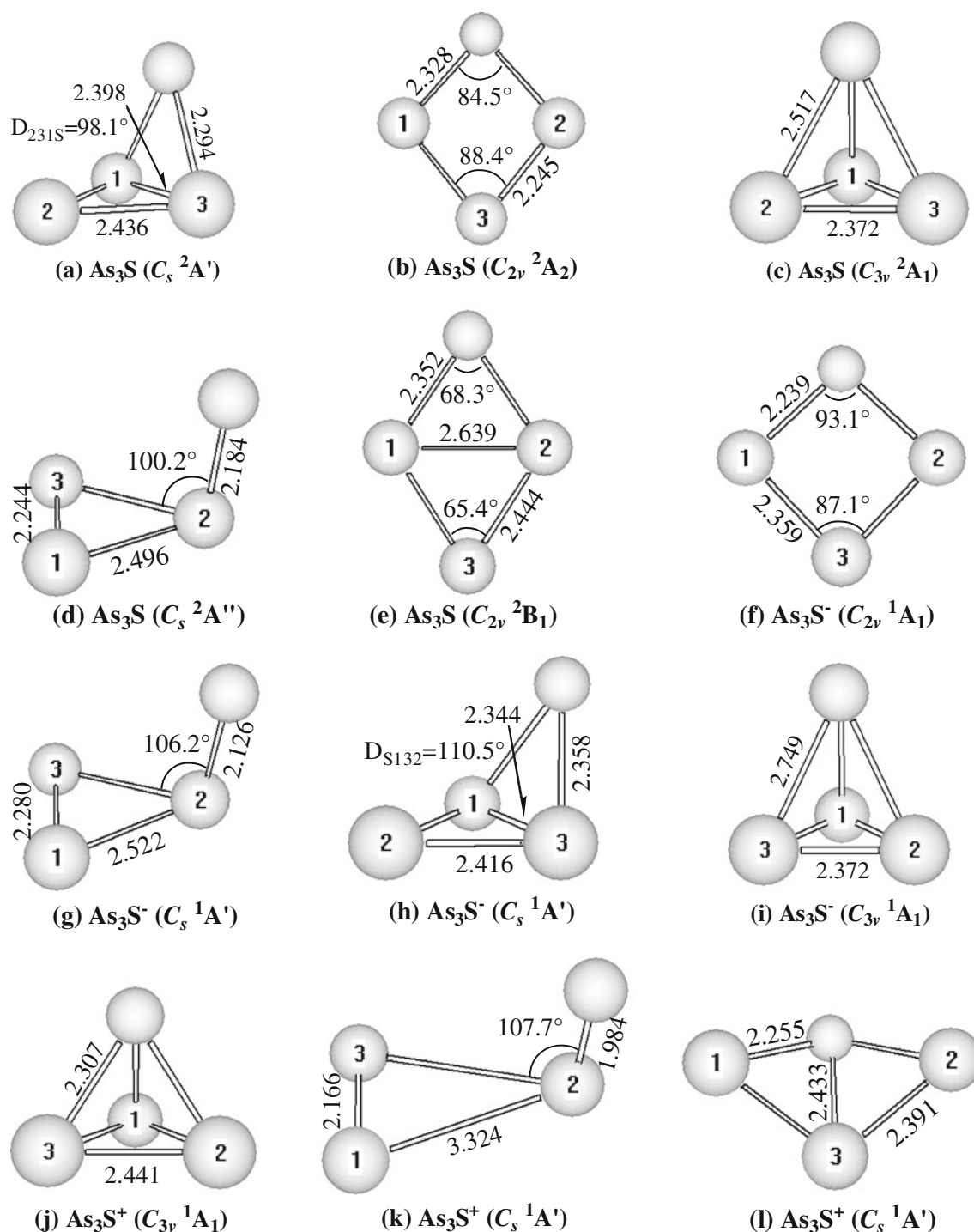
Fig. 3 Geometries of neutral As$_3$S and its charged species optimized at MP2(full)/6-31G(d) level. Only arsenic atoms are numbered. The bond lengths are in angstrom. The bond angles and dihedral angles are in angstrom and degree

electronic state (similarly to **3(a)**, not shown in Fig. 3). It is higher than the ground-state **3(j)** by 1.83 eV in energy. The As–As and S–As bond distances of the lowest-energy **3(j)** are calculated to be 2.441 and 2.307 Å, respectively.

From the discussion above, we can see that the ground-state structures of the As$_3$S, As$_3$S$^-$, and As$_3$S$^+$ are different from each other.

As$_4$S and its charged molecules

The equilibrium geometries of the As$_4$S and its charged species are shown in Fig. 4. For neutral As$_4$S, three isomers are presented. Both C_{2v}-symmetry **4(a)** of $^1A_1$ state and C_s-symmetry **4(c)** of $^1A'$ state can be viewed as being derived from not only the ground-state *distorted trigonal bipyramid* of
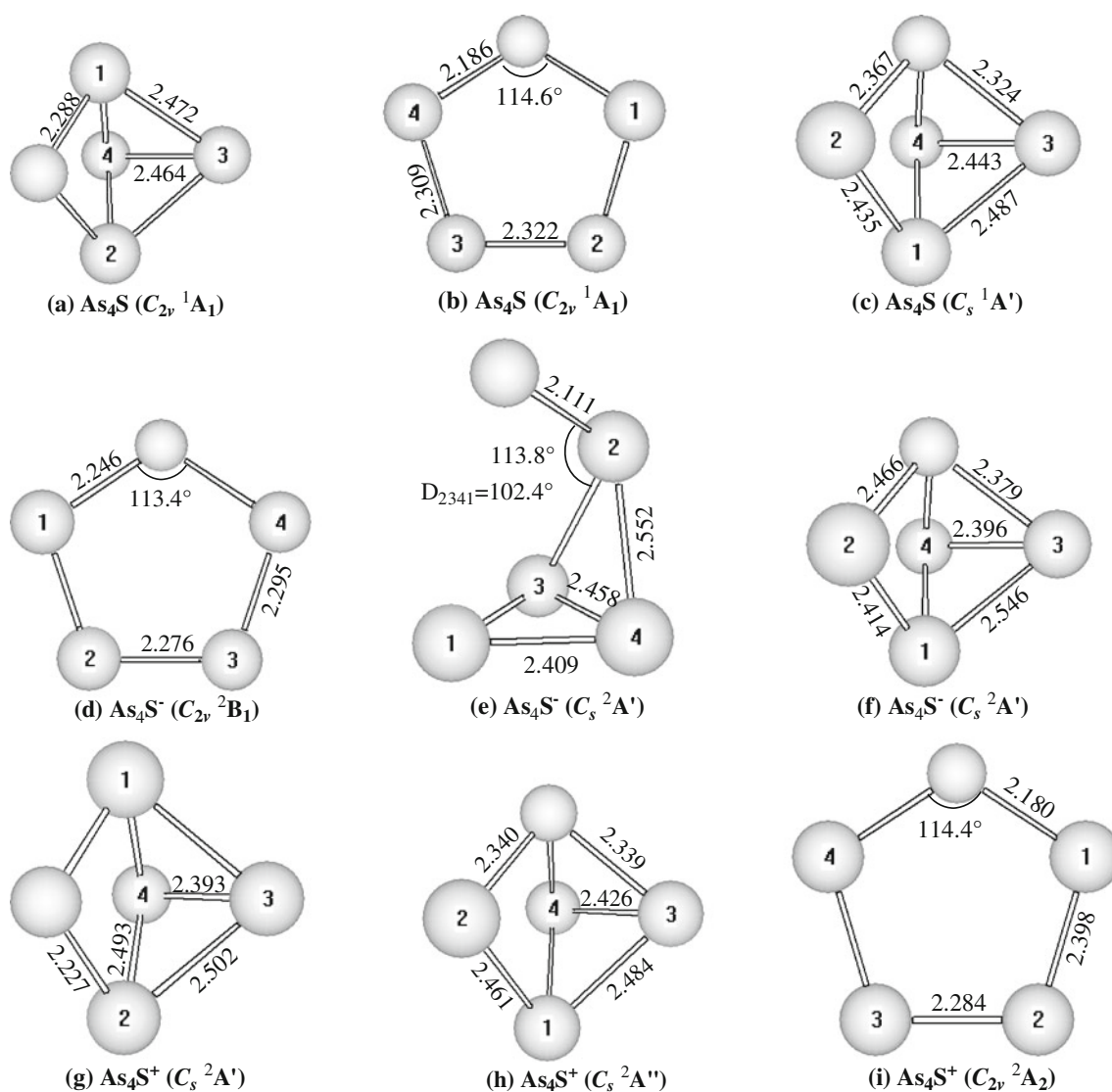
Fig. 4 Geometries of neutral As₄S and its charged species optimized at MP2(full)/6-31G(d) level. Only arsenic atoms are numbered. The bond lengths are in angstrom. The bond angles and dihedral angles are in angstrom and degree

As₅ [2, 3, 7] by replacing an As atom with a S atom but also the ground-state *tetrahedral* geometry of As₄ [1–4] by edge-bridging or face-capping with a S atom. The C_{2v}-symmetry structure **4(b)** of $^1A_1$ state can be regarded as the ground-state *pentagonal* geometry of As₅⁻ [2, 3, 7] by replacing an As atom with a S atom. Energetically, the ground-state structure **4(a)** more stable than the isomer **4(b)** and **4(c)** by 0.10 and 1.72 eV, respectively. The bond distances of ground-state **4(a)** are calculated to be 2.288 Å for two equivalent S–As bonds, 2.472 Å for four equal As–As bonds, and 2.464 Å for another As–As bond.

For negatively charged ion As₄S⁻, three isomers are also presented. Attaching an electron to the neutral **4(a)** results in an anionic As₄S⁻ with C_{2v} symmetry and $^2B_2$ state, which is a saddle point on the potential surface due to an imaginary b_2 frequency of 450 cm⁻¹. Following the mode b_2, it collapses to

the C_s-symmetry structure **4(e)** of $^2A'$ state. The isomer **4(f)**, corresponding to neutral **4(c)**, possesses C_s symmetry with $^2A'$ state. The structure **4(d)**, corresponding to **4(b)**, has C_{2v} symmetry with $^2B_1$ ground state. Energetically, the ground-state structures **4(d)** are more stable than the isomers of **4(e)** and **4(f)** by 0.19 and 1.74 eV, respectively. The bond distances of global minimum **4(d)** are evaluated to be 2.246 Å for two equivalent S–As bonds, 2.295 Å for two equal As–As bonds, and 2.276 Å for another As–As bond. The ground-state structure of anionic As₄S⁻ is different from that of neutral As₄S.

For positively charged ion As₄S⁺, three geometries are presented. The C_s-symmetry structure **4(g)** of $^2A'$ ground state can be viewed as being derived from not only the ground-state structure of As₄⁺ by edge-bridging with a S atom, but also the ground-state *square pyramid* of As₅⁺ [3, 7] by replacing an As atom of the base of the *square pyramid* with a

S atom. The isomers **4(h)** and **4(i)**, corresponding to neutral **4(c)** and **4(b)**, display C_s symmetry with $^2A''$ state and C_{2v} symmetry with $^2A_2$ state, respectively. Energetically, they are less stable than the ground-state structure **4(g)** by 0.34 and 0.84 eV, respectively. The bond distances of ground-state **4(g)** are calculated to be 2.227 Å for two equal S–As bonds, 2.393–2.502 Å for five As–As bonds. The ground-state structure of cationic As_4S^+ is somewhat different from that of neutral As_4S.

As_5S and its charged molecules

The equilibrium geometries of the As_5S and its charged species are shown in Fig. 5. For neutral As_5S, five isomers are presented. The potential surfaces of the As_6 clusters are very shallow, and two types of *benzvalene* form and *trigonal prism* compete with each other for the ground-state structure [3]. So the two types in the geometry optimization process were taken into account. The C_s-symmetry structure **5(a)** of $^2A''$ state can be considered as the *benzvalene* form of As_6 by replacing the As atom with a S atom. The C_s-symmetry structure **5(c)** of $^2A'$ state can be considered as the *trigonal prism* of As_6 by replacing an As atom with a S atom. The C_s-symmetry structure **5(b)** of $^2A''$ state can be viewed as being derived from the ground-state *square pyramid* of As_5^+ [3, 7] by edge-bridging of square base with a S atom. The C_s-symmetry isomer **5(d)** of $^2A'$ state can be viewed as being derived from the ground-state *distorted trigonal bipyramid* of As_5 [2, 3, 7] by apex-connecting with a S atom, respectively. The C_s-symmetry structure **5(e)** of $^2A''$ state can be regarded as the ground-state *pentagonal* geometry of As_5^- [2, 3, 7] by edge-bridging with a S atom. Energetically, the ground-state structure **5(a)** is more stable than isomers **5(b)**, **5(c)**, **5(d)**, and **5(e)** by 0.40, 0.45, 0.71, and 0.96 eV, respectively. The two S–As bond distances of ground-state **4(a)** are respetively 2.202 and 2.253 Å, and the six As–As bond distances range from 2.414 to 2.492 Å.

For negatively charged ion As_5S^-, five isomers are also presented. The geometry **5(f)**, corresponding to neutral **5(d)**, is predicted to be the ground-state structure with C_s symmetry and $^1A'$ state. It is interesting to note that sulfur is incorporated in this ground-state structure as a terminal atom on two-fold coordinated As of As_5. The isomers **5(g)** and **5(h)**, corresponding respectively to neutral **5(c)** and **5(e)**, possess C_s symmetry with $^1A'$ state. Energetically, they are only less stable than the ground-state structure **5(f)** by 0.06 and 0.11 eV, respectively, indicating the potential surfaces of the As_5S^- species are very shallow. Attaching an electron to the neutral **5(a)** results in an anionic As_5S^- with C_s symmetry and $^1A'$ state, which is a saddle point on the potential surface on account of having an imaginary a'' frequency of 37 cm^{-1}. It undergoes John-Teller distortion to give the C_1-symmetry structure **5(i)**. The isomer **5(j)**, corresponding to neutral

5(b), displays C_s symmetry with $^1A'$ state. Energetically, the isomers **5(i)** and **5(j)** are higher than the ground-state **5(f)** by 0.23 and 0.52 eV, respectively. The bond distances of ground-state **5(f)** are calculated to be 2.117 Å for exclusive S–As bond, 2.448–2.551 Å for seven As–As bonds.

For positively charged ion As_5S^+, five isomers are also presented. The global minimum for As_5S^+ is predicted to be C_s symmetry structure **5(k)** of $^1A'$ ground state, which can be considered as being derived from ground-state *square pyramid* of As_5^+ [3, 7] by edge-bridging in the base of the *square pyramid* with a S atom. Both isomers **5(l)** and **5(m)**, corresponding respectively to neutral **5(a)** and **5(c)**, have C_s symmetry with $^1A'$ state. The isomer **5(n)**, corresponding to neutral **5(d)**, displays C_{2v} symmetry with $^1A_1$ state. Attaching an electron to the neutral **5(e)** results in a cationic As_5S^+ with C_s symmetry and $^1A'$ state, which is a saddle point on the potential surface on account of having an imaginary a'' frequency of 155 cm^{-1}. It undergoes John-Teller distortion to give finally the C_s-symmetry structure **5(o)** of $^1A'$ state. Energetically, the isomers **5(l)**, **5(m)**, **5(n)** and **5(o)** are higher than the ground-state **5(k)** by 0.29, 0.40, 0.56 and 0.66 eV, respectively. The bond distances of ground-state **5(f)** are calculated to be 2.216 Å for two equal S–As bonds, 2.391–2.603 Å for seven As–As bonds.

From the discussion above, we can see that the ground-state structures of the As_5S, As_5S^-, and As_5S^+ are different from each other.

As_6S and its charged molecules

Three minimal structures for neutral As_6S, three for anionic As_6S^-, and three for cationic As_6S^+ are shown in Fig. 6. The global minimum for neutral can be predicted to be structure **6(a)** with C_{2v} symmetry and $^1A_1$ ground state, which can be considered as being derived from not only the *trigonal prism* of As_6 [3, 9] by edge-bridging with a S atom but also the ground-state structure of As_7 by replacing an As atom with a S atom. Both isomers **6(b)** and **6(c)** with C_s symmetry and $^1A'$ state can be viewed as being derived from the benzalene form and trigonal prism of As_6 [3, 9] by edge-bridging with a S atom, respectively. Energetically, the **6(a)** structure is more stable than the **6(b)** and the **6(c)** by 0.30 and 0.31 eV, respectively. The bond distances of ground-state **6(a)** are calculated to be 2.216 Å for two equal S–As bonds, 2.432–2.508 Å for eight As–As bonds.

For negatively charged ion As_6S^-, the global minimum is predicted to structure **6(d)** with C_s symmetry and $^2A''$ ground state. Compared with the ground-state structure of the neutral As_6S, the largest change is an As–As bond breaking in As_6S^-. The isomers **6(e)** and **6(f)**, corresponding respectively to neutral **6(c)** and **6(b)**, display C_s symmetry with $^1A'$ state. Energetically, they are less stable than the ground-state structure **6(d)** by 0.56 and 0.69 eV, respectively. The bond
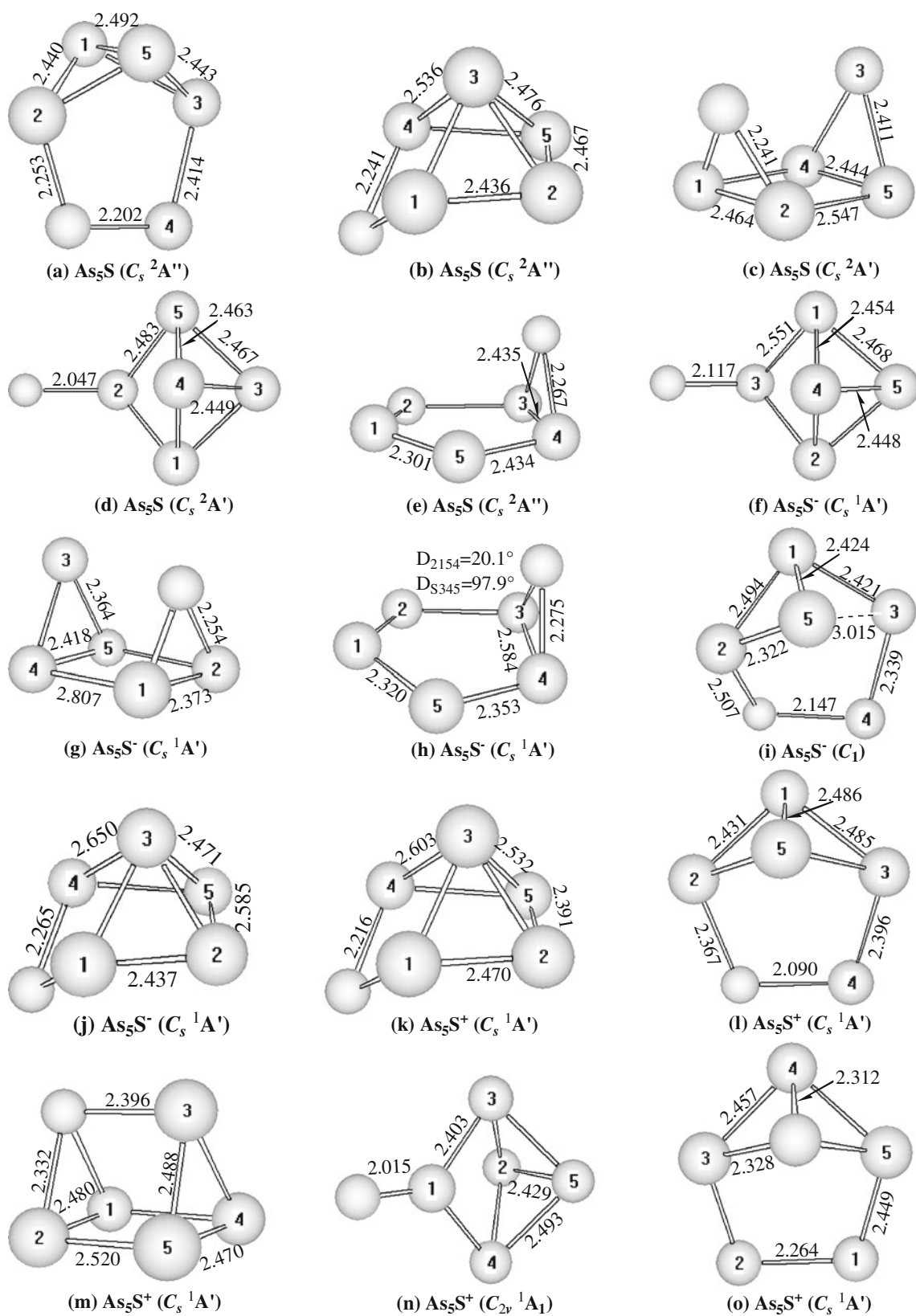
Fig. 5 Geometries of neutral As$_5$S and its charged species optimized at MP2(full)/6-31G(d) level. Only arsenic atoms are numbered. The bond lengths are in angstrom. The bond angles and dihedral angles are in angstrom and degree
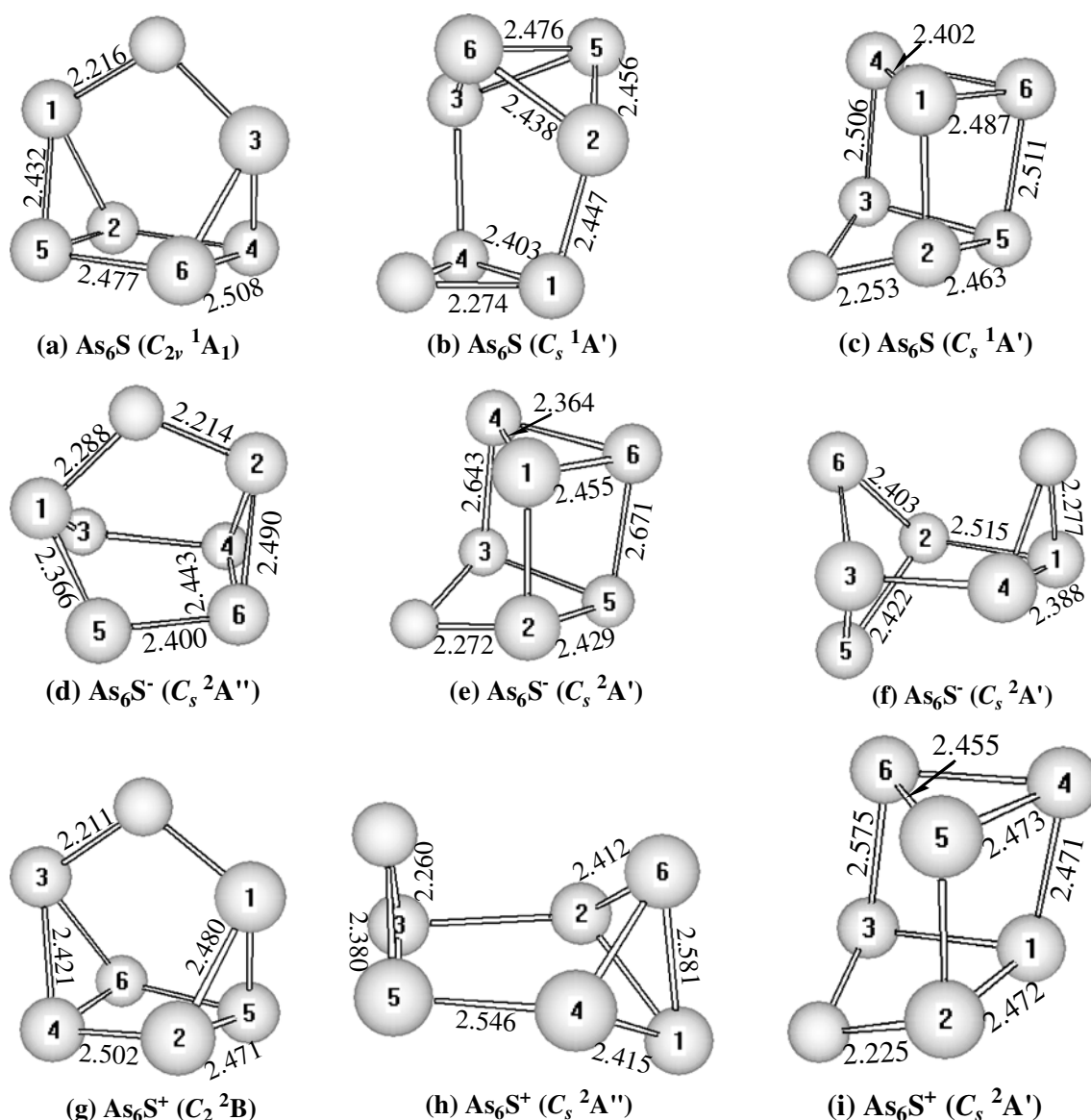
Fig. 6 Geometries of neutral As_6S and its charged species optimized at MP2(full)/6-31G(d) level. Only arsenic atoms are numbered. The bond lengths are in angstrom

distances of ground-state **6(d)** are calculated to be 2.214 and 2.288 Å for two S–As bonds, 2.366–2.490 Å for seven As–As bonds.
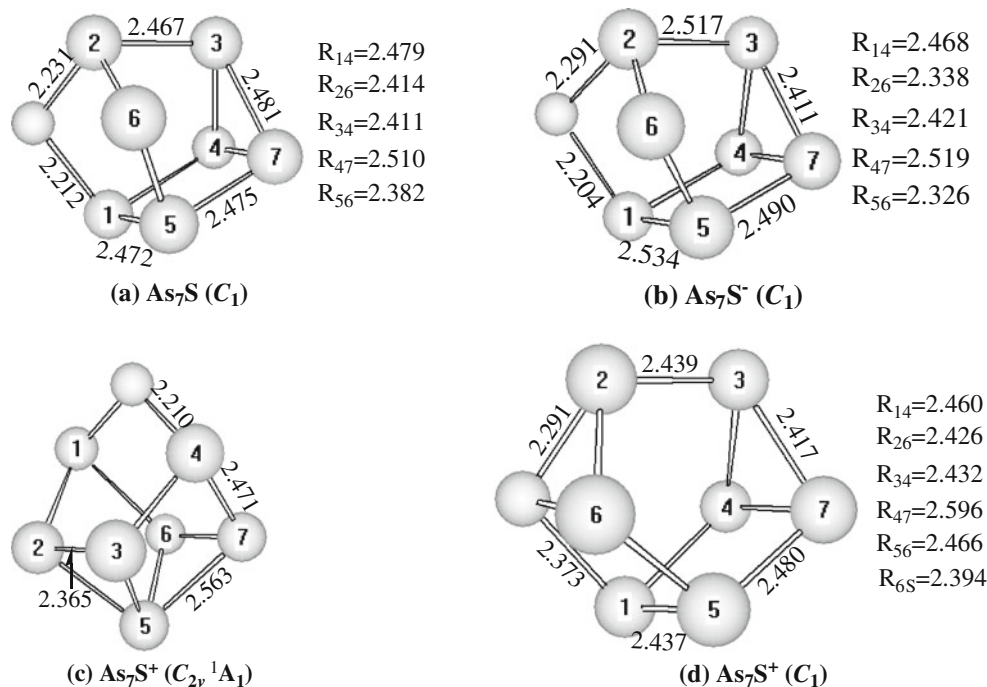
For positively charged ion As_6S^+, the global minimum is predicted to structure **6(g)** with C_2 symmetry and ^2B ground state. The isomers **6(h)** and **6(i)**, corresponding to neutral **6(b)** and **6(c)**, have C_s symmetry with $^2A''$ and $^2A'$ state, respectively. Energetically, they are less stable than the ground-state structure **6(g)** by 0.16 and 0.17 eV, respectively. The bond distances of ground-state **6(g)** are calculated to be 2.211 Å for two equal S–As bonds, 2.421–2.502 Å for eight As–As bonds.

The ground-state structures of As_6S, As_6S^-, and As_6S^+ are somewhat different from each other.

As_7S and its charged molecules

One minimum for neutral As_7S, one for anionic As_7S^-, and two for cationic As_6S^+ are shown in Fig. 7. The ground-state structures of neutral As_7S and its anion are predicted to be C_1-symmetry geometries of **7(a)** and **7(b)**, respectively. Both can be regarded as being derived from the ground-state *wedgelike* structure of As_8 (and/or As_8^-) [9] by replacing an As atom with a S atom. The ground-state structure **7(c)** of As_7S^+ is predicted to be C_{2v} symmetry with $^1A_1$ state. It can be viewed as the ground-state structure of As_7^+ by edge-bridging with a S atom. The C_1-symmetry isomer **7(d)**, corresponding to neutral **7(a)**, is higher 0.84 eV in energy than the **7(c)**. The ground-state structure of cationic As_7S^+ differs from that of

Fig. 7 Geometries of neutral As₇S and its charged species optimized at MP2(full)/6-31G(d) level. Only arsenic atoms are numbered. The bond lengths are in angstrom

(a) As₇S (C_1)

$R_{14}=2.479$
$R_{26}=2.414$
$R_{34}=2.411$
$R_{47}=2.510$
$R_{56}=2.382$

(b) As₇S⁻ (C_1)

$R_{14}=2.468$
$R_{26}=2.338$
$R_{34}=2.421$
$R_{47}=2.519$
$R_{56}=2.326$

(c) As₇S⁺ (C_{2v} $^1A_1$)

(d) As₇S⁺ (C_1)

$R_{14}=2.460$
$R_{26}=2.426$
$R_{34}=2.432$
$R_{47}=2.596$
$R_{56}=2.466$
$R_{6S}=2.394$

the neutral and/or the anion. The bond distances of the neutral ground-state structure are calculated to be 2.212 and 2.231 Å for two S–As bonds, 2.382–2.510 Å for nine As–As bonds. The bond distances of the anionic ground-state structure are evaluated to be 2.204 and 2.291 Å for two S–As bonds, 2.326–2.534 Å for nine As–As bonds. The bond distances of the cationic ground-state structure are calculated to be 2.210 Å for two equal S–As bonds, 2.365–2.563 Å for ten As–As bonds.

From the discussion above we can conclude that the ground-state structures of As$_n$S can be considered as the lowest-energy structure of neutral As$_{n+1}$ by replacing an As atom with a S atom, that is, "substitutional structure", in which the feature of sulfur bonding is edge-bridging. The global minima of As$_n$S⁺ tend to be derived from the lowest-energy structure of cation As$_n$⁺ by attaching to a S atom, that is, "attaching structure", in which the feature of sulfur bonding is either edge- or face-bridging (for example, As₃S⁺). There is no rule to be found for the ground state structure of anion As$_n$S⁻, in which the feature of sulfur bonding is either edge-bridging or a terminal atom (for instance, As₅S⁻). The reason can be explained as follows. The sulfur has four 3p electrons and a lone pair of 3s electrons, i.e., with a coordination number of two the octet rule is fulfilled. Therefore, in As$_n$S the sulfur bonding is edge-bridging. In As$_n$S⁻ if sulfur gains an electron resulting in coordination number of one the octet rule is met, then sulfur bonding can be a terminal atom. In As$_n$S⁺ if sulfur loses an electron resulting in coordination number of three the octet rule is fulfilled, then sulfur bonding can be face-capped. Of course, if arsenic in As$_n$S⁺ (or As$_n$⁺)

loses an electron resulting in four electrons in its outermost shell (arsenic has three 4p electrons and a lone pair of 4s electrons, i.e., with a coordination number of three the octet rule is met.), then arsenic can be four-fold coordinated (for example, the As atom numbered 3 in As₅S⁺ (**5(k)**)).

Electron affinity and ionization potential

The adiabatic electron affinity (AEA) (defined as the difference of total energies in the manner AEA = E (the ground-state structure of neutral) − E (the ground-state structure of anion)) of As$_n$S species was evaluated at the G3 level of theory. The ZPVE-corrected AEAs were calculated to be 1.73 eV for AsS, 1.57 eV for As₂S, 2.37 eV for As₃S, 1.64 eV for As₄S, 2.35 eV for As₅S, 1.87 eV for As₆S, and 3.07 eV for As₇S. To facilitate comparison, Fig. 8 sketched the AEAs of As$_n$S and As$_n$ clusters as a function of the size of the compounds. From Fig. 8 we can see that (i) the odd-even alternation in AEAs is unchanged when S atom is bound to As$_n$ clusters. That is, the AEAs of As$_n$S species are larger when n is odd, and are smaller when n is an even number. This odd-even alternation may be readily explained. With odd n, As$_n$S clusters possess an open shell electronic structure. When they gain an electron, the electronic structures change to a closed shell, where the electronic repulsions are minimized according to the Pauli exclusion principle [49] (except for AsS⁻ species, its ground state is triplet). With an even n, As$_n$ possesses a closed shell electronic structure. The situation is the opposite. So the AEAs are smaller. (ii) The AEAs of

Fig. 8 The AEA and the AIP versus the number of atoms n for As$_n$S and As$_n$ species. The AEA and AIP of As$_n$ clusters are taken from ref [3]
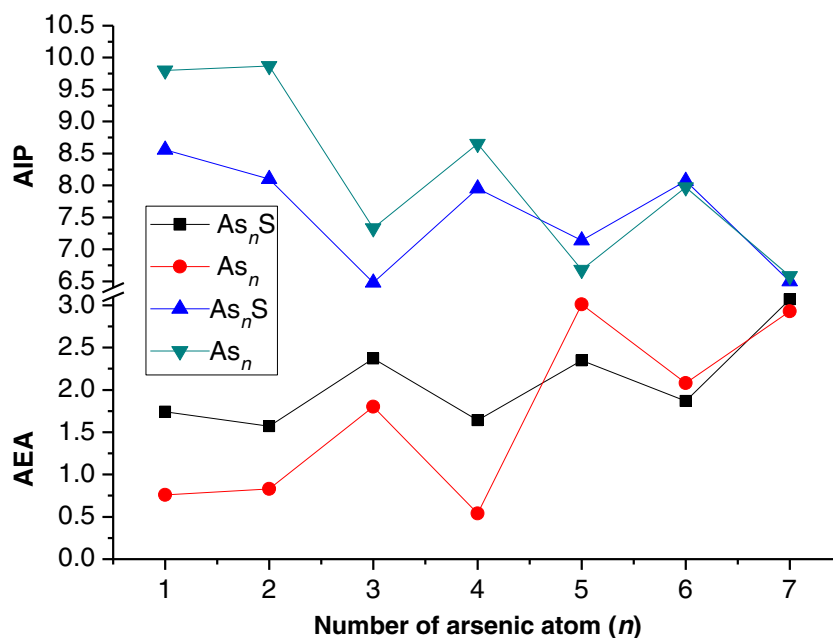
As$_n$S are smaller than those of As$_n$ with $n=5$ and 6. There are no experimental values for comparison.

The adiabatic ionization potential (AIP) (defined as the difference of total energies in the manner AIP $= E$ (the ground-state structure of cation) $- E$ (the ground-state of neutral) of As$_n$S clusters were calculated at the G3 level of theory). The ZPVE-corrected AIPs were estimated to be 8.56 eV for AsS, 8.10 eV for As$_2$S, 6.48 eV for As$_3$S, 7.95 eV for As$_4$S, 7.14 eV for As$_5$S, 8.07 eV for As$_6$S, and 6.50 eV for As$_7$S. To facilitate comparison, the AIPs of As$_n$S and As$_n$ as a function of the size of the compounds were also exhibited in Fig. 8. Similarly to AEAs, the odd-even alternations in AIPs are unaltered when S atom is bound to As$_n$ species with the exception of $n=1$. But the AIPs of As$_n$S species are smaller when n is odd, and are larger when n is an even number. The reason as mentioned above is that As$_n$S is a closed shell electronic structure when n is an even number. It is more stable than that of an open shell electronic structure. In other words, for species of open shell electronic structure, it is easier to remove an electron than for those of closed shell electronic structure. There are no experimental values for comparison.

Dissociation energy

The energies of S (and/or its ion S$^{(-/+)}$) from As$_n$S clusters and their ions were calculated and listed in Table 1. From Table 1 we can see that (i) for neutral As$_n$S ($n=1$–7), the DEs (defined as DE $= E$(S) $+ E$(As$_n$) $- E$(As$_n$S)) were estimated to be 3.94, 2.72, 3.44, 2.47, 3.53, 3.97, and 3.62 eV, respectively. Unlike in AEAs and in AIPs, in DEs there are no odd-even alternations. (ii) For anionic As$_n$S$^-$, two types of DEs were

presented. One is the As$_n$S$^- \rightarrow$ S $+$ As$_n^-$, and other is As$_n$S$^- \rightarrow$ S$^- +$ As$_n$. The DEs for the former are larger than those of the latter for $n=1$–4, approximately equal for $n=6$, and smaller for $n=5$ and 7. The reason can be explained as follows. The EA of S atom (2.07 eV at the G3 level) is larger than the EA of As (0.76 eV at the G3 level), As$_2$ (0.83 eV [3]), As$_3$ (1.80 eV [3]), and As$_4$ (0.54 eV [3]), close to the EA of

Table 1 DEs of S, S$^-$ and S$^+$ from As$_n$S ($n=1$–7) and their ions[a]

Dissociation	DE	Dissociation	DE
AsS$^- \rightarrow$ S $+$ As$^-$	4.94	AsS$^- \rightarrow$ S$^- +$ As	3.61
As$_2$S$^- \rightarrow$ S $+$ As$_2^-$	3.46	As$_2$S$^- \rightarrow$ S$^- +$ As$_2$	2.23
As$_3$S$^- \rightarrow$ S $+$ As$_3^-$	4.02	As$_3$S$^- \rightarrow$ S$^- +$ As$_3$	3.75
As$_4$S$^- \rightarrow$ S $+$ As$_4^-$	3.56	As$_4$S$^- \rightarrow$ S$^- +$ As$_4$	2.04
As$_5$S$^- \rightarrow$ S $+$ As$_5^-$	2.86	As$_5$S$^- \rightarrow$ S$^- +$ As$_5$	3.81
As$_6$S$^- \rightarrow$ S $+$ As$_6^-$	3.75	As$_6$S$^- \rightarrow$ S$^- +$ As$_6$	3.78
As$_7$S$^- \rightarrow$ S $+$ As$_7^-$	3.75	As$_7$S$^- \rightarrow$ S$^- +$ As$_7$	4.61
AsS$^+ \rightarrow$ S $+$ As$^+$	5.19	AsS$^+ \rightarrow$ S$^+ +$ As	5.65
As$_2$S$^+ \rightarrow$ S $+$ As$_2^+$	4.50	As$_2$S$^+ \rightarrow$ S$^{++} +$ As$_2$	4.89
As$_3$S$^+ \rightarrow$ S $+$ As$_3^+$	4.32	As$_3$S$^+ \rightarrow$ S$^+ +$ As$_3$	7.23
As$_4$S$^+ \rightarrow$ S $+$ As$_4^+$	3.17	As$_4$S$^+ \rightarrow$ S$^+ +$ As$_4$	4.79
As$_5$S$^+ \rightarrow$ S $+$ As$_5^+$	3.07	As$_5$S$^+ \rightarrow$ S$^+ +$ As$_5$	6.66
As$_6$S$^+ \rightarrow$ S $+$ As$_6^+$	3.86	As$_6$S$^+ \rightarrow$ S$^+ +$ As$_6$	6.17
As$_7$S$^+ \rightarrow$ S $+$ As$_7^+$	3.70	As$_7$S$^+ \rightarrow$ S$^+ +$ As$_7$	7.39
AsS $\rightarrow$ S $+$ As	3.94	As$_2$S $\rightarrow$ S $+$ As$_2$	2.75
As$_3$S $\rightarrow$ S $+$ As$_3$	3.49	As$_4$S $\rightarrow$ S $+$ As$_4$	2.52
As$_5$S $\rightarrow$ S $+$ As$_5$	3.57	As$_6$S $\rightarrow$ S $+$ As$_6$	4.02
As$_7$S $\rightarrow$ S $+$ As$_7$	3.68		

[a] The values are corrected with ZPVE and in eV

As$_6$ (2.06 eV [3]), and smaller the EA of As$_5$ (3.01 eV [3]) and As$_7$ (2.93 eV [3]). (iii) For cationic As$_n$S$^+$, two types of DEs were also reported. One is the As$_n$S$^+ \rightarrow$ S + As$_n^+$, and the other is As$_n$S$^+ \rightarrow$ S$^+$+As$_n$. The DEs of S are smaller than the DEs of S$^+$. That is, the As$_n$S$^+$ prefer to dissociate S and As$_n^+$ rather than to dissociate S$^+$ and As$_n$, because the AIP of S atom is larger than that of As$_n$. The AIPs of S atom are 10.27 eV at the G3 level. The AIPs of As$_n$ ($n = 1$–7) are respectively 9.80, 9.87, 7.33, 8.65, 6.68, 7.97, and 6.58 eV at the G3 level (ref 3). (iv) As expected, the ground-state structures for As$_n$S and their ions are predicted to be stable with respect to As–S bond breaking, because the minimal DEs are 2.04 eV.

Conclusions

The structures and energies of neutral and charged arsenic sulfides As$_n$S$^{(-1,0,+1)}$ ($n = 1$–7) have been systematically investigated with the G3 scheme. The bonding properties and the stabilities of As$_n$S and their ions have been discussed. The AEAs and AIPs have been calculated. The results can be summarized as follows: (i) the ground-state structures of As$_n$S can be considered as the lowest-energy structure of neutral As$_{n+1}$ by replacing an As atom with a S atom, that is, "substitutional structure", in which the feature of sulfur bonding is edge-bridging. The global minima of As$_n$S$^+$ tend to be derived from the lowest-energy structure of cation As$_n^+$ by attaching to a S atom, that is, "attaching structure", in which the sulfur can be three-fold coordinated. There is no rule to be found for the ground state structure of anion As$_n$S$^-$, in which the sulfur can be a terminal atom. (ii) The reliable AEAs of As$_n$S were estimated to be 1.73 eV for AsS, 1.57 eV for As$_2$S, 2.37 eV for As$_3$S, 1.64 eV for As$_4$S, 2.35 eV for As$_5$S, 1.87 eV for As$_6$S, and 3.07 eV for As$_7$S. And the reliable AIPs were evaluated to be 8.56 eV for AsS, 8.10 eV for As$_2$S, 6.48 eV for As$_3$S, 7.95 eV for As$_4$S, 7.14 eV for As$_5$S, 8.07 eV for As$_6$S, and 6.50 eV for As$_7$S. There are odd-even alternations in both AEAs and AIPs as a function of size of As$_n$S. (iii) The theoretical values of DEs revealed that the As$_n$S$^+$ prefer to dissociate S and As$_n^+$ rather than to dissociate S$^+$ and As$_n$. The As$_n$S$^-$ prefer to dissociate S$^-$ and As$_n$ rather than to dissociate S and Asn^- for $n = 1$–4, but prefer to dissociate S and As$_n^-$ rather than to dissociate S$^-$ and As$_n$ for $n = 5$ and 7. The ground-state structures for As$_n$S and their ions are predicted to be stable with respect to As–S bond breaking, as expected. To the best of our knowledge, there are no experimental data and other theoretical results regarding the AEAs, AIPs, and DEs for As$_n$S system. We hope that our predictions will provide strong motivation for further experimental investigation of these important arsenic sulfides species.

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