

Probing the electronic structures and properties of neutral and charged arsenic sulfides $[\text{As}_n\text{S}_2^{(-1,0,+1)}]$, $n=1-6$ with Gaussian-3 theory

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Abstract The structures and energies of neutral and charged arsenic sulfides $\text{As}_n\text{S}_2^{(-1,0,+1)}$ ($n=1-6$) were investigated systematically by means of the Gaussian-3 (G3) scheme. The ground-state structures of these species are presented. The ground-state structures of As_nS_2 can be viewed as the lowest-energy structure of neutral As_{n+1}S by replacing an As atom with a S atom. To be more precise, the ground-state structures of As_nS_2 can be viewed as the lowest-energy structure of neutral As_{n+2} by replacing two As atoms with two S atoms, in which the feature of sulfur bonding is edge-bridging. No rule could be found for the ground state structure of As_nS_2^- and As_nS_2^+ . In As_nS_2^- , the feature of sulfur bonding is either edge-bridging or a terminal atom, and in As_nS_2^+ the feature of sulfur bonding is edge-bridging analogous to As_nS_2 . The potential energy surfaces of As_4S_2 and its charged species are very flat. So co-existence for many isomers of As_4S_2 and its charged species are possible. The reliable adiabatic electron affinities (AEAs) and adiabatic ionization potentials (AIPs) of As_nS_2 were estimated. There are odd-even alternations in both AEAs and AIPs as a function of size of As_nS_2 . The dissociation energies (DEs) of S [and/or its ion $\text{S}^{(-/+)}$] from As_nS_2 clusters and their ions were calculated and used to reveal relative stability.

Keywords Arsenic sulfides · Ground-state structure · Electron affinity · Ionization potential · Dissociation energy

Introduction

During the past two decades, arsenic and its compounds have attracted a lot of attention due to their use as pigments and components to modify the mechanical properties of lead and copper alloys [1–14]. Wide application of their unique electronic, magnetic, optical, mechanical, and pharmacological properties in such fields as semiconductors, optoelectronics, and bio-pharmaceutics is well known. Arsenic and its compounds are one of the most toxic and carcinogenic species, raising a very important environmental issue [15]. For instance, arsenic contamination of groundwater has led to massive epidemics of arsenic poisoning in such areas as South and South East Asia [16]. The ions of arsenic attack the –SH groups present in enzymes and alter their functions. Therefore, arsenic concentrations in the environment are controlled by strict guidelines [17].

Arsenic sulfides are found as naturally occurring minerals. They play an important role in the field of novel functional optical materials due to their distinctive characteristics such as broad transparency in the near and far infrared spectra region, high refractive indices, and excellent photochemical sensitivity [18–22]. For example, they are used as infrared sensors, optical fibers, p–n junctions, and photoresists in optical and ultraviolet lithography, optical memory devices, switches, modulators and optical computing [23–27]. There have been some previous studies on arsenic sulfides. On the experimental side, pulsed laser ablation and time-of-flight mass spectrometry was used to identify the formation of arsenic sulfide clusters such as AsS_n ($n=1-8$), As_2S_n ($n=1-7$), As_3S_n ($n=1-7$), As_4S_n ($n=3,4$), As_3S_n^+ ($n=1-4$), and AsS_n^+ ($n=1-7$) species [17, 21, 25]. X-ray diffraction, Raman, and/or infrared

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spectroscopy was employed to monitor the photoinduced transformation of arsenic-sulfur clusters in the realgar form to pararealgar [22, 28–31]. The infrared, Raman, and/or UV-visible spectra of As_2S_2 , As_2S_3 , As_2S_5 , As_4S_3 , As_4S_4 , As_4S_6 , As_6S_9 , and As_8S_9 were measured and compared with theoretical calculated spectra [32–37]. Mass spectrometric and vapor pressure techniques was applied to investigate the nature of sublimation processes of As_2S_3 and As_4S_4 [38–43]. On the theoretical side, Banerjee et al. [24] studied the structure, bonding, electron distribution, normal mode frequencies and the corresponding vibrational assignments of tetrasenic tetrasulfide (As_4S_4) using the HF, MP2 and B3LYP methods and the 6-311G(d) basis set. Babić et al. [44, 45] performed local-density pseudopotential calculations for As_4S_4 , As_4S_5 , and As_4S_6 , and found that the As–As bonds in As_4S_4 and As_4S_5 are the main reason for the stability of these species, and the charge density of As–S bonds have excellent transferability. Recently, we [2, 5] calculated the structures and energies of neutral and charged $\text{As}_n^{(-1,0,-1)}$ ($n \leq 8$) and $\text{As}_n\text{S}^{(-1,0,+1)}$ ($n=1-7$), discussed the bonding properties and the stabilities, and presented the adiabatic electron affinities (AEAs) and adiabatic ionization potentials (AIPs) using the Gaussian-3 (G3) method.

This report focuses on neutral and charged $\text{As}_n\text{S}_2^{(-1,0,+1)}$ ($n=1-6$) in the gas phase. The objective of this research involves (1) predictions of the ground state structures of neutral As_nS_2 ($n=1-6$) and their charged species; (2) predictions of AEAs and AIPs of As_nS_2 ; (3) evaluation of other properties including dissociation energies (DEs); and (4) continuation of previous work on arsenic clusters [2–5]. The information gained on these properties and structures may provide the required theoretical guidance for the design and synthesis of novel functional materials of arsenic sulfides. In addition, both EA and IP are the key spectroscopic values and vitally important for use in the chemical cycle to determine bond dissociation energies. A knowledge of 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 method used in this paper is the G3 scheme [46, 47], which provides accurate energies of molecular systems for calculation of IPs, EAs, and atomization energies (AEs). The mean absolute deviation from experiment for 188 (23 for AEs, 63 for EAs, and 102 for IPs) reactions are $1.05 \text{ kcal mol}^{-1}$ [46, 47]. Recently, we predicted the EAs, IPs, and DEs of As_n and Si_n clusters using the G3 method. The mean absolute error from experiments involving 21 reactions is only 0.05 eV [5, 48, 49].

Computational methods

All calculations using the extension of G3 theory [46, 47] were performed using the Gaussian 09 package [50]. The G3

theory is a composite technique in which geometry optimization is carried out at the MP2(full)/6-31G(d) level. The energies, a series of single-point energy calculation at the levels of QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(full)/G3large, are calculated. These energies are then modified by a series of corrections. Finally, the HF/6-31G(d) vibrational frequencies, scaled by 0.8929, are applied for zero-point vibrational energy (ZPVE) correction at 0 K [46, 47]. In addition to the HF/6-31G(d) vibrational frequency, MP2(full)/6-31G(d) harmonic frequency analysis for all species reported in this paper was also performed to guarantee that the optimized structure is local minimum.

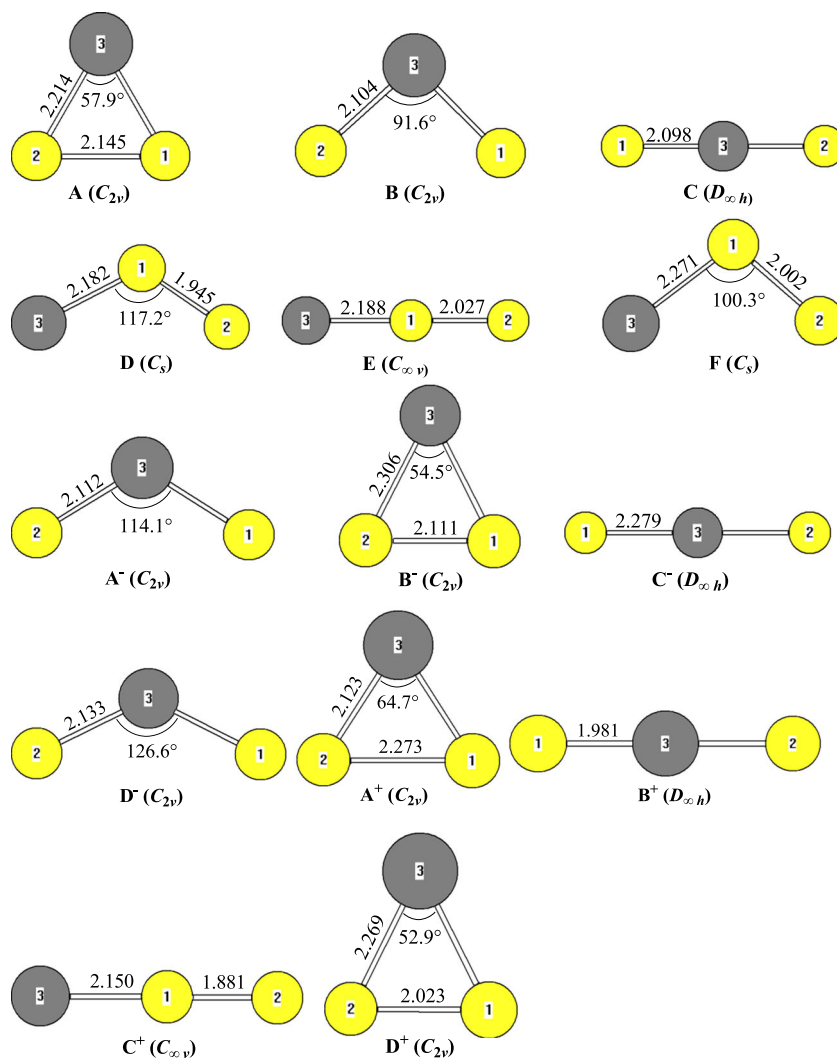
As described previously [2], a large amount of isomers need to be explored to obtain the ground state structure, especially as there are no experimental values for comparison. Consequently, in the optimization process of cluster geometries, we took into account many isomers generated from the following three types: “substitutional structures”, which can be regarded as being derived from the lowest-energy structure of As_{n+1}S ($\text{As}_{n+1}\text{S}^-$ and/or $\text{As}_{n+1}\text{S}^+$) by replacing an As atom with a S atom; “attaching structures”, in which the S atom is connected to various positions on surface or edge or apex of the lowest-energy structure of As_nS (As_nS^- and/or As_nS^+); and the “third type” (our nomenclature), i.e., several structures designed by us. Starting with these structures, we obtained as many of the refined low-lying structures as possible at the B3LYP/6-311+G* level. Then, we refined the energies of the selected low-energy isomer using the G3 scheme. In addition, the spin multiplicities of the singlet, doublet, triplet, and quartet state were taken into account for AsS_2 species.

Results and discussion

AsS_2 and its charged compounds

Six minimal geometries for neutral AsS_2 , four for anionic AsS_2^- , and four for cationic AsS_2^+ are displayed in Fig. 1. For neutral AsS_2 , the ground-state structure is predicted to be isosceles triangle **1A** with C_{2v} symmetry and 2B_1 ground state. The isomer **1B** is also C_{2v} symmetry, but 2B_2 state. It is higher than the structure **1A** by 0.12 eV in energy. Two linear isomers of **1C** and **1E** have $D_{\infty h}$ symmetry with $^2\Sigma_g$ and $C_{\infty v}$ symmetry with $^2\Sigma$ state, respectively. They are less stable than the structure **1A** by 1.23 and 2.62 eV in energy, respectively. The isomer **1D** possesses C_s symmetry with $^2A'$ state. It is higher in energy than the ground-state structure **1A** by 1.60 eV . The lowest lying quartet state is predicted to be bent structure **1F** with C_s symmetry and $^4A'$ electronic state, which is predicted to lie 1.40 eV above the ground-state **1A**. The As–S and S–S bond distances of structure **1A** are calculated to be 2.214 and 2.145 \AA , respectively. Compared with the ground-state

Fig. 1 Geometries of neutral AsS_2 and its charged species optimized at MP2(full)/6-31G(d) level. Sulfur atoms are numbered 1 and 2. The bond lengths and bond angles are in Ångstroms and degrees, respectively



structure of As_2S , the As–S bond distances of the ground-state structure of AsS_2 decrease by 0.096 Å [2].

For anion AsS_2^- , isosceles triangle structures **1A⁻** and **1B⁻** have C_{2v} symmetry with 1A_1 electronic state. Energetically, the lowest-energy structures of obtuse triangle **1A⁻** are more stable than that of acute triangle **1B⁻** by 1.61 eV. The $D_{\infty h}$ -symmetry linear isomer (**1C⁻**) of the $^1\Sigma_g$ electronic state is higher in energy by 2.29 eV than the lowest-energy structure. The lowest lying triple state is predicted to be isosceles triangle isomer (**1D⁻**) with C_{2v} symmetry and 3B_1 electronic state. Energetically, it is higher by 1.59 eV than the ground-state **1A⁻** structure. Compared with the neutral **1A**, the S–S bonds of the anion **1A⁻** are breaking and the As–S bonds are shortened by 0.102 Å.

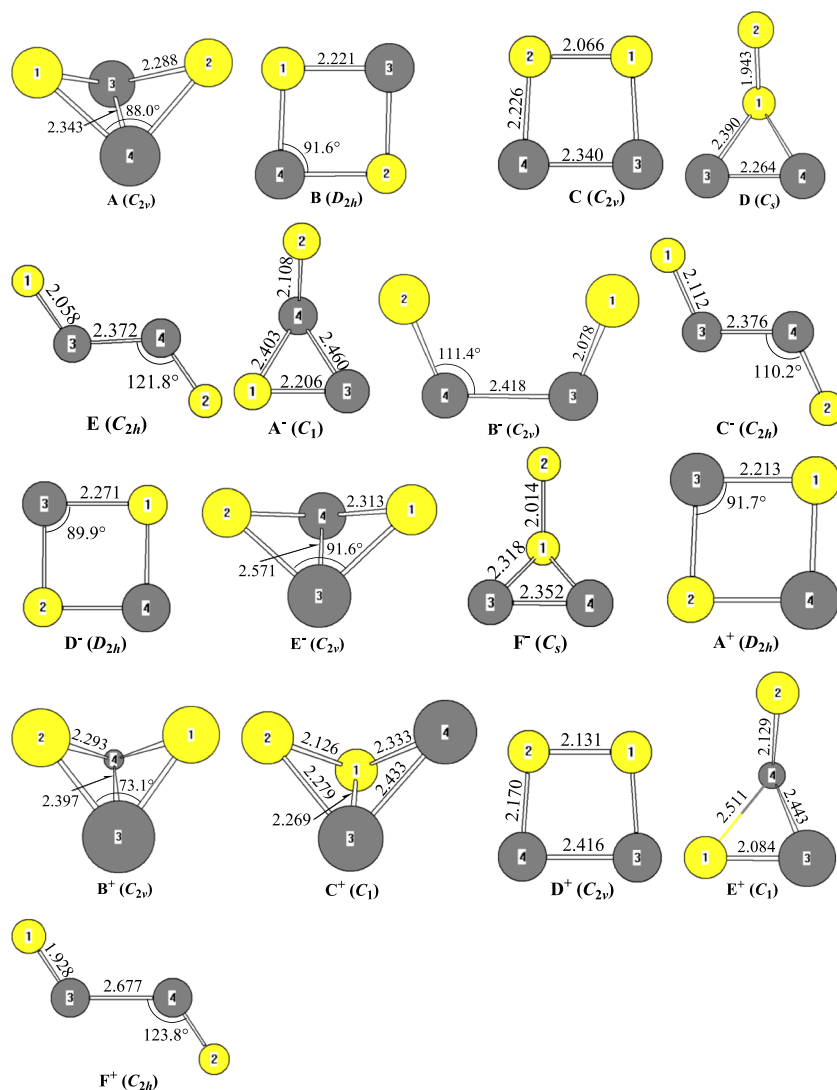
For cation AsS_2^+ , the lowest-energy structure is predicted to be isosceles acute triangle structures **1A⁺** with C_{2v} symmetry and 1A_1 ground state. Two linear isomers of **1B⁺** and **1C⁺** have $D_{\infty h}$ symmetry with $^1\Sigma_g$ and $C_{\infty v}$ symmetry with $^1\Sigma$ state, respectively. They are less stable than the structure **1A⁺** by 0.66 and 1.67 eV in energy, respectively. The lowest lying

triple state is predicted to be isosceles triangle isomer (**1D⁺**) with C_{2v} symmetry and 3B_2 electronic state. Energetically, it is higher 0.38 eV than the ground 1A_1 state. The As–S and S–S bond distances of the lowest-energy **1A⁺** are shorter by 0.091 and 0.034 Å than their neutral counterparts, respectively. The reason is that the orbital occupied by removing electron has antibonding character.

As_2S_2 and its charged compounds

The structures of the As_2S_2 and its charged species are exhibited in Fig. 2. For neutral As_2S_2 , five isomers are reported. The C_{2v} -symmetry structure **2A** of 1A_1 state can be regarded as being derived from not only the isosceles triangle ground-state structure of As_2S [2] by tilted edge-bridging with a S atom but also the V-shapes ground-state structure of As_3S [2] by replacing an As atom with a S atom. The D_{2h} -symmetry **2B** of 1A_g state and the C_s -symmetry **2D** of $^1A'$ state belongs to the “attaching structure”. The C_{2v} -symmetry **2C** of 1A_1 state and the C_{2h} -symmetry **2E** of 1A_g state belongs to “third type”.

Fig. 2 Geometries of neutral As_2S_2 and its charged species optimized at MP2(full)/6-31G(d) level. Sulfur atoms are numbered 1 and 2. The bond lengths and bond angles are in Ångstroms and degrees, respectively



Energetically, the V-shaped **2A** structures are more stable than the **2B**, **2C**, **2D**, and **2E** isomers by 0.22, 0.53, 1.54 and 2.14 eV, respectively. The four equivalent S–As bond distances of the ground-state **2A** are 2.288 Å, and the As–As bond lengths are 2.343 Å.

For anion As_2S_2^- , six isomers are presented. The ground-state structure is predicted to be C_1 -symmetry geometry **2A⁻**, which can be regarded as a tilted attachment of a S atom to an As atom of the ground state structure of As_2S (or As_2S^-) [2], i.e., an “attaching structure”. The isomers **2E⁻** with C_{2v} symmetry and 2B_2 state and **2F⁻** with C_s symmetry and $^2A''$ state are also “attaching structures”. Adding an electron to the neutral **2C** produces an anion As_2S_2^- isomer with C_{2v} symmetry and 2A_2 state. It is a saddle point due to having an imaginary a_2 frequency of $20i \text{ cm}^{-1}$ at the MP2(full)/6-31G(d) level. It undergoes Jahn-Teller distortion to give finally the structure **2B⁻** with C_{2v} symmetry and 2B_1 state. The isomer **2C⁻**, corresponding to neutral **2E**, displays C_{2h} symmetry with 2A_g state. The D_{2h} -symmetry **2D⁻** isomer of $^2B_{3u}$ can

be regarded as not only attaching a S atom to the ground state of As_2S (or As_2S^-) but also replacing an As atom of the ground state of As_3S^- [2] with a S atom. Energetically, the isomers **2B⁻**, **2C⁻**, **2D⁻**, **2E⁻**, and **2F⁻** are less stable than the **2A⁻** structure by 0.38, 0.55, 0.68, 0.75, and 0.87 eV, respectively. Three S–As bond distances of the lowest-energy **2A⁻** are calculated to be 2.108, 2.206, and 2.403 Å, respectively. One As–As bond length is predicted to be 2.460 Å.

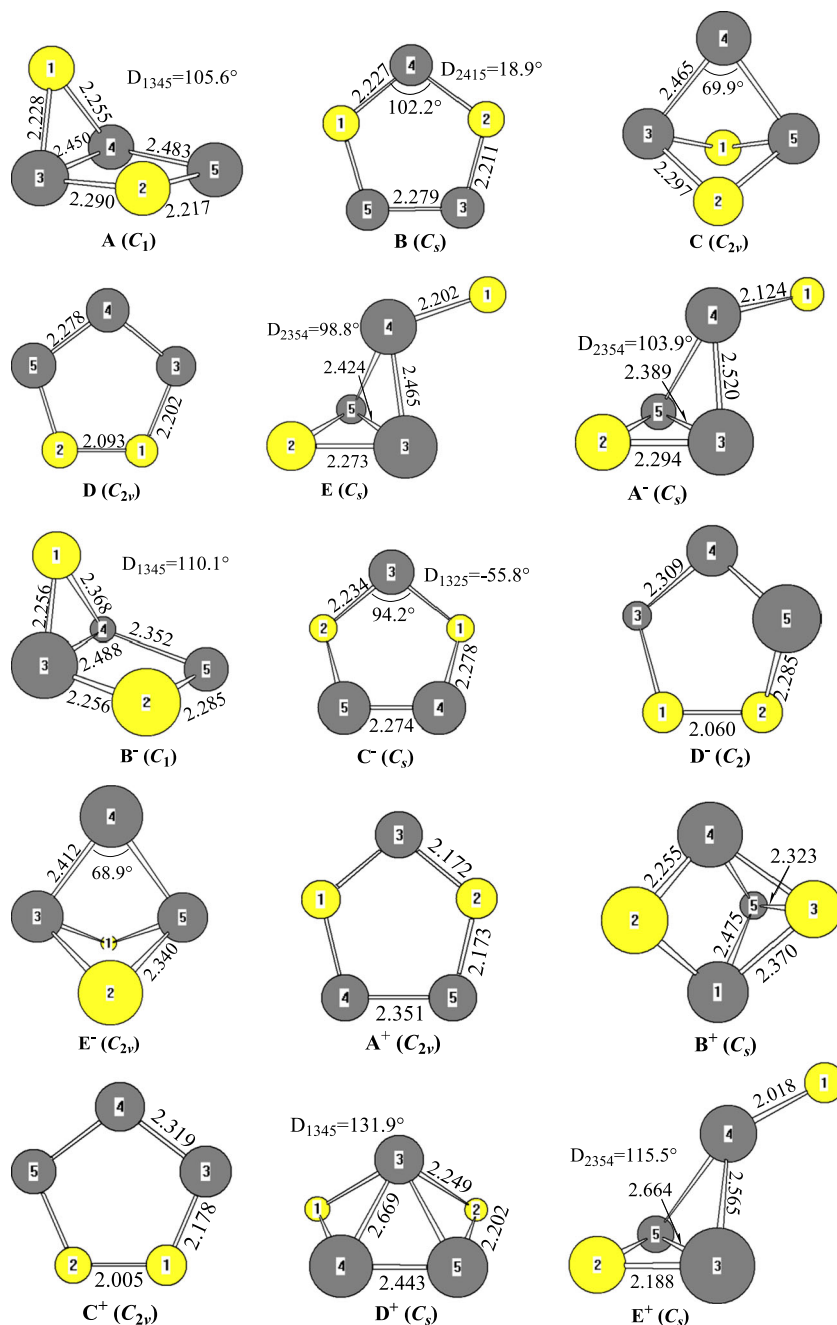
For cation As_2S_2^+ , six isomers are presented. The ground-state structure is approximate square **2A⁺** with D_{2h} symmetry and $^2B_{2g}$ state, which can be regarded as connecting a S atom to the base of isosceles triangle of the ground state structure of As_2S (or As_2S^+) [2]. The ground-state structures of the As_2S_2^+ , As_2S_2^- , and As_2S_2 differ from each other. Both **2B⁺** and **2D⁺** isomers, corresponding respectively to neutral **2A** and **2C**, possess C_{2v} symmetry. But the electronic states are 2B_2 and 2B_1 , respectively. The C_1 -symmetry isomer **2C⁺** can be regarded as replacing an As atom of the ground state tetrahedral structure of As_3S^+ [2] with a S atom. The C_1 -symmetry

isomer $2E^+$ belongs to an “attaching structure”. The isomer $2F^+$, corresponding to neutral $2E$, has C_{2h} symmetry with 2A_u electronic state. Energetically, the isomers $2B^+$, $2C^+$, $2D^+$, $2E^+$, and $2F^+$ are less stable than the most stable structure $2A^+$ by 0.18, 0.36, 0.92, 1.17, and 1.78 eV, respectively. The four equivalent As–S bond distances of the approximate square $2A^+$ are predicted to be 2.213 Å.

As₃S₂ and its charged compounds

The equilibrium geometries of As₃S₂ and its charged species are shown in Fig. 3. For neutral As₃S₂, five isomers are

Fig. 3 Geometries of neutral As₃S₂ and its charged species optimized at MP2(full)/6-31G(d) level. Sulfur atoms are numbered 1 and 2. Bond lengths in Ångstroms; bond angles and dihedral angles in degrees



presented. The C_1 -symmetry geometry $3A$ is predicted to be the ground state structure, which can be regarded as not only attaching a S atom to the edge of the ground state of As₃S [2] but also replacing an As atom of the ground state structure of As₄S [2] with a S atom. Both C_s -symmetry $3B$ of $^2A'$ state and the C_{2v} -symmetry $3D$ of the 2A_2 state can be regarded as replacing an As atom of planar five-membered ring of the As₄S⁻ ground state structure [2] with a S atom. Both C_{2v} -symmetry $3C$ of 2B_1 state and C_s -symmetry $3E$ of $^2A'$ state can be regarded as connecting a S atom to the ground state structure of As₃S [2], that is, an “attaching structure”. Energetically, the isomers $3B$, $3C$, $3D$, and $3E$ are less stable than

the ground state **3A** by 0.16, 0.52, 0.57 and 0.67 eV, respectively. The bond distances of ground-state **3A** are calculated to be 2.217, 2.228, 2.255, and 2.290 Å for four S–As bonds, 2.450 and 2.483 Å for two As–As bonds.

For negatively charged ion As_3S_2^- , five isomers are also presented. The **3A**[−] isomer, corresponding to the neutral **3E**, is predicted to be the ground state structure, which possesses C_s symmetry with ¹A' ground state. It is interesting to note that the S atom labeled 1 is incorporated in this ground-state structure as a terminal atom on the two-fold coordinated arsenic atom labeled 4. The isomers of C_1 -symmetry **3B**[−], C_s -symmetry **3C**[−] of ¹A', and C_{2v} -symmetry **3E**[−] of ¹A₁ correspond respectively to the neutral **3A**, **3B**, and **3C**. Energetically, they are less stable than the lowest-energy **3A**[−] structure by 0.46, 0.63, and 0.86 eV, respectively. Attaching an electron to the neutral **3D** results in an anionic As_3S_2^- with C_{2v} symmetry and ¹A₁ state, which is a saddle point on the potential surface because of having an imaginary a_2 frequency of 136 cm^{−1} at the MP2(full)/6-31G(d) level. Following mode a_2 , it collapses to the C_2 -symmetry structure **4D**[−] of ¹A state. It is less stable than the ground-state structure **3A**[−] by 0.69 eV in energy. The bond distances of the structure **3A**[−] are evaluated to be 2.294 Å for two equivalent S–As bonds, 2.124 Å for another S–As bond, 2.520 Å for two equal As–As bonds, and 2.389 Å for another As–As bond.

For the positively charged ion As_3S_2^+ , five geometries are also presented. The lowest-energy **3A**⁺ structure is predicted to be a planar five-membered ring with C_{2v} -symmetry and ¹A₁ ground state, which can be viewed as being derived from the lowest-energy As_5^- structure [5, 10, 11] by replacing two arsenic atoms with two S atoms. That is, the ground-state structures of the As_3S_2 , As_3S_2^- , and As_3S_2^+ differ from each other. The C_s -symmetry isomer **3B**⁺ of ¹A' state can be regarded as replacing an arsenic atom of the ground state structure of As_4S^+ [2] with a S atom. Energetically, it is less stable than the ground state **3A**⁺ by 0.11 eV. The C_{2v} -symmetry **3C**⁺, C_s -symmetry **3D**⁺, and C_s -symmetry **3E**⁺ isomers correspond to neutral **3B**, **3A**, and **3E**, respectively. They are ¹A₁, ¹A', and ¹A' electronic state, and less stable than the **3A**⁺ by 0.45, 0.49, and 1.39 eV in energy, respectively. The two pairs of equal As–S bond lengths for the lowest-energy **3A**⁺ structure are predicted to be 2.172 and 2.173 Å. The bond distances of As–As are evaluated to be 2.351 Å.

As_4S_2 and its charged compounds

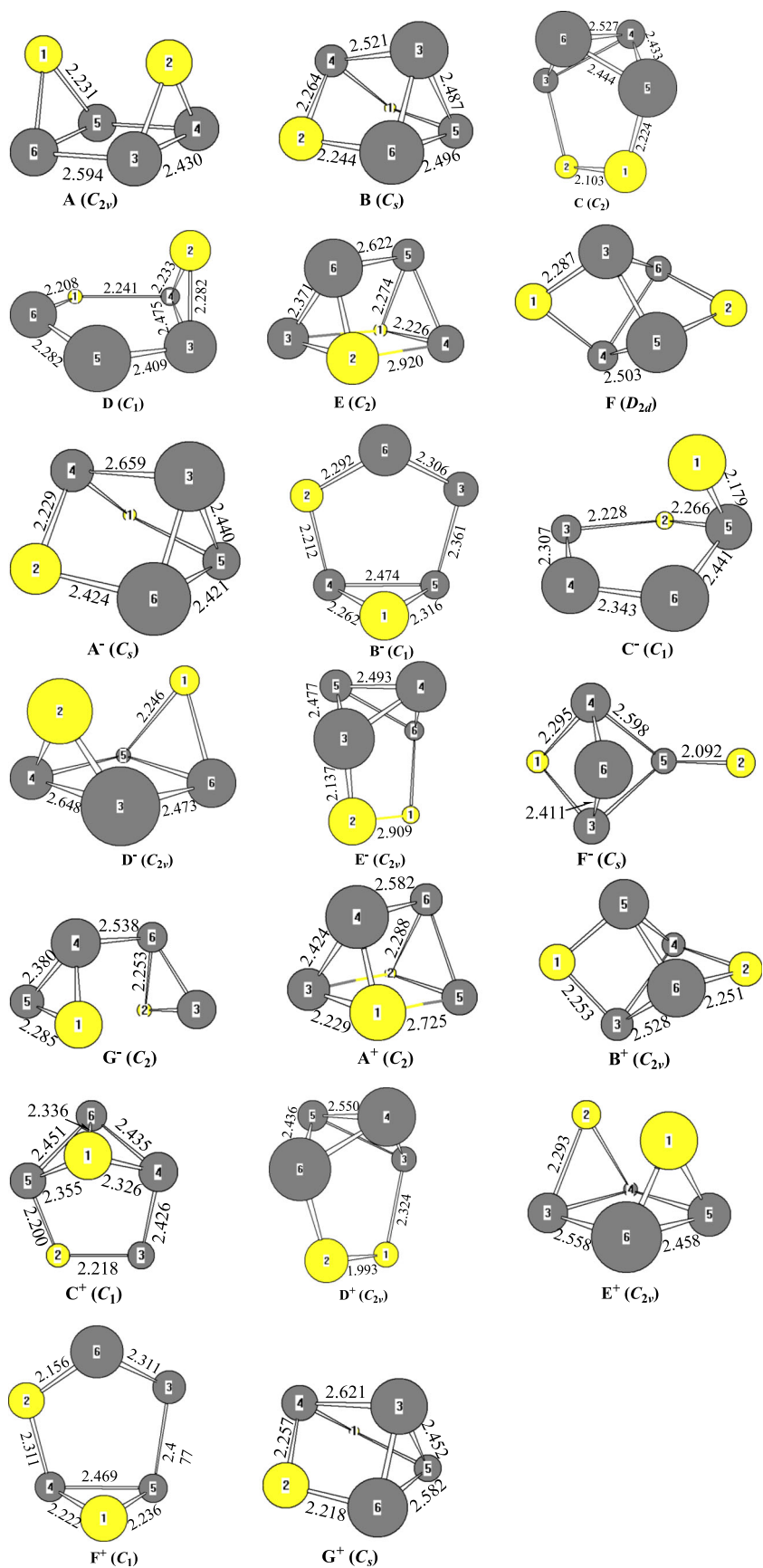
The equilibrium geometries of the As_4S_2 and its charged species are shown in Fig. 4. For neutral As_4S_2 , six isomers are presented. Two types of benzvalene form and trigonal prism for As_6 species compete with each other for the lowest-energy structure because their potential surfaces are very shallow [5, 8, 13]. Hence, the two types in the geometry optimization process were taken into account. Isomers **4A**,

4B, and **4E** can be considered as the trigonal prism of As_6 by replacing two arsenic atoms with two S atoms. They possess C_{2v} , C_s , and C_2 symmetry with ¹A₁, ¹A', and ¹A electronic state, respectively. Energetically, the ground-state **4A** structure is more stable than that of **4B** and **4E** by 0.09 and 0.46 eV, respectively. Both isomers **4C** and **4D** can be considered as the benzvalene form of As_6 by replacing two arsenic atoms with two S atoms (the **4D** isomer can also be considered as attaching a S atom to the bond of the ground state structure of anionic As_4S^- [2]). The C_2 -symmetry **4C** of ¹A state and C_1 -symmetry **4D** isomers are less stable than the ground-state **4A** structure by 0.19 and 0.30 eV in energy, respectively. The D_{2d} -symmetry isomer of ¹A₁ state, **4F**, can be viewed as being derived from the ground state structure of As_4S [2] by edge-attaching with a S atom. It is less stable than that of **4A** by 0.47 eV in energy. The four equal S–As bond distances of the ground-state **4A** are predicted to be 2.231 Å. And the two pairs of equal As–As bond lengths are evaluated to be 2.430 and 2.594 Å, respectively.

For negatively charged ion As_4S_2^- , seven isomers are reported. The C_s -symmetry **4A**[−] of ²A' state and C_1 -symmetry **4B**[−] isomers are nearly identical in energy at the G3 level theory. This indicates that the potential energy surfaces of As_4S_2^- are very flat analogous to that of As_6 [5] and Si_5H^- [51]. Advanced quantum mechanical investigations would be required for accurate predictions of the equilibrium geometries. The **4A**[−] isomers belong to a trigonal prism and the **4B**[−] belongs to the benzvalene form as can be seen from Fig. 4. The C_1 -symmetry **4C**[−] isomer can be regarded as attaching a S atom to an As atom of the ground-state structure of As_4S^- [2]. Both **4D**[−] and **4E**[−] isomers, corresponding to neutral **4A** and **4C**, possess C_{2v} symmetry with ²B₁ and ²B₂ state, respectively. When neutral isomer **4F** obtains an additional electron and becomes negative ion **4F**[−], the As6–S2 bond is broken, and the symmetry changes from C_{2v} to C_s . That is, the S atom labeled 2 is incorporated in this structure as a terminal atom on the two-fold coordinated arsenic atom labeled 5. The electronic state of the **4F**[−] is ²A'. Isomer **4G**[−], corresponding to neutral **4E**, has C_2 symmetry with ²A state. Energetically, these **4C**[−], **4D**[−], **4E**[−], **4F**[−], and **4G**[−] isomers are less stable than that of **4A**[−] (and/or **4B**[−]) by 0.34, 0.39, 0.49, 0.64, and 1.01 eV, respectively. The bond distances of **4A**[−] are calculated to be 2.117 Å for a pair of equal S–As bond lengths, 2.421, 2.424, and 2.440 Å for three pairs of equal As–As bond lengths, and 2.659 Å for another As–As bond lengths. The ranges of bond distances of **4B**[−] are 2.212–2.316 Å for four S–As bonds and 2.306–2.474 Å for three As–As bonds.

For the positively charged ion As_4S_2^+ , seven isomers are also presented. The lowest-energy structure **4A**⁺, corresponding to neutral **4E**, is predicted to be C_2 symmetry with ²B ground state. Isomer **4B**⁺, corresponding to neutral **4F**, displays C_{2v} symmetry with ²B₁ electronic state. Both isomers **4C**⁺ and **4D**⁺ can be considered as the benzvalene form of As_6

Fig. 4 Geometries of neutral As_4S_2 and its charged species optimized at MP2(full)/6-31G(d) level. Sulfur atoms are numbered 1 and 2. Bond lengths in Ångstroms



by replacing two arsenic atoms with two S atoms. Their symmetries are C_1 and C_{2v} , respectively. The electronic state of $4D^+$ is 2A_2 . Energetically, these $4B^+$, $4C^+$, and $4D^+$ are less stable than that of $4A^+$ by only 0.03, 0.04, and 0.09 eV, respectively. That is, the potential surface of the $As_4S_2^+$ species is very shallow. Isomers $4E^+$, $4F^+$, and $4G^+$, corresponding to neutral $4A$, $4D$, and $4B$, possess C_{2v} symmetry with 2B_2 state, C_1 symmetry, and C_s symmetry with ${}^2A'$ state, respectively. They are less stable in energy than that of $4A^+$ by 0.49, 0.57, and 1.64 eV, respectively. The bond distances of ground-state $4A^+$ are calculated to be 2.229 and 2.288 Å for two pairs of equal S–As bonds, 2.424 Å for two equal As–As bonds, and 2.582 Å for another As–As bonds.

From the discussion above, we can see that the ground-state structures of the As_4S_2 , $As_4S_2^-$, and $As_4S_2^+$ are different from each other, although they are considered as being derived from the trigonal prism of As_6 by replacing two As atoms with two S atoms.

As_5S_2 and its charged compounds

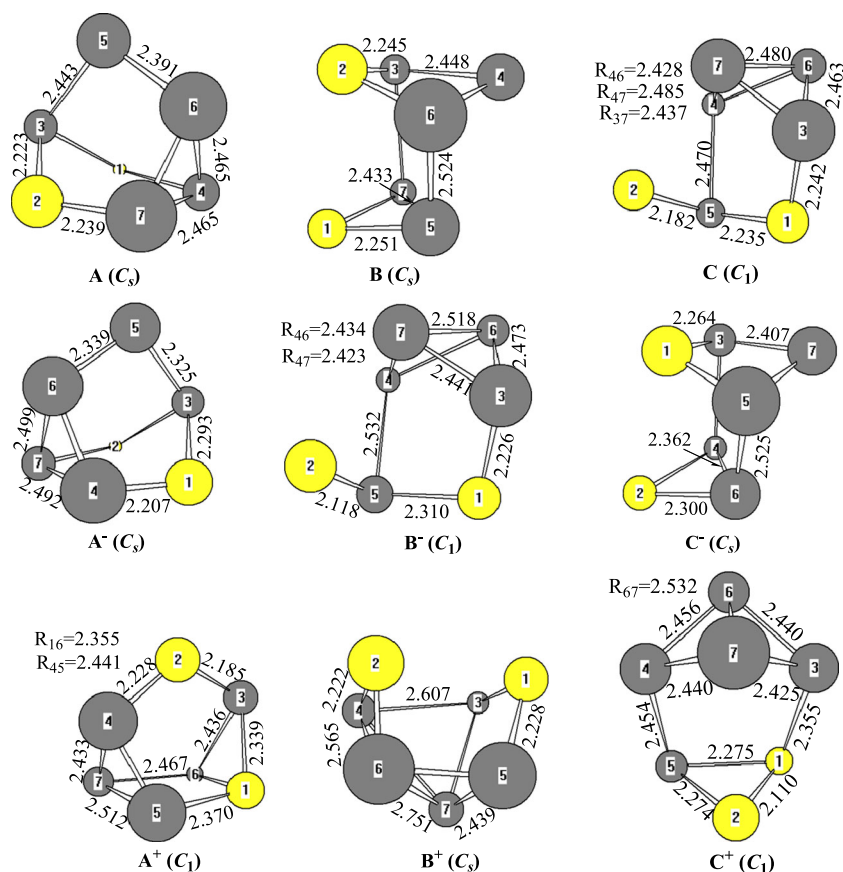
Three minimal structures for neutral As_5S_2 , three for anionic $As_5S_2^-$, and three for cationic $As_5S_2^+$ are shown in Fig. 5. The lowest-energy structure for neutral can be predicted to be geometry $5A$ with C_s symmetry and ${}^2A'$ ground state, which

can be viewed as replacing an arsenic atom of the ground state structure of As_6S [2] with a S atom. The C_s -symmetry $5B$ of ${}^2A'$ belongs to “third type”, which can be viewed as attaching an arsenic atom to the ground state structure of As_4S_2 . The C_1 -symmetry $5C$ can be viewed as adding a S atom to the ground state benzvalene structure of As_5S [2]. Energetically, the ground-state $5A$ structure is more stable than the $5B$ and the $5C$ by 0.74 and 0.88 eV, respectively. The bond distances of ground-state $5A$ are calculated to be 2.223 and 2.239 Å, respectively, for two pairs of equal S–As bonds, 2.465 Å for a pair of equal As–As bonds, 2.391, 2.443, and 2.465 Å for remaining three As–As bonds.

For negatively charged ion $As_5S_2^-$, the lowest-energy structure $5A^-$ is similar to the ground-state geometry of neutral. The symmetry is also C_s , but ${}^1A'$ ground state. The C_1 -symmetry $5B^-$ and C_s -symmetry $5C^-$ of ${}^1A'$ state corresponds respectively to neutral $5C$ and $5B$. Energetically, they are less stable than that of $5A^-$ by 0.61 and 1.22 eV, respectively. The bond lengths of $5A^-$ are predicted to be 2.207 and 2.293 Å for two pairs of equal S–As bonds, 2.499 Å for a pair of equal As–As bonds, 2.325, 2.339, and 2.492 Å for the remaining three As–As bonds.

For the positively charged ion $As_5S_2^+$, the lowest-energy structure is predicted to $5A^+$ geometry with C_1 symmetry, which is a “substitutional structure”. The isomers $5B^+$ and

Fig. 5 Geometries of neutral As_5S_2 and its charged species optimized at MP2(full)/6-31G(d) level. Sulfur atoms are numbered 1 and 2. Bond lengths in Ångstroms



$5C^+$, corresponding to neutral **5B** and **5C**, have C_s symmetry with $^1A'$ and C_1 symmetry, respectively. Energetically, they are less stable than that of $5A^+$ by 0.18 and 0.79 eV, respectively. The bond distances of $5A^+$ are calculated to be 2.185–2.375 Å for five S–As bonds and 2.436–2.512 Å for five As–As bonds.

As₆S₂ and its charged molecules

One minimum for neutral As₆S₂, one for anionic As₆S₂[−], and one for cationic As₆S₂⁺ are shown in Fig. 6. The lowest-energy structures of As₆S₂, As₆S₂[−], and As₆S₂⁺ are predicted to be C_s -symmetry with $^1A'$, $^2A''$, and $^2A''$ ground state, respectively. They can be regarded as replacing an As atom of the ground-state structure of As₇S [2] with a S atom. The bond distances of the neutral **6A** structure are calculated to be 2.217 and 2.233 Å for two pairs of equal S–As bonds, 2.425 and 2.468 Å for two pairs of equal As–As bonds, and 2.484, 2.493, and 2.525 Å for remaining three As–As bonds. Compared the bond lengths of the anion **6A**[−] with their neutral counterparts, a pair of equal S–As bonds shared by the As atom is shortened slightly by 0.004 Å, but another pair of equal S–As bond with unshared As atom is elongated by 0.052 Å. In addition to the As₃–As₇ breaking bond, the two pairs of equal As–As bonds are shortened by 0.034 and 0.081 Å, and remaining two As–As bonds are elongated by 0.019 and 0.062 Å, respectively. For cationic As₆S₂⁺, a pair of equal S–As bond lengths sharing the As atom is predicted to be 2.238 Å, which is 0.005 Å slightly longer than their neutral counterparts. Another pair of equal S–As bond lengths is calculated to be 2.269 Å, which is 0.030 Å shorter than their neutral counterparts. The two pairs of equal As–As bond lengths are predicted to be 2.426 and 2.542 Å, i.e., longer than their neutral counterparts by 0.001 and 0.074 Å, respectively. The remaining three As–As bond distances are predicted to be 2.459, 2.479, and 2.517 Å, respectively. The first two are shorter than their neutral counterparts by 0.066 and 0.014 Å, respectively, while the latter is 0.033 Å longer than that of neutral.

From the discussion above, we can conclude that, with the exception of As₄S₂, the ground-state structures of As_{*n*}S₂ can be viewed as the ground-state structure of neutral As_{*n*+1}S by

replacing an As atom with a S atom, that is, a “substitutional structure”, in which the feature of sulfur bonding is edge-bridging. To be more precise, the ground-state structures of As_{*n*}S₂ can be viewed as the lowest-energy structure of neutral As_{*n*+2} by replacing two As atoms with two S atoms because the ground-state geometry of As_{*n*}S can be regarded as the global minimum of neutral As_{*n*+1} by replacing an As atom with a S atom [2]. No rule was found for the ground state structure of As_{*n*}S₂[−] and As_{*n*}S₂⁺. In anion As_{*n*}S₂[−], the feature of sulfur bonding is either edge-bridging or a terminal atom (for example, As₂S₂[−] and As₃S₂[−]). The reason for this is explained in Ref. [2]. In As_{*n*}S₂⁺ the feature of sulfur bonding is edge-bridging analogous to As_{*n*}S₂.

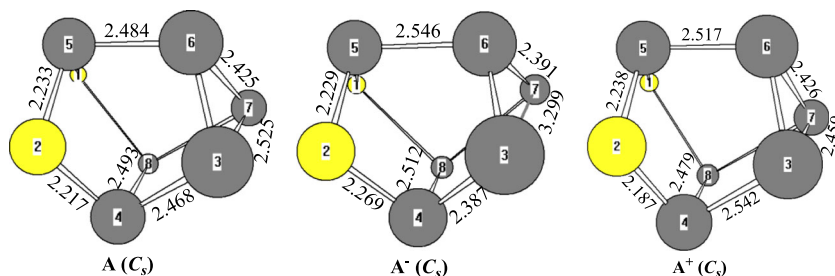
Comparison with CCSD(T)/aug-cc-pVTZ-DK results

Due to the flat potential energy surfaces of As₄S₂ and its charged species, the CCSD(T)/aug-cc-pVTZ-DK//MP2/cc-pVTZ calculations for As₄S₂, As₄S₂[−], and As₄S₂⁺ were performed and compared with G3 results. At the CCSD(T)/aug-cc-pVTZ-DK level of theory, the **4A** structure is slightly more stable than that of **4B** by 0.02 eV in energy. The **4B**[−] isomer is 0.03 eV above **4A**[−]. And the **4B**⁺ geometry is more stable than that of **4A**⁺, **4C**⁺, and **4D**⁺ by 0.09, 0.09, and 0.11 eV in energy, respectively. In other words, the CCSD(T)/aug-cc-pVTZ-DK results agree with the G3 results for As₄S₂ and As₄S₂[−], but not for As₄S₂⁺. In short, many isomeric arrangements for As₄S₂ and its positively and negatively charged species are possible because of the flat potential energy surfaces. This information may be important for further experiments. In addition, more attention should be paid in experiments because all these isomers may be co-existence and it is not easy to distinguish them experimentally.

Electron affinity and ionization potential

The AEA [defined as the difference of total energies as follows: AEA = E (the ground-state structure of neutral) – E (the ground-state structure of anion)] of As_{*n*}S₂ species was predicted at the G3 level. The AEAs corrected with ZPVE were calculated to be 3.22 eV for AsS₂, 1.69 eV for As₂S₂, 2.67 eV for As₃S₂, 1.81 eV for As₄S₂, 3.08 eV for As₅S₂,

Fig. 6 Geometries of neutral As₆S₂ and its charged species optimized at MP2(full)/6-31G(d) level. Sulfur atoms are numbered 1 and 2. Bond lengths in Angstroms



and 1.75 eV for As_6S_2 . To facilitate comparison, Fig. 7 sketches the AEAs of As_nS_2 , As_nS and As_n clusters as a function of the size of the compounds. From Fig. 7 we can conclude that the odd-even alternation in AEAs is unchanged when S atoms are bound to As_n clusters. The curve of As_nS_2 is roughly parallel to that of As_n , but converse to that of As_nS . The AEAs of As_nS_2 species are larger when m (m = number of As atoms plus number of S atoms) is odd, and are smaller when m is an even number. The reason is that As_nS_2 clusters with odd m are 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 Pauli's exclusion principle [52]. There are no experimental values for comparison.

The AIP [defined as the difference of total energies as follows: $\text{AIP} = E(\text{the ground-state structure of cation}) - E(\text{the ground-state of neutral})$] of As_nS_2 clusters were evaluated at the G3 level. The AIPs corrected with ZPVE were calculated to be 8.18 eV for AsS_2 , 8.22 eV for As_2S_2 , 7.13 eV for As_3S_2 , 8.10 eV for As_4S_2 , 7.17 eV for As_5S_2 , and 7.93 eV for As_6S_2 . To facilitate comparison, the AIPs of As_nS_2 , As_nS and As_n are shown in Fig. 8 as a function of the size of the compounds. Similarly to AEAs, the odd-even alternations in AIPs are unaltered when S atoms are bound to As_n species. The AIP curve of As_nS_2 is roughly parallel to that of As_n , but converse to that of As_nS . The AIPs of As_nS_2 species are smaller when m is odd, and larger when m is an even number. As mentioned above, the reason is that As_nS_2 is a closed shell electronic structure when m is an even number, and more stable than that of an open shell electronic structure. That is to say, it is easier to remove an electron for a species of open shell electronic structure than for those of closed shell electronic structure. There are no experimental values for comparison.

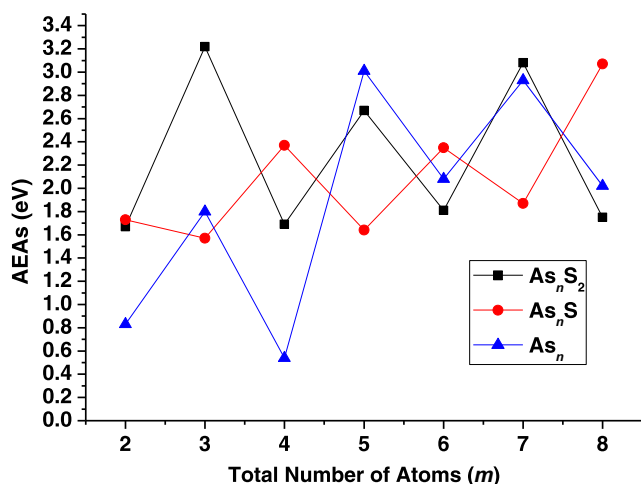


Fig. 7 Adiabatic electron affinities (AEAs) versus the total number of atoms m (number of As atoms plus number of S atoms) for As_nS_2 , As_nS , and As_n species. The AEAs of As_nS , As_n , and S_2 are taken from Refs. [2], [5] and [46] respectively

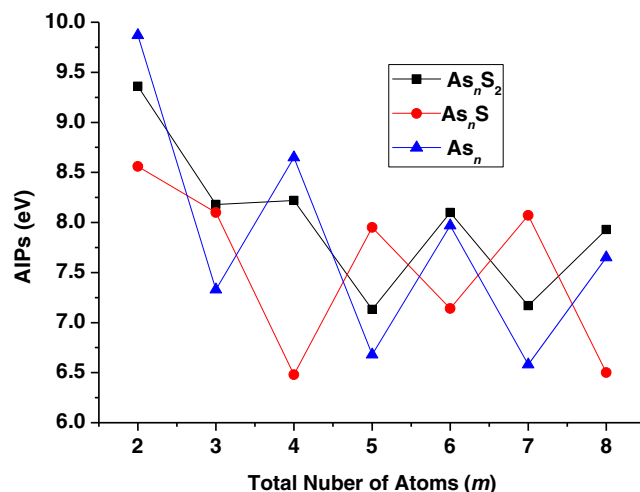


Fig. 8 The adiabatic ionization potentials (AIPs) versus the total number of atoms m (number of As atoms plus number of S atoms) for As_nS_2 , As_nS , and As_n species. The AIPs of As_nS , As_n , and S_2 are taken from Refs. [2], [5], [46], respectively

Dissociation energy

The energies of S (and/or its ion $\text{S}^{(-/+)}$) from As_nS_2 clusters and their ions were calculated and listed in Table 1. From Table 1 we can see that (1) for neutral As_nS_2 ($n=1-6$), the DEs [defined as $\text{DE} = E(\text{S}) + E(\text{As}_n\text{S}) - E(\text{As}_n\text{S}_2)$] were calculated to be 2.81, 3.76, 3.35, 3.30, 3.60 and 3.68 eV, respectively. Similarly to the DEs of As_nS [2], there are no odd-even alternations for the DEs of As_nS_2 . (2) For anionic As_nS_2^- , two types of DEs were reported. One is the $\text{As}_n\text{S}_2^- \rightarrow \text{S}^- + \text{As}_n\text{S}$

Table 1 Dissociation energies (DEs) of S, S^- and S^+ from As_nS_2 ($n=1-6$) and their ions. Values (eV) are corrected with zero-point vibrational energy (ZPVE)

Dissociation	DE	Dissociation	DE
$\text{AsS}_2^- \rightarrow \text{S} + \text{AsS}^-$	4.31	$\text{AsS}_2^- \rightarrow \text{S}^- + \text{AsS}$	3.97
$\text{As}_2\text{S}_2^- \rightarrow \text{S} + \text{As}_2\text{S}^-$	3.88	$\text{As}_2\text{S}_2^- \rightarrow \text{S}^- + \text{As}_2\text{S}$	3.38
$\text{As}_3\text{S}_2^- \rightarrow \text{S} + \text{As}_3\text{S}^-$	3.65	$\text{As}_3\text{S}_2^- \rightarrow \text{S}^- + \text{As}_3\text{S}$	3.95
$\text{As}_4\text{S}_2^- \rightarrow \text{S} + \text{As}_4\text{S}^-$	3.47	$\text{As}_4\text{S}_2^- \rightarrow \text{S}^- + \text{As}_4\text{S}$	3.04
$\text{As}_5\text{S}_2^- \rightarrow \text{S} + \text{As}_5\text{S}^-$	4.33	$\text{As}_5\text{S}_2^- \rightarrow \text{S}^- + \text{As}_5\text{S}$	4.61
$\text{As}_6\text{S}_2^- \rightarrow \text{S} + \text{As}_6\text{S}^-$	3.57	$\text{As}_6\text{S}_2^- \rightarrow \text{S}^- + \text{As}_6\text{S}$	3.37
$\text{AsS}_2^+ \rightarrow \text{S} + \text{AsS}^+$	3.19	$\text{AsS}_2^+ \rightarrow \text{S}^+ + \text{AsS}$	4.90
$\text{As}_2\text{S}_2^+ \rightarrow \text{S} + \text{As}_2\text{S}^+$	3.64	$\text{As}_2\text{S}_2^+ \rightarrow \text{S}^+ + \text{As}_2\text{S}$	5.81
$\text{As}_3\text{S}_2^+ \rightarrow \text{S} + \text{As}_3\text{S}^+$	2.69	$\text{As}_3\text{S}_2^+ \rightarrow \text{S}^+ + \text{As}_3\text{S}$	6.49
$\text{As}_4\text{S}_2^+ \rightarrow \text{S} + \text{As}_4\text{S}^+$	3.15	$\text{As}_4\text{S}_2^+ \rightarrow \text{S}^+ + \text{As}_4\text{S}$	5.46
$\text{As}_5\text{S}_2^+ \rightarrow \text{S} + \text{As}_5\text{S}^+$	3.57	$\text{As}_5\text{S}_2^+ \rightarrow \text{S}^+ + \text{As}_5\text{S}$	6.70
$\text{As}_6\text{S}_2^+ \rightarrow \text{S} + \text{As}_6\text{S}^+$	3.83	$\text{As}_6\text{S}_2^+ \rightarrow \text{S}^+ + \text{As}_6\text{S}$	6.02
$\text{AsS}_2 \rightarrow \text{S} + \text{AsS}$	2.81	$\text{As}_2\text{S}_2 \rightarrow \text{S} + \text{As}_2\text{S}$	3.76
$\text{As}_3\text{S}_2 \rightarrow \text{S} + \text{As}_3\text{S}$	3.35	$\text{As}_4\text{S}_2 \rightarrow \text{S} + \text{As}_4\text{S}$	3.30
$\text{As}_5\text{S}_2 \rightarrow \text{S} + \text{As}_5\text{S}$	3.60	$\text{As}_6\text{S}_2 \rightarrow \text{S} + \text{As}_6\text{S}$	3.68

Table 2 DE ratio [DEs(As_nS)/DEs(As_{n-1}S₂⁺) and DEs(As_nS₂/As_{n+1}S⁻)]

Species	G3 ratio	Species	G3 ratio
As ₂ S/AsS ₂ ⁺	0.85	AsS ₂ /As ₂ S ⁻	0.81
As ₃ S/As ₂ S ₂ ⁺	0.95	As ₂ S ₂ /As ₃ S ⁻	0.94
As ₄ S/As ₃ S ₂ ⁺	0.92	As ₃ S ₂ /As ₄ S ⁻	0.94
As ₅ S/As ₄ S ₂ ⁺	1.12	As ₄ S ₂ /As ₅ S ⁻	1.15
As ₆ S/As ₅ S ₂ ⁺	1.11	As ₅ S ₂ /As ₆ S ⁻	0.96
As ₇ S/As ₆ S ₂ ⁺	0.95	As ₆ S ₂ /As ₇ S ⁻	0.98

As_nS⁻, and other is As_nS₂⁻→S⁻+As_nS. The DEs for the former are larger than those of the latter for $n=1, 2, 4$ and 6 , and smaller for $n=3$ and 5 . The reason is that the EA of the S atom (2.07 eV at the G3 level) is larger than that of AsS, As₂S, As₄S and As₆S, and smaller than that of As₃S and As₅S (see [2]). (iii) For cationic As_nS⁺, two types of DEs were also reported. One is the As_nS₂⁺→S+As_nS⁺, and other is As_nS₂⁺→S⁺+As_nS. The DEs of S are smaller than the DEs of S⁺. So As_nS₂⁺ prefers to dissociate S and As_nS⁺ rather than to dissociate S⁺ and As_nS. The reason is that the AIP of S atom (10.3 eV at the G3 level) is larger than that of As_nS (see [2]).

Regularity in DEs of type AB species

Similarly to the discussions of bond enthalpy ratio of isoelectronic species performed by Deakynne et al. [53, 54], we discussed the DEs ([AB][±]→A[±]+B) ratio for the isoelectronic AB compounds, where B=S with A=As_n and As_{n-1}S⁺, or As_nS and As_{n+1}⁻. The DEs ratio [DEs(As_nS)/DEs(As_{n-1}S₂⁺) and DEs(As_nS₂/As_{n+1}S⁻)] were collected in Table 2. As can be seen from Table 2, there is a roughly constancy in the DEs(As_nS)/DEs(As_{n-1}S₂⁺) and DEs(As_nS₂/As_{n+1}S⁻) ratios. The DEs(As_nS)/DEs(As_{n-1}S₂⁺) display a roughly constant ratio of 0.98±0.09 and the DEs(As_nS₂/As_{n+1}S⁻) exhibit a roughly constant ratio of 0.96±0.07.

Conclusions

The structures and energies of neutral and charged arsenic sulfides As_nS₂^(-1,0,+1) ($n=1-6$) were investigated systematically by means of the G3 scheme, and the ground-state structures of these species are presented. The ground-state structures of As_nS₂ can be viewed as the lowest-energy structure of neutral As_{n+1}S by replacing an As atom with a S atom. To be more precise, the ground-state structures of As_nS₂ can be viewed as the lowest-energy structure of neutral As_{n+2} by replacing two As atoms with two S atoms, in which the feature of sulfur bonding is edge-bridging. No rule was found for the ground state structure of As_nS₂⁻ and As_nS₂⁺. In As_nS₂⁻, the feature of sulfur bonding is either edge-bridging or a terminal

atom, and in As_nS₂⁺ the feature of sulfur bonding is edge-bridging analogous to As_nS₂. The potential energy surfaces of As₄S₂ and its charged species are so very flat that co-existence for many isomers of As₄S₂ and its charged species are possible. The reliable AEAs of As_nS₂ were estimated to be 3.22 eV for AsS₂, 1.69 eV for As₂S₂, 2.67 eV for As₃S₂, 1.81 eV for As₄S₂, 3.08 eV for As₅S₂, and 1.75 eV for As₆S₂. And the reliable AIPs were evaluated to be 8.18 eV for AsS₂, 8.22 eV for As₂S₂, 7.13 eV for As₃S₂, 8.10 eV for As₄S₂, 7.17 eV for As₅S₂, and 7.93 eV for As₆S₂. There are odd-even alternations in both AEAs and AIPs as a function of size of As_nS₂. The DEs of S (and/or its ion S^(-/+)) from As_nS₂ clusters and their ions were calculated and used to reveal relative stability. The theoretical DEs revealed that As_nS₂⁺ prefers to dissociate S and As_nS⁺ rather than to dissociate S⁺ and As_nS. The As_nS₂⁻ prefer to dissociate S⁻ and As_nS rather than to dissociate S and As_nS⁻ for $n=1, 2, 4$, and 6 , but prefer to dissociate S and As_nS⁻ rather than to dissociate S⁻ and As_nS for $n=3$ and 5 . To the best of our knowledge, there are no experimental or other theoretical data regarding the AEAs, AIPs, and DEs for the As_nS₂ system. Our results may thus provide a reference for further experimental investigation of these important arsenic sulfides species.

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