

The formation energies of the clusters of As-S materials vapor phase

A.V. DALEKOREY, V.P. IVANYTSKY, V.S. KOVTUNENKO, R.O. MESHKO
National University of Uzhhorod, Engineering department, 88000, Uzhhorod, Ukraine

The self-consistent field (SCF), spin-unrestricted methods (UHF) and density functional theory (DFT) methods have been applied for first-principles calculations on small As_nS_m atomic clusters of As-S materials vapor phase. 7 two-atomic and 17 three-atomic probable isomeric forms of clusters have been studied among which 10 have the lowest formation energy and may be stable in the vapor phase. It has been revealed that the energy per one atom for the most stable two- and three-atomic As_nS_m clusters is within the range from 1.9 to 2.3 eV/atom with the average value of ~ 2.1 eV/atom. The calculated chemical bonds energies in As_nS_m clusters agree well with the experimental data available. The efficiency of combining the experimental mass-spectroscopic studies with quantum-mechanical calculations to study the structure and energy of vapor flows particles under evaporation of covalent chalcogenide materials has been shown.

(Received June 09, 2015; accepted April 05, 2016)

Keywords: Arsenic-sulfur clusters, Mass-spectroscopy, Chemical bonds energy

1. Introduction

Amorphous and glassy materials have been intensely studied because of their technological importance and fundamental interest. Chalcogenide As-S films and glasses are excellent sensitive media for optical recording, useful optoelectronic elements and materials for potential applications in different electronic, laser-technology and photonic devices as well as perfect materials for fundamental studies and modeling [1-2]. Past year's investigations of the microscopic structure of chalcogenides show that the approximation of the simplest structural units only cannot explain the realistic nature and properties of its amorphous state.

Theoretical and experimental investigations show that chalcogenide As-S amorphous films are formed in a wider variety of basic short range order structural units than their crystal analogs [3]. The majorities are combined into different middle range ordering grouping (clusters), depending on the concentration of additives and producing technology [4]. The ordering grouping geometry in As-S films determines its physical properties [5]. During a few years a great importance has started to be given to structural fluctuations and separated nano-scale phases to interpret photo-induced phenomena in binary As-S films and glasses [6].

During the last few years many scientists have intensely studied the structure of As-S glasses and films in combination with first-principles quantum-mechanical calculations of As_nS_m clusters to understand the compositional dependence of clustering and structural transformation in these materials during laser irradiation [7, 8]. Nowadays elemental arsenic and its clusters have also begun to be important for high technology [9, 10]. For example, they have important effects on the molecular-beam epitaxial grow of GaAs semiconductors on Si surfaces. There have been several previous theoretical studies of As_n clusters up to $n = 11$ using different methods [11, 12].

Despite numerous experimental and theoretical studies the physical processes responsible for different photo-stimulated changes in As-S films remain unclear. The implicit fact is that they are all determined by the atomic structure of the given materials [13]. The repeated attempts to "decode" this structure have not given real results so far [14]. To our mind, this task may be solved only by taking into account all physicochemical formation processes of the atomic net of As-S amorphous films under their vacuum condensation. As an example in works [15-16] a strong effect of the cluster structure of vapor particles under evaporation of As-S glasses on the structure formation of amorphous films of these materials has been shown. Besides, the presence of stable many-atomic complexes in the vapor and hardening of their disordered structures in condensed films is an important factor of the formation of different structural units of the atomic net in chalcogenide As-S layers.

That's why some important experimental studies of the mass-spectra for the vapour phase of As-S materials have been carried out. In a series of well-known publications the role of the composition of vapour phase in forming the structure of As_2S_3 thin films has been discussed [17-23]. The general idea of these publications is that the stable component in vapour phase is labile in condensed films. For example, As_4S_4 molecule is the most stable component in the vapour phase of g- As_2S_3 . It was shown by T.P. Martin that quenching of the vapour phase of As_2S_3 structure in super cold helium leads to the formation of different As_nS_m molecules. The most intense component in vapor phase is also As_4S_4 molecule [21]. It is considered that two and three atomic components in the vapor phase of As_2S_3 may appear as a result of ionization of more complex molecules in the mass-spectra [17, 20].

Our mass-spectrometric studies of evaporation processes of As_xS_{1-x} glasses at $x < 0.3$ show that two, three and four atomic clusters become the main ones in vapor

phase [24]. Therefore, they will play an essential role in forming the structure of As-S amorphous films with a small content of arsenic. We think that the nature of small atomic components of the vapour phase of As-S materials may be connected with evaporation of glasses rich in sulphur as well as with the process of fragmentation of more complex molecules, which were formed during mass-spectrometric investigations of glasses in the vicinity of As_2S_3 compositions.

By using up-to-date mass-spectroscopic studies one can only determine the chemical composition and concentration of different particles in vapour phase. What is the form of these particles in it, what is their structure and energy – the mass-spectroscopy can't give answers to these questions. In order to get answers to them one can use up-to-date first-principles methods of quantum-mechanical calculations of different particles, i.e. As_nS_m vapour flows of the clusters formed under evaporation of As-S materials. Such studies also allow us to solve a lot of other unsolved actual problems of modern nanophysics of covalent materials: 1. Why is the concentration of some clusters in vapors very big, of the others - small, and why are some clusters not met in the vapor phase at all? 2. What is the distribution of vapor phase particles according to the energies of their formation? 3. Which structural and energy parameters of chemical bonding of atoms determine the stability of covalent clusters? 4. Does the ionization process of many-atomic vapor particles which takes place in the mass-spectrometer influence their energy state and structure much? 5. How intensively can the dissociation of many-atomic clusters into simpler particles go on? 6. How effective may the combination of mass-spectroscopy methods with quantum-mechanical calculations be?

The density functional theory (DFT) [25] has become a widely applicable computational first-principles tool, requiring much less computational effort than convergent quantum mechanical methods, such as a coupled cluster theory. The application of gradient-corrected DFT has been shown to be effective for many inorganic clusters [26, 27]. The given method is often used by different authors in quantum-mechanical calculations of clusters and molecules with arsenic and sulfur [28 – 30]. The works [12, 31] have also shown that some DFT methods with carefully chosen basis sets allow to calculate energy parameters of As-containing clusters with the accuracy up to 0.2 eV.

That's why the object of the present study is to systematically apply DFT to determine the formation energies of short and middle order chemical bonds in the clusters of As-S materials vapor phase. The given system is chosen as a model because there are a lot of experimental results of both the evaporation processes of materials with different chemical composition and structure and physicochemical properties of thin amorphous films for it. But theoretically, such studies are actual for all substances with a covalent type of bonding which have the prospects of practical application in the form of thin $As-S$ films prepared by vacuum evaporation technologies.

2. Modeling methods

The computations consist of first-principles calculations on two- and three As_nS_m ($n, m = 0, 1, 2, 3$) clusters. These all clusters are represented in mass-spectra of As-S materials vapor phase. All calculations were performed using the GAMESS (USA) quantum-chemical program package.

The self-consistent field (SCF), spin-unrestricted methods (UHF) and density functional theory (DFT) methods were applied for geometry optimizations of all species using the Berny optimization procedure. The use of DFT method allowed to take into account the contribution of electron correlation into the energy of clusters which is considerable for many-electron systems. The triple-zeta valence Pople 6-311G* [26] basis set was used for As and S atoms. The Becke's three-parameter hybrid functional (B3) that defines the exchange functional as a linear combination of Hartree-Fock, local and gradient-corrected exchange terms (B3LYP) was used here. For separate calculations the corrected exchange functional proposed by Becke and gradient-corrected correlation functional of Lee, Yang, and Parr (BLYP) were used, too. Subsequent second derivative calculations, using the same method and basis set verified the obtained structures as true energy minimum geometries.

The triple-zeta valence basis set for sulfur and arsenic was constructed from the standard set of contracted Gaussian functions by adding a set of three pure d -type and one f -type polarization functions on each atom.

Zero-point vibrational energy is quite small for all the As_nS_m clusters and it was not taken into account in calculations. In the process of studies it was revealed that for many clusters the formation energy depends on the kind of the potential used in DFT method. In particular, our calculations by DFT method gave such values of atoms energies (in atomic units of energy): $E(As) = -2235.438$, $E(S) = -398.049$, $E(H) = -0.497$ for B3LYP potential and $E(As) = -2235.579$, $E(S) = -398.093$, $E(H) = -0.498$ for BLYP potential. At the same time the calculations by UHF method without correlation errors give bigger values of the energies of arsenic and sulfur atoms in the basic state [12] that was observed in our studies, too. It should be noted that the energies indicated above relate to the most stable states of atoms with multiplicity $M=4$ for arsenic (in this state the atom has three free bonds conditioned by $4p$ – atomic orbitals) and $M = 3$ for sulfur (the given stable state of the atom has two free bonds conditioned by $3p$ -atomic orbitals). The geometry optimization of some clusters with indicated two different potentials also gave their different geometric parameters. Therefore to define the energy of clusters such parameters of quantum-mechanical calculations under fully similar conditions were taken at which the structural data close to the experimental ones were obtained. Besides, in many cases for more precise determination of average energies of chemical bonds in different clusters free valences in calculations were saturated by fictitious hydrogen atoms.

3. Results

3.1 Calculation of simple S- and As-containing molecules

The reason for the formation of different associates from several atoms is the decrease in total energy of such a system when its atoms draw together at the distance of the order of fractions of a nanometer. Besides, in the clusters formed those parameters of the structure are fixed at which the given cluster gets a minimal total energy. For As-S system the formation of clusters responds to the formation of covalent chemical bonds between interacting atoms. The energy minimum of each chemical bond between two atoms corresponds to a strictly defined value of

equilibrium distance l_0 between them which we will call the length of the given bond. For many-atomic complexes the energy and spacious displacement of atoms will be defined by the parameters of all molecular orbitals formed in such a system. In particular, the complex interaction between divided and undivided electron pairs of the given orbitals will set the equilibrium angles between chemical bonds θ_0 .

To check the accuracy of the method at the first stage of studies we conducted the calculations of the formation energies E_f and energies of different chemical bonds E_b for several simple molecules with the participation of S, As and H atoms for which reliable experimental data exist. The results obtained by us are given in Table 1 alongside with the average experimental values borrowed from [32].

Table 1. The formation energies and chemical bonds energies of simple molecules (multiplicity equals to 1, except for S_2 molecule) calculated by different methods and with different potentials.

Molecule	Bond	E_f , eV (UHF)	E_f , eV (DFT, B3LYP)	E_f , eV (DFT, BLYP)	E_b , eV (UHF)	E_b , eV (DFT, B3LYP)	E_b , eV (DFT, BLYP)	E_b , eV (experiment)
H ₂	H-H	-3.56	-4.76	-4.63	3.56	4.76	4.63	4.45
S ₂	S=S	-1.56	-4.45 (-3.46)	-	1.56	4.45 (3.46)	-	4.34; 4.4
As ₂	As≡As	-0.38	-3.85	-4.23	0.38	3.85	4.23	3.3
H ₂ S	H-S	-5.45	-7.6	-7.67	2.72	3.8	3.83	3.6; 3.7
S ₃	S-S	-2.40	-6.45	-6.75	0.80	2.15	2.25	2.86; 2.78; 2.3
As ₄	As-As	-2.62	-9.90	-10.48	0.44	1.65	1.75	1.7 (1.52)
AsH ₃	As-H	-4.67	-9.67	-9.33	1.57	3.2	3.1	3.19; 2.8

The experimental data for energies of bonds H-H, As≡As, H-S, S=S are taken as dissociation energies of two-atomic molecules H₂, As₂, HS and S₂. Given in Table 1 the calculated value E_b (H-S) within the error coincides with the average energy value of two dissociation reactions H₂S → HS + S and HS → H + S, equal to 3.78 eV [32]. It should be noted that for HS radical the dissociation energy is a bit higher: the experimental value is equal to 3.85 eV and the values calculated by different methods are within the limits of 3.95 – 4.20 eV [35]. At the same time the calculations by DFT method for different potentials and basic functions by authors [35, 36] give the values for H-S bond energy equal to 3.50 – 3.63 eV. For further analysis of formation energies of different As_nS_m clusters we must choose the fixed averaged value of calculated H-S bond energy. Taking into account the data of Table 1 and the analysis conducted above, we can take for DFT method using the potential E_b (H-S) = 3.8 eV which is 3 – 6 % higher than the experimental value for H₂S molecule. The double S=S bond for clusters of As-S system can be found in S₂ dimer. But the results of studies of S₂ molecules with a double chemical bond is not so unambiguous as for previous molecules. The use of BLYP potential in DFT method did not allow us to obtain the formation energy of S₂ molecule. Yet the calculations with B3LYP potential for the state of S₂ molecule with the multiplicity $M = 1$ gave the value E_b (S=S) = 3.5 eV which is 20 % less in comparison with the experiment. At the same time for a triplet state ($M = 3$) of the given molecule the calculations give the value very close to the

experimental one, i.e. E_b (S=S) = 4.4 eV. At that, the calculated total valence of atoms in this state was equal to 2.6, and the bound one was equal to 2. The calculations of authors [34-37] for S=S bond energy gave the value within the limits of 4.0 – 4.5 eV. This is very close both to experimental values and to calculated data at $M=3$ obtained by us. Besides, it should be noted that this result obtained by us is close to the data cited by authors [37] for calculations of dissociation energies of S₂ molecules while using other programs (Gaussian and Priroda) and other bases (basis4.in and relativistic errors), other methods (PM3) and with other potentials (non-empiric exchange-correlation PBE functional). That's why one can consider that in the couple for S₂ atomic complexes-molecules a triplet state with the energy of S=S double bond, equal to 4.4 eV is realized.

The triple As≡As bond in clusters of As-S system is found in As₂ molecules only. The value of energies of this bond equal to 3.9 eV and calculated using B3LYP potential is close to the experimental one.

The average experimental As-H bond energy is taken by us as the energy of AsH₃ → AsH₂ + H reaction [32]. It should be noted that in work [38] for the bond energy of As-H radical the experimental value E_b (As-H) = 2.8 eV is cited which is a little bit lower in comparison with the data for AsH₃ molecules. Our calculations by different methods give different results, too. If optimize the geometry of AsH₃ molecule with B3LYP potential, the lengths of As-H bonds are a bit shorter (0.148 nm) in

comparison with the optimization by UHF method (0.151 nm) and with BLYP potential (0.155 nm). In the first case the calculated As-H bonds energy is equal to 2.6 eV, whereas in the last – 3.1 eV. But if to calculate the energy of AsH₃ molecule with B3LYP potential at the interatomic distances of 0.151 nm, the As-H bonds energy is equal to 3.2 eV. The same energy calculated at the distances of 0.151 nm with BLYP potential is equal to 3.1 eV. So, the calculations of bonds energies of clusters with B3LYP potential are very sensitive to the value of the interatomic distances. Therefore when considerable discrepancies in the calculations of clusters energies by different methods appeared, we conducted additional studies on the dependence of their energy of the interatomic distances. Taking into account the experimental data, results of our calculations and data [34], we can take the average energy of As-H bond equal to 3.2 eV (Table 1) for further analysis of modeling clusters with B3LYP potential.

To define the value $E_b(\text{S-S})$ in S₃ molecule-triangle the experimental data of five energies of bonds uncoupling reaction for chains of S_n → S_{n-1} + S type, where n = 3 – 8 [33] and the results [38] were averaged. They gave us the average value $E_b(\text{S-S}) = 2.86$ eV. Other data for S_n chains [33] give the experimental value $E_b(\text{S-S}) = 2.78$ eV which is very close to the previous one, for rings S₈ $E_b(\text{S-S}) = 2.3$ eV [33]. Practically the same value of the average S-S bond value was obtained by us while calculating S₃ molecule. Therefore we can assume that for ring-like or closed areas of clusters $E_b(\text{S-S}) = 2.3$ eV, and for branched chain-like areas of As_nS_m clusters this energy may appear to be closer to 2.8 eV. We'll turn back to the analysis of this question a bit later.

Literary sources [32] for single As-As chemical bond in As₄ molecules give two values of average energy given in Table 1. One of them (1.70 eV) practically coincides with the value calculated by us. Therefore it can be taken for postulating the average energy of As-As bond in As_nS_m molecular clusters. Such $E_b(\text{As-As})$ value is obtained in calculations [38].

The analysis of data in Table 1 allows to indicate some relationships.

1. The program GAMESS with standard parameters used by us often incorrectly calculates the energy parameters of S₂ and As₂ molecules with double and triple bonds, respectively, within BLYP potential. At the same time the use of B3LYP potential provides good calculated results.

2. The formation energies of some molecules calculated by UHF and DFT methods differ sufficiently. This indicates to a considerable influence of the correlation component on the value of formation energy of clusters in As-S system.

3. Within DFT method both potentials indicated above give close calculated values of bonds energies.

4. Calculated by DFT method the values of chemical bonds energies in simple molecules with sulfur and arsenic are close enough to the experimental data (some differences are observed only for S₂ molecule).

5. The energies of chemical bonds of simple S- and As-containing molecules which may be calculated by using both BLYP and B3LYP potentials differ less than for 1 % between themselves (except for As₂ molecule).

6. There exists quite a clear correlation between calculated values of bonds energies by DFT method with B3LYP potential and experimental ones.

7. DFT method with B3LYP potential gives good results of calculations of the formation energy and average energies of chemical bonds of different ratio for simple S- and As-containing molecules. As a result all energy parameters of As_nS_m clusters were afterwards calculated by just this method.

3.2 Calculation of two-atomic clusters-radicals

For two-atomic complexes of vapor phase of As-S system only five isomeric forms of clusters-radicals are possible. They have various quantities of unbound valences (from 1 to 4). In Table 2 the data of clusters with the formation energies calculated by DFT method with B3LYP potential are given. For comparison the experimental data are taken from [12. 32-34].

Table 2. The formation energies of two-atomic clusters-radicals of As-S system.

Cluster	E_f , eV (direct calculations)	E_f , eV (calculations via bonds with hydrogen)	E_b , eV (experiment)
-S-S-	-	-2.3	2.8 (2.3)
=As-As=	+0.13	-0.3	2.1 (1.7)
-As=As-	-0.9	-2.3	-
=As-S-	-1	-2.3	2.6
-As=S	-3.9	-3.4	-

We could not calculate the energy of S₂ cluster-radical with a single chemical bond by DFT method (B3LYP potential). Such a bond in accordance with [39] has a low-lying triplet state. Yet the program in the calculations of both a singlet and triplet state shows the formation of only a double chemical bond between atoms within the limits of the interatomic distances from 0.17 nm to 0.22 nm. The length of a single S-S chemical bond (~0.21 nm) falls into this range, too, but it isn't fixed under conditions chosen by us. When increasing the interatomic distances above 0.22 nm the program stops calculating the total energy of S₂ cluster at all.

In the given context we'd like to mention some remarks made while analyzing the structure and energies of sulfur clusters in work [39]. Here it is mentioned that in sulfur atoms the energy of *d*-orbitals makes up approximately 10 % of the energy of *p*-orbitals. Therefore the supposition about a considerable contribution of *d*-orbitals into S-S bonds in different chains and rings is unjustified. But for excited states of different sulfur molecules the theoretical data are obtained to be much closer to the experiment if *d*-orbitals are taken into account in the calculations. Taking into account such peculiarities we tried to calculate the formation energy of S₂ cluster with a single chemical bond without introducing *d*-orbitals into the basis. But in this case we did not obtain the final result with getting a stable state by S₂ cluster either. We could not make clear the reason for such behavior of GAMESS program.

In quantum-mechanical computations free valences are very often saturated by hydrogen atoms in the calculations of energies and properties of clusters [5,8]. We have applied this method for two-atomic clusters-radicals of As-S system. The results of such calculations are also given in Table 2. At that for H_2S_2 cluster with a single S-S chemical bond the formation energy which gives the value $E_b(S-S) = 2.3$ eV has been already calculated. Not taking into account the branched chain geometry of H_2S molecules the value obtained coincides with both calculated and experimental energies of chemical bonds in closed S_3 molecule-triangle.

Similar to -S-S-clusters picture was observed by us for other two-atomic radicals of As-S system (Table 2). Thus, for =As-As= cluster the calculations give a positive value (+0.13 eV) of the formation energy. The saturation of free valences by hydrogen with the formation of As_2H_4 cluster gives the value of $E_b(As-As) = 0.3$ eV in the calculations that is much less than the experimental value. We have similar relationships for -As=As- ($E_b(As=As) = 0.9$ eV) and As_2H_2 ($E_b(As=As) = 2.3$ eV). Thus, DFT method with B3LYP potential for two-atomic As_2 clusters-radicals both without saturation and at saturation of free valences by hydrogen atoms gives much lower energy values of single and double chemical bonds between As atoms in comparison with the experiment. At that for clusters with saturating hydrogen atoms such discrepancies are sufficiently smaller. The difference between calculated and experimental energies for such clusters with smaller quantity of unpaired electrons decreases much (Table 2). It is difficult to analyze in detail the behavior of bonds energy of As_2 clusters as we haven't found the experimental value of energy $E_b(As=As)$ in the literature. Note that mentioned relationships in the behavior of chemical bonds energies of two-atomic As_2 radicals are characteristic for As-S clusters, too. The analysis of the latter is also complicated because of the absence of experimentally measured value $E_b(As=S)$.

For two-atomic molecules it is considered that their formation energy is equal to the energy of a chemical bond. It is weakly dependent of the temperature of the system and the given energy may be considered equal to the dissociation energy of molecules, that is to that energy which is necessary for breaking of two-atomic molecule into two separate atoms. That is why at experimental and theoretical studies of chemical bonds energies of two-atomic molecules the problems of methodical character do not appear what is confirmed by the results of our quantum-mechanical calculations. At the same time, in calculations of the interatomic chemical bonds energies there appear some difficulties even for two-atomic radicals. This is connected with the fact that they represent a system of atoms bound presumably by a covalent type which has some unpaired electrons. Therefore, to our mind, it is more expedient to conduct quantum-mechanical calculations of bonds energy of As-S two-atomic clusters-radicals under the condition of saturation of free valences by hydrogen atoms.

For such clusters we defined such theoretical values of chemical bonds energies: $E(As-As) = 0.3$ eV, $E(As=As) = 2.3$ eV, $E(As-S) = 2.3$ eV, $E(As=S) = 3.4$ eV.

On the whole, in accordance with the data of Table 2 in mass-spectra of As-S substances two-atomic vapor

particles will be realized in the form of the most stable complexes: As_2 , S_2 molecules and As=S radical.

3.3 Calculation of three-atomic clusters

The number of different isomeric forms of three-atomic clusters of As-S system is equal to 17. The majority of them are radicals (Table 3). All studied clusters as to the peculiarities of the structure are divided into three groups by us: chain-like – 11 clusters; radicals of triangular form – 4 clusters; triangular molecules – 2 clusters. The formation energies of the given clusters calculated by DFT method are given in Table 3. The results of calculations with fictitious H atoms are given in the table in brackets (As-H and S-H bonds energies do not enter the formation energy of clusters).

4. Discussion

Using the data of Table 3 we calculated the average energies of covalent chemical bonds which are realized in As_nS_m three-atomic clusters. For this we used the calculated data for molecules and clusters with saturating hydrogen atoms only. To our mind, to calculate the energies of chemical bonds simply from the formation energies of clusters-radicals is incorrect. This is conditioned by the fact that valence orbitals with single unpaired electrons realized in such atomic formations will influence the energies of their formation a lot. Besides, the contribution of such orbitals in different clusters will be different. As the chemical bonds energies in this case may be defined while taking into account the formation energies of the clusters different in the structure only, the nonequivalent role of these orbitals in different three-atomic clusters will give the unrealistic values of chemical bonds energies. Indeed, we calculated the energies of one and the same bond, for example As-S, from the formation energies of different combinations of three-atomic cluster-radicals. The obtained energy values were revealed to depend strongly on which output clusters are taken for calculations. We consider that because of this reason quantum-mechanical calculations give substantial discrepancies of chemical bonds energies in both two-atomic clusters with saturating hydrogen atoms and without them (see Table 2).

Taking into account the above mentioned, one can find the average As-S bonds energy, approximately equal to 2.3 eV from the formation energies of clusters 1 and 7 (Table 3). Then from the analysis of clusters 2 and 10 it follows that the average value $E_b(As-As) \approx 1.6$ eV. Correspondingly, from the data for clusters 5 and 6 we calculate the average value $E_b(S-S) \approx 2.6$ eV. If to assume that the determined average energies of single bonds are typical for other triple As_nS_m clusters, too, then for the energies of double chemical bonds there appear visible discrepancies when analyzing clusters-chains different in their chemical composition. In particular, $E_b(As=As) = 2.8$ eV in case of cluster 3 and $E_b(As=As) = 2.1$ eV in case of cluster 11. Similarly, $E_b(As=S) = 3.7$ eV in case of cluster 4 and $E_b(As=S) = 4.1$ eV for clusters 8 and 3.3 eV for cluster 9.

Table 3. The formation energies of different isomers of As-S three-atomic clusters (in brackets the energies calculated using saturating hydrogen atoms are indicated)

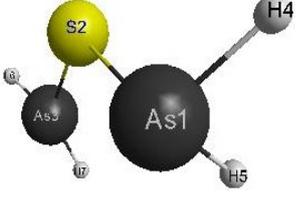
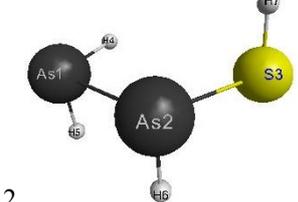
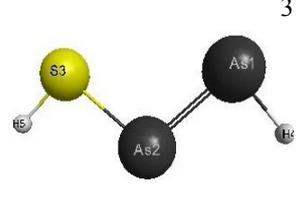
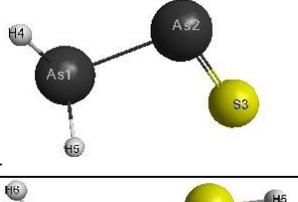
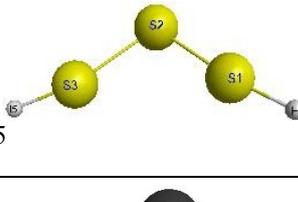
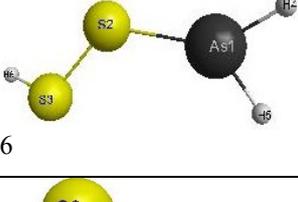
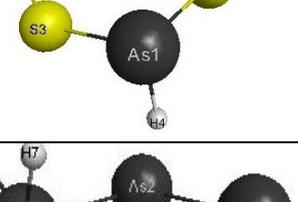
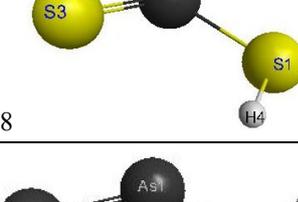
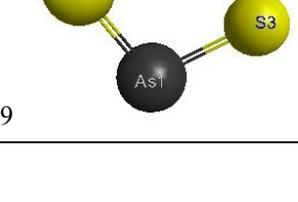
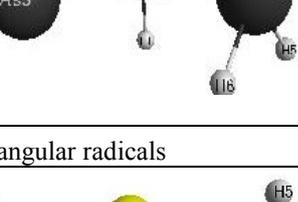
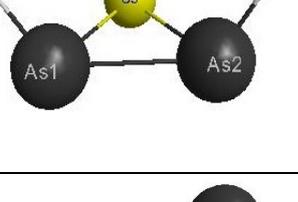
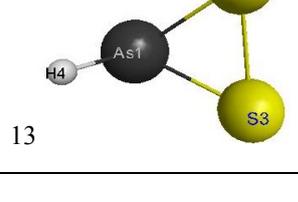
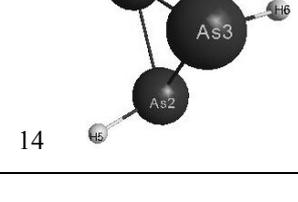
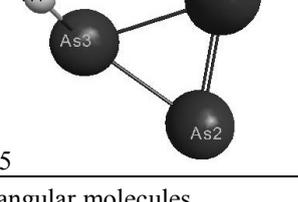
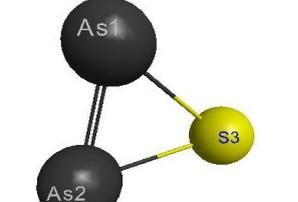
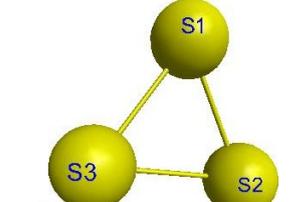
Chain-like clusters					
Cluster	E_f , eV	Cluster	E_f , eV	Cluster	E_f , eV
	3.6 (4.4)		– (3.8)		5.3 (5.1)
	4.5 (5.3)		4.4 (5.3) (8.9)		4.0 (4.7)
	5.0 (4.5)		6.2 (6.4)		6,6
	– (3.7)		6.6		
Triangular radicals					
	6.3 (5.8)		6.6 (6.3)		– (5.0)
	5.9 (5.7)				
Triangular molecules					
	6.4		6.8		

Table 4. Energies of chemical bonds (in eV) for small clusters of As-S systems with saturating hydrogen atoms (in brackets the data are given when saturating atoms are absent).

Bonds	Two-atomic molecules	Two-atomic radicals	Tree-atomic clusters			Experiment
			Chains	Triangles-radicals	Triangles-molecules	
S-S	–	2.3 (–)	2.6 (1.5; 2.2)	2.1 (2.5)	2.3	2.8; 2.3
S=S	4.4	–	–	–	–	4.3
As-As	–	0.3 (–)	1.6 (–)	1.7 (–)	–	2.1; 1.7
As=As	–	2.3 (0.9)	2.1; 2.8 (3.5)	2.3 (2.5)	2.2	–
As≡As	3.9	–	–	–	–	3.9
As-S	–	2.3 (1)	2.3 (1.8; 2.5)	2.1 (2.3)	2.1	2.6
As=S	–	3.4 (3.9)	3.7; 4.1; (2.9; 3.3)	–	–	–

According to such methodology we calculated the average energies of chemical bonds for two other groups of As_nS_m clusters. The results obtained are given in Table 4. For clusters-radicals the data are given in Table 4 for the case of saturation of their free valences by hydrogen atoms and without such saturation (the values in brackets). For comparison the data for two-atomic clusters studied earlier are given.

It is known that clusters with equilibrium geometric parameters have a minimum internal energy. Its basic part falls on the chemical bonds energies. The values of such energies for different bonds in the materials of As-S system were defined both theoretically and experimentally [6-8]. On the basis of data analysis of indicated literary sources we determined the average values of chemical bonds energies $E_b(As-S) = 250$ kJ/mol, $E_b(As-As) = 198$ kcal/mol and $E_b(S-S) = (267 - 277)$ kJ/mol at their equilibrium length for open chain-like configurations. The same values but in electron-volts are given in Table 4 (the first value corresponds to molecules-chains, the second – to molecules in the form of polyhedrons).

The analysis of the data given in Table 4 reveals some general relationships in the behavior of the obtained bonds energies, for each of which, however, there are exceptions. First, the calculated energies are close to experimental ones or within the limits up to 10 % are smaller than they are. Second, the calculated energies of certain bonding are close both to two-atomic and three-atomic clusters, with the exception of As-As bond. Third, both calculated and experimental energies of one and the same bond in triangular clusters are approximately 10-20 % smaller in comparison with clusters-chains (again, with the exception of As-As bond). That is, in ring-like and closed molecules-polyhedrons the bonds energies are a bit smaller than the values for chain-like atomic formations. To our mind, such distinction is conditioned by the fact that for closed atomic configurations the fixation of strict bonding lengths and angles between them is necessary, which are defined by the geometric structure and symmetry of appropriate clusters. And this is accomplished by introducing some “tension” into chemical bonds between atoms that defines the decrease in their energy. That is in ring-like and closed molecules-polyhedrons the bonds energies are a bit smaller than the values for chain-like atomic formations.

So, the value of the certain chemical bond energy depends on the shape of configuration (open or closed) of the atom net into which the given chemical bond is included. Such peculiarities were observed by the authors of other studies [12]. According to them the calculated average bonds values for As-S system are 10 – 20 % smaller for rings with 3 – 4 chemical bonds and they gradually, within the limits of error, become proportionate with bonds energies of chain-like clusters for more large-scale rings. The experimental data mentioned above confirm this relationship. But quantitative differences of experimental bonds energies in various types of atomic configurations of As – S materials are quite different. In particular, in As_4 molecules the average bond energy As-As in three-member rings is equal to 1.3 eV, that is 30 % smaller than the bonds energy of open configurations. The average bonds energy in molecule S_8 $E_b(S-S) = 2.3$ eV that is 20 % smaller than the energy of such bonds of open configurations. Such behavior of bonds energies is connected with enforcing the interaction between undivided pairs of atomic electrons which enter closed atomic complexes.

Taking into account the results of quantum-mechanical calculations obtained we consider that while modeling the structures of As-S vapor phase particles one should introduce errors into the energies of chemical bonds between atoms, which enter atomic configurations different in type. These errors have to gradually decrease the value of chemical bonds energy with decreasing the sizes of closed ring-like configurations in atomic complexes. But quantitative proportions of such decrease can't be defined well from the available data of three-atomic clusters only. This problem should be additionally analyzed after the calculations done for more large-scaled clusters of As-S system.

On the whole, among 17 probable three-atomic As_nS_m clusters the most energy-favorable are 7 atomic formations: one triangular As_3 molecule-radical (15 in table 3); one triangular S_3 molecule (17 in table 3); one triangular molecule and one triangular As_2S radical (16 and 12 in table 3); one chain-like molecule, one chain-like and one triangular AsS_2 radicals (9, 8 and 13 in table 3). To our mind, just in such structural form three-atomic particles exist in the vapor phase of As-S system. All other isomeric forms of three-atomic clusters in the vapor form

should be revealed with much less probabilities, as they are less energy-favorable.

Interesting is the fact that for all energetically most stable two- and three-atomic clusters the energies per one atom are the closest and distributed within the range from 1.9 to 2.3 eV/atom with the maximum at 2.0 – 2.1 eV/atom. That is within the limits of the average error of quantum-mechanical energy calculations of 10 % for two- and three –atomic As_nS_m clusters the energy per one atom is approximately equal for all atomic formations studied by us.

5. Conclusions

The first-principles investigations on small As_nS_m atomic clusters were performed using the density functional theory. As a result the formation energies have been calculated and chemical bonds energies of two- and three-atomic particles which are contained in the vapor phase under evaporation of As-S materials have been determined. It has been established that from seven probable two-atomic particles in the vapor with the greatest probability the clusters in the form of As_2 and S_2 molecules and AsS radical with a double bond should be realized. For As_nS_m three-atomic particles 17 different isomeric forms of As_3 , As_2S , AsS_2 and S_3 clusters have been studied, among which seven have much lower formation energy and, consequently, may be present in vapor flows of As-S materials. Five from such stable atomic particles have a triangular geometric form and two AsS_2 clusters have a chain-like form. Within the limits of the average error of quantum-mechanical energy calculations the energy per one atom for 10 most stable As_nS_m two- and three-atomic clusters is within the range from 1.9 to 2.3 eV/atom with the average value of ~2.1 eV/atom.

The calculated chemical bonds energies in As_nS_m clusters agree well with the experimental data available. Besides, in clusters-triangles the calculated bonds energies are 10 – 20 % less in comparison with chain atomic formations. Such behavior also correlates with experimental values of bonds energies of As-S materials. The results obtained by us show the efficiency of combining experimental mass-spectrometric studies with quantum-mechanical calculations to study the structure and energy of vapor flows under evaporation of covalent materials.

References

- [1] M. A. Popescu, *Physics and Applications of Disordered Materials*, INOE Publishing House, Stanford (2002).
- [2] J. Singh, K. Shimakawa, *Advances in Amorphous Semiconductors*, Gordon&Breach, London (2003).
- [3] M. Popescu, F. Sava, A. Lorinczi, *Chalcogenide Lett.* **1**, 111 (2004).
- [4] S. I. Simdyankin, S. R. Elliott, *Phys. Rev.* **B69**, 144202 (2004).
- [5] R. M. Holomb, V. M. Mitsa, *J. Optoelectron. Adv. Mater.* **6**, 1177 (2004).
- [6] A. V. Kolobov, *Photo-Induced Metastability in Amorphous Semiconductors*, Wiley-VCH, Weinheim (2003).
- [7] R. Holomb, V. Mitsa, P. Johansson, N. Mateleshko, A. Matic, M. Veresh, *Chalcogenide Lett.* **2**, 63 (2005).
- [8] R. Holomb, M. Veres, V. Mitsa, *J. Optoelectron. Adv. Mater.* **11**, 917 (2009).
- [9] O. Neugebauer, T. Zywiets, M. Scheffler, J. E. Northrup, C. G. Van de Walle, *Phys. Rev. Lett.* **80**, 3097 (1998).
- [10] R. Shiraishi, T. Ito, *Surface Sci.* **57**, 451 (1996).
- [11] M. Shen, H. F. Schaefer, *J. Chem. Phys.* **101**, 2261 (1994).
- [12] Y. Zhao, W.G. Xu, Q. S. Li, Y. Xie, V. Henry, H. F. Schaefer, *J. Comput. Chem.* **25**, 907 (2004).
- [13] K. Tanaka, K. Shimakawa, *Amorphous Chalcogenide Semiconductors and related materials*, Springer, New York (2011).
- [14] R. P. Wang, *Amorphous Chalcogenides: Advances and Applications*, CRC Press, London (2014).
- [15] A. Popescu, D. Savastru, M. Ciobanu, S. Miclos, V. T. Dolghier, *J. Optoelectron. Adv. Mater.* **13**, 1193 (2011).
- [16] A. Popescu, *Moldavian J. Phys. Scien.* **1**, 130 (2002).
- [17] V.P. Zakharov, V.S. Gerasimenko, *Strukturnije osobennosti poluprovodnikov v amorphnom sostojanii*, Naukova Dumka, Kiev (1976).
- [18] AA Popescu, V.T. Dolghier, I.I. Vataman, A.I. Buzdugan, K.M. Yndrychan, *Molekuljarnij phazovij analiz tonkich plenok amorphnich As_xS_{100-x} : Stekloobraznije poluprovodniki dlja optoelektroniki*, Ed. House "Shtynytsa.", Chisinau. P. 98-107 (1997).
- [19] K. White., B. Kumar., K.Rai Amarendra, Effect of deposition rate on structure and properties of As_2S_3 films, *Thin Solid Films.* **161**, 139 (1988).
- [20] A.S. Pashynkyn, A.D. Molodik, V.I. Belousov, S.S. Strelchenko, V.L. Fedorov, *Sostav para As_2S_3* , *Izv. USSR Academy of Sciences. Neorhanycheskye materials.* **16**, 1600 (1974).
- [21] T.P. Martin, Arsenic sulfide clusters, *Solid State Communication.* **44**, 111 (1984).
- [22] L. Gutzov, I. Avramov, On the mechanism of formation of amorphous condensates from the vapour phase (I). General theory, *J. Non-Cryst. Sol.* **16**, 128 (1974).
- [23] A.J. Leadbetter, A.J. Apling, M.F. Daniel, Structure of vapour-deposited amorphous films of arsenic chalcogenides, *J. Non-Cryst. Sol.* **21**, 47 (1976).
- [24] A.V. Dalekorey, Sh.Sh. Demesh, V.S. Kovtunenکو, R.O. Meshko, *Mas-spectry parovyh potokov pri ispareniji materialov systemi As-S*, *Naukovyj visnyk Uzgorod state university: physics.* **N31**, 79 (2012).
- [25] W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **100**, 12974 (1996).

- [26] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*; Wiley-VCH, Weinheim, (2000).
- [27] W. G. Xu, G. L. Li, G. Yu, Y. Zhao, Q.S. Li, Y. Xie, H. F. Schaefer, *J. Phys. Chem.* **A107**, 258 (2003).
- [28] A. Orthaber, A. F. Sax, K. A. Francesconi, *J. Comput. Chem.* **33**, 112 (2012).
- [29] A. H. Edwards, P. C. Taylor, K. A. Campbell, A. C. Pineda, *J. Phys.: Cond. Mat.* **23**, .
- [30] J. D. Kubicki, K. D. Kwon, K. W. Paul, D. L. Sparks, *European J. Soil Scien.* **58**, 932 (2007).
- [31] J. C. Rienstra-Kiracofe, G. S. Tschumper, H. F. Schaefer, S. Nandi, G. B. Ellison, *Chem. Rev.* **102**, 231 (2002).
- [32] D. L. Perry, *Handbook of Inorganic Compounds (Second Edition)*, CRC Press, London (2011).
- [33] D. Ralf Steudel, *Properties of Sulfur-Sulfur Bonds, Angewandte Chemie International Edition in English*, **14**, No10, 655 (1975).
- [34] Y. Mochizuki, K. Tanaka, *Chem. Phys. Lett.*, **274**, 264 (1997).
- [35] A. V. Nemuhin, B. L. Grigorenko, A.A. Granovckiy, *Vestnik MGU: Chem.* **45**, 75 (2004) (Russian).
- [36] G. I. Sabahova, *Fundamentalnye issledovaniya*, **No6**, 1137 (2013).
- [37] A. A. Taskin, *Phys. Tech. Poluprovodnikov.* **36**, 1163 (2002) (Russian).
- [38] S. S. Bacanov, *Structure Chemistry, Dialog, Moscow*, (2000) (Russian).
- [39] B. Meyer, *Elemental Sulfur*, **76**, 367 (1976).

*Corresponding author: ivancvp@yandex.ua