

SIMULATION OF RAMAN SPECTRA OF As_xS_{100-x} GLASSES BY THE RESULTS OF *AB INITIO* CALCULATIONS OF As_nS_m CLUSTERS VIBRATIONS

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We here present *ab initio* calculations on small As_nS_m clusters that are building blocks for the formation of continuous random networks (CRN) generally found in As_xS_{100-x} glasses. The calculations were performed by density functional theory (DFT). Geometries, vibrational frequencies, Raman intensities for the clusters have been calculated using the modified Stuttgart RLC ECP basis set at DFT/B3LYP level. Using the calculated and experimental data the relative contributions of different small clusters in the glasses structure matrix and the implications are discussed.

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1. Introduction

Amorphous materials or glasses exhibit physical properties different from crystalline solids. These differs arises from structure differs between glassy and crystalline solids. The structural origins of amorphous/glassy materials are very important in science up today [1]. Amorphous chalcogenides, in particular, show a number of interesting photo- and radiation-induced changes [2], not only structural, but furthermore also in their electronic and optical properties [3], that is the ground for various applications [1].

For chalcogenide glasses in general, the short-range order (SRO) has been used to obtain the nearest neighbor atomic configuration i.e. the coordination numbers, the bond lengths, and the bond angles [4]. The obvious next step is to try to identify the medium-range order (MRO) of these materials and thereby perhaps also to increase our understanding of defect structures [5]. However, for the MRO, there is no unique and obvious experimental technique that can be used single-handedly. Raman spectroscopy has been an important tool for investigating the properties of chalcogenide glasses for over two decades. Application of the Raman tool has ranged from early investigations of the SRO in the glasses, later to support MRO hypotheses, and very recently as a probe of network rigidity [4,5,6]. Recently, *ab initio* methods have been very successful in calculating the structural and vibrational properties of materials in general, much due to the increase in computational power and their inherent possibility of high accuracy in the solving of the Schrödinger equation [7]. By combining calculated vibrational spectra for different clusters, which together can form the CRN of the glass, with experimental spectra we aim to define and understand not only the SRO, but furthermore the MRO structure and properties of the glassy systems.

In the present work, first of all we used first-principles methods based on the HF approximation, and subsequently add DFT to increase the accuracy, to study the optimal geometries, vibrational frequencies, and Raman intensities of a series of the most important clusters for the As-S glass system. Using computed vibrational spectra of different atomic clusters the evolution of their Raman spectra were find. Using knowledge gathered above, the broad stretching vibration bands found in the Raman spectra of g- As_xS_{100-x} glasses were analyzed.

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2. Experimental

The glasses for the investigation were synthesized by melt quenching and cooled with cooling rate $V=1$ K/s.

Right angle Raman spectra were measured with the use of DFS-24 spectrometer. A spectral slit width was 1 cm^{-1} . The polarization of incident light was parallel and that of scattered light was normal to the scattering plain. Excitation laser beam 632.8 nm was used.

3. Calculations

The calculations were carried out with the quantum-chemical program package GAMESS (US) [8]. The self-consistent field calculations were HF and subsequently DFT (taking into account the electron exchange-correlation energy). All initial calculations were made at the HF level. A hybrid functional, the Becke's three-parameter functional (B3) [9] that defines the corrected exchange functional {proposed by Becke [10] and the widely used gradient-corrected correlation functional of Lee, Yang, and Parr (BLYP) [11]} as a linear combination of Hartree-Fock, local and gradient-corrected exchange terms (B3LYP) was used in the DFT part of the study. The basis set used for the As and S atoms for the HF calculations was 6-31G* [12]. For the DFT calculations the Stuttgart Relativistic Large Core ECP (Stuttgart RLC ECP) [13] basis set was used. The Stuttgart RLC ECP basis was modified by the addition of one polarization d-function (*) identical to that of the 6-31G* basis set.

4. Model

To study the Raman modes of the As-S glasses we used finite clusters of atoms expected to be important in the glasses. Hydrogen atoms saturated the dangling bonds of the clusters in order to improve the model of chemical environment within the clusters. The model cluster geometries are shown in Fig. 1.

To allow atomic relaxation all cluster geometries were optimized using standard algorithms. All geometry optimizations were followed by second derivative calculations using the same method and basis set to verify the structures found as true minima. The vibrational frequencies, Raman activities, and eigenvectors were computed using standard techniques for the closed As-S clusters. For the H-terminated clusters, we eliminate the influence of the hydrogen atoms on the vibrational spectra by assigning the masses of these atoms a very small value ($\sim 10^{-4}$ a.u.). In addition, the dipole derivatives and alpha polarizability tensor elements for the H atoms were changed to zero and the Raman spectra were re-calculated using these modified tensors. Consequently, the resulting spectra do not practically contain any influence from the hydrogen atoms.

4. Result and discussion

A. Optimal geometries, total energies and formation energies

Selected geometry parameters for the As_nS_m clusters are listed as mean values in Table 1. All As and S atoms of the clusters were used for calculating the mean values of the bond distances and bond angles.

B. Calculated and modelled vibrational Raman spectra

The vibrational spectra for major part of As_nS_m clusters were calculated using all the HF/6-31G* and DFT (BLYP and B3LYP)/Stuttgart RLC ECP methods. But we present here the frequency position of As-S stretching modes calculated using DFT (B3LYP)/Stuttgart RLC ECP level of theory only. This method are in best accordance with experimental Raman spectra. As for the frequencies, no scaling was applied on the DFT results. After calculation vibration frequencies and their Raman intensities we have added independent Gaussian-shape functions with a halfwidth of 10 cm^{-1} to each computed peak and integrated the spectra. The resulting modelled Raman spectra of As_nS_m clusters shown in Fig. 3, Fig. 4, Fig. 5 together with experimental Raman spectra.

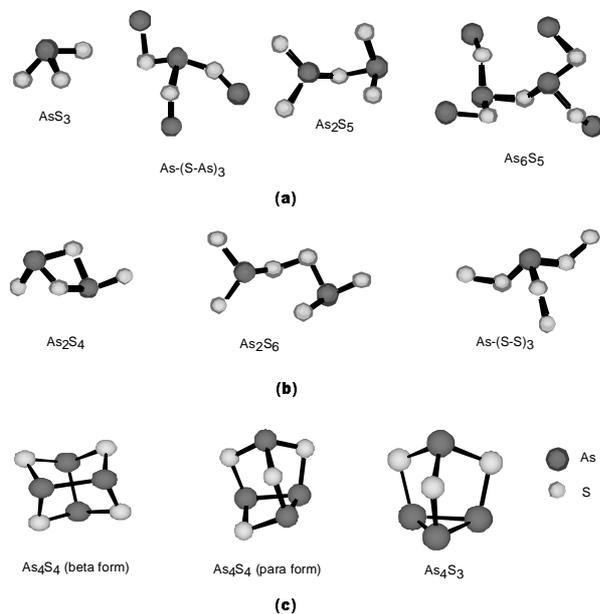


Fig. 1. Geometry models of the arsenic sulfide As_nS_m clusters: standard clusters obtained as differently sized structures from of As_2S_3 crystal (a); defect clusters with bonds not present in the structure of the crystalline As_2S_3 , expected to be important for S-rich (b), and for As-rich (c) As-S glasses. (Saturating hydrogen atoms and corresponding bonds are not shown for clarity).

Table 1. Mean values of optimized geometry parameters of As_nS_m clusters calculated at RHF/6-31G* level.

Cluster	Bond distances [\AA]		Bond angles [degree]		
AsS_3	As-S	2.236	S-As-S	97.3	
As-(S-As)_3	As-S	2.247	S-As-S	100.3	
			As-S-As	102.0	
As_2S_5	As-S	2.239	S-As-S	98.7	
			As-S-As	100.6	
As_6S_5	As-S	2.245	S-As-S	99.1	
			As-S-As	100.0	
As_2S_4	As-S	2.249	S-As-S	95.9	
			As-S-As	86.8	
As_2S_6	As-S	2.242	S-As-S	97.8	
	S-S		2.076	As-S-S	99.6
As-(S-S)_3	As-S	2.246	S-As-S	99.8	
	S-S		2.068	As-S-S	102.4
As_4S_4 (beta)	As-S	2.223	As-As-S	100.1	
	As-As	2.500	S-As-S	95.1	
			As-S-As	99.5	
As_4S_4 (para)	As-S	2.233	S-As-S	101.6	
	As-As		2.444	As-As-S	96.6
				As-As-As	85.3
				As-S-As	103.1
As_4S_3	As-S	2.221	S-As-S	99.3	
	As-As		2.429	As-As-As	60.0
				As-As-S	102.4
			As-S-As	104.0	

C. Raman spectra of As_xS_{100-x} glasses and As_nS_m cluster's spectra evolution.

The current interest in Raman spectra of glass systems is due to the excellent relationships that can be found for the local structure (i.e. SRO) and the vibrational spectra of disordered materials. To understand the atomic order in amorphous or glassy As_2S_3 it is important at first to examine the atomic arrangements in its crystalline counterpart $c-As_2S_3$.

To compare our calculated spectra, a detailed analysis of the broad stretching band of As_xS_{100-x} ($x=30, 40, 45$) glasses is made. Ultimately, such analysis can be helpful to understanding SRO and MRO of these materials. The broad Raman band of $g-As_2S_3$ (Fig. 2) consists of at least three individual peaks with maxima at 306, 340, and 385 cm^{-1} , as obtained by peak fitting. The Raman spectrum of polycrystalline As_2S_3 has four unique peaks in this region centered at 292, 310, 355, and 382 cm^{-1} . Descriptions of the structure of $a-As_2S_3$ are most often beginning with an AsS_3 pyramidal unit as in $c-As_2S_3$. The arguments for the existence of such units are based on vibrational data, and there is general agreement that these pyramids provide a convenient framework for a further discussion of the glass network. Using a molecular model Lucovsky and Martin [14] were able to determine empirical force constants associated with bond length and bond angle deviations. They also suggested that the AsS_3 pyramid structure is the basic building block of $a-As_2S_3$.

When the Raman spectrum of As_2S_3 glass is analysed we assume that the As-S stretching vibration region of polycrystalline As_2S_3 is similar to the same region of the glass. The vibrational modes are, however, significantly broadened in the disordered phase.

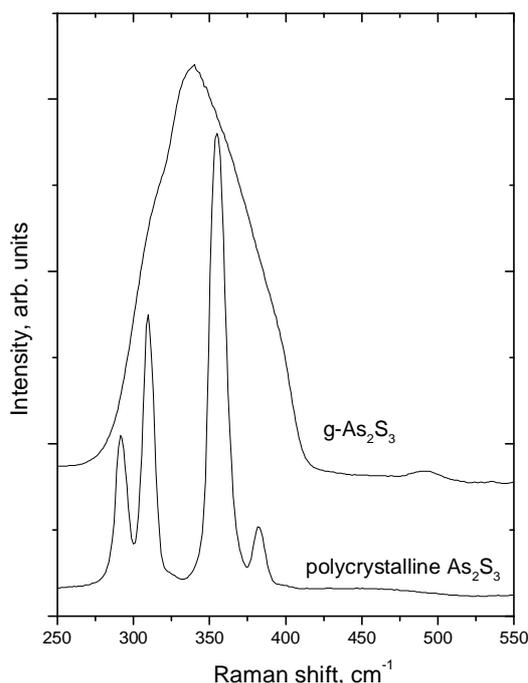


Fig. 2. Experimental Raman spectra of glassy and polycrystalline As_2S_3 .

However, the vibrational properties of $a-As_2S_3$ and furthermore As_xS_{100-x} glassy system are not yet well understood. The vibrational modes of $a-As_2S_3$ basically consist of many different stretching modes in the range from 300-400 cm^{-1} and bending modes below 200 cm^{-1} . The large broadening of experimental band of stretching modes in the Raman spectrum of $a-As_2S_3$ compared with $c-As_2S_3$ can certainly not be understood only by deviations of geometry parameters (bond lengths and bond angles) in pyramidal units. Thus, variation in As-S bond lengths in $a-As_2S_3$ can be expected to be large, but on the contrary great deviations in As-S bond lengths are not found experimentally [15,16]. Furthermore, the distribution in apex angles produces only a slight

broadening of the mode frequencies and cannot generate the continuous Raman spectrum observed experimentally.

The stretching mode band observed has three main components at 310, 340, and 380 cm^{-1} . The two lowest frequency modes are attributed to asymmetric and symmetric stretching in the AsS_3 pyramidal unit, respectively [14], but the highest frequency mode is suggested to be due to interactions between pyramidal units.

The origin of the bending modes can hardly be explained by studying the vibrations of one pyramidal unit only. The very LF peak (*i.e.* the Boson peak) of the Raman spectrum ($\sim 25 \text{ cm}^{-1}$) is interpreted as the rigid layer shear mode [17], and the discussion on the nature of this peak is still vivid [18]. Structural investigations show that regions of well-ordered atoms accommodated in glasses are found in larger domains than the dimension of one structural unit (s.u.). This brought the appearance of the concept of medium-range order (MRO) in glasses [19,20,21].

By optical structural research, using low frequency (LF) Raman spectra, the cluster dimensions (dimensions of the MRO) can be calculated and related with the CRN model radius of structural correlation [18,22]. These facts and our torsional type vibrations hypothesis [18] and previous investigations of Raman spectra of chalcogenides implanted into pores of zeolites [23], together indicate that the vibrational spectra of $g\text{-As}_2\text{S}_3$ (and $\text{As}_x\text{S}_{100-x}$ glass system) should be able to be interpreted from large cluster models.

The broadening of peaks in the spectra of glasses are due to constrained and therefore distorted AsS_3 s.u. Such a simple interpretation, based on comparison with crystalline (polycrystalline) analogues, using AsS_3 units only and crystal-like rings, is not sufficient to describe the complicated nature of the broad main band in the As_2S_3 glass and besides it is difficult to apply for different glass compositions or to understand the MRO of these glasses. Larger clusters based on variously interconnected AsS_3 pyramids are needed for an interpretation of the broad band of $g\text{-As}_2\text{S}_3$ and to understand the MRO in these materials.

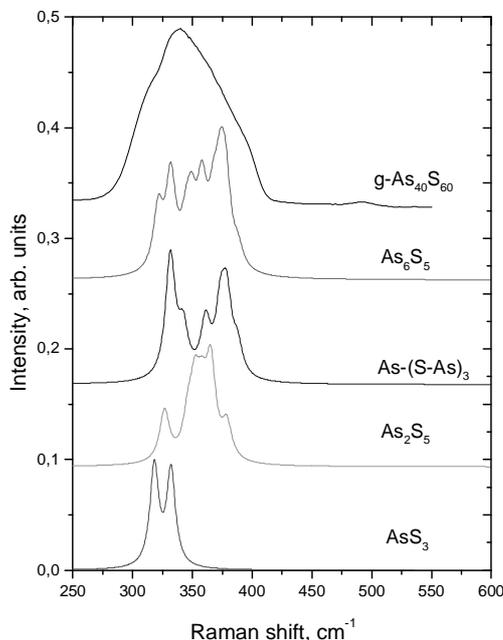


Fig. 3. Raman spectra of $g\text{-As}_2\text{S}_3$ and evolution of Raman spectra of different sizes As_nS_m clusters (See. Fig. 1, a).

As seen in Fig. 2 there are many differences between Raman spectra of polycrystalline As_2S_3 and the glass samples. In Fig. 3 we show the experimental Raman spectra of As_2S_3 glass together with our calculated data. The calculated Raman spectra of the As_nS_m clusters which can form CRN of the $g\text{-As}_2\text{S}_3$: AsS_3 , $\text{As}(\text{S-As})_3$, As_2S_5 , As_6S_5 , are shown. The calculations show no features outside the region of the band found experimentally and accurately describe the

experimental Raman spectra of the As_2S_3 glass in the low frequency side of the broad band. Fig. 3 shown evolution of Raman spectra of different sized As_nS_m clusters also.

The experimental spectrum contains at least three bands centered at 306 and 340, and 385 cm^{-1} . The first of them can be attributed to a mode of asymmetric vibrations in simple AsS_3 cluster (318 cm^{-1}). The second band can be attributed to integrated Raman spectra of other three clusters: As_2S_5 , $\text{As}-(\text{S}-\text{As})_3$, and As_6S_5 . The band at 385 cm^{-1} found by the peak fitting of the $g\text{-As}_2\text{S}_3$ spectra can also be attributed to an As-S stretching mode. The frequency position is very similar to that observed for polycrystalline As_2S_3 (383 cm^{-1}). A high frequency mode can be found in the calculated spectra of the As_6S_{12} ring cluster (not presented here), but as we can see $\text{As}-(\text{S}-\text{As})_3$ and As_6S_5 has peaks in their integrated Raman spectra at 377 and 375 cm^{-1} respectively. They can influence to 385 cm^{-1} mode of $g\text{-As}_2\text{S}_3$ also. Finally, we turn attention to broadened of experimental Raman spectra by influence of differently sized clusters.

In order to study excess sulfur As-S glasses we use defect clusters, using S-S bond or non-typically connected AsS_3 pyramids not to be found in the structure of $c\text{-As}_2\text{S}_3$. In Fig. 4 we show the Raman spectrum of $g\text{-As}_{30}\text{S}_{70}$ together with calculated data. The calculated Raman spectra in Fig. 9 are from clusters describing defect structures in the glass - "wrong" chemical S-S bonds (As_2S_6 and $\text{As}-(\text{S}-\text{S})_3$), and the cluster As_2S_4 built by two edge-sharing AsS_3 pyramids. The Raman spectrum for excess sulfur $\text{As}_x\text{S}_{100-x}$ glass, $x=30$ (Fig. 4), show a continuous increasing of the two bands at 472 and 494 cm^{-1} with lowering x . These are related to the presence of S-S bonds [24]. The characteristic stretching modes at 456 cm^{-1} and 475 cm^{-1} found experimentally were attributed to S_n chains and S_8 rings respectively [25]. According to our calculation results the observed maximum at 472 cm^{-1} can be assigned to S-S stretching vibrations in an As_2S_6 cluster ($\sim 467\text{ cm}^{-1}$). Therefore the mode at 472 cm^{-1} is attributed to stretch vibrations in S_8 rings [24,26] and in As_2S_6 clusters. Some authors assigned the band at 494 cm^{-1} to presence of S-S bonds in S dimers in the glass structure [27]. Our results show that this band can be attributed also to the presence of S-S bond at the ends of $\text{As}-(\text{S}-\text{S})_3$ clusters ($\sim 487\text{ cm}^{-1}$). As bands at 472 and 494 cm^{-1} are not found for $x=40$, while obtained in the clusters $\text{As}-(\text{S}-\text{S})_3$, and As_2S_6 , we concluded that these clusters are not useful building blocks to obtain the MRO of $\text{As}_x\text{S}_{100-x}$ ($x \geq 40$).

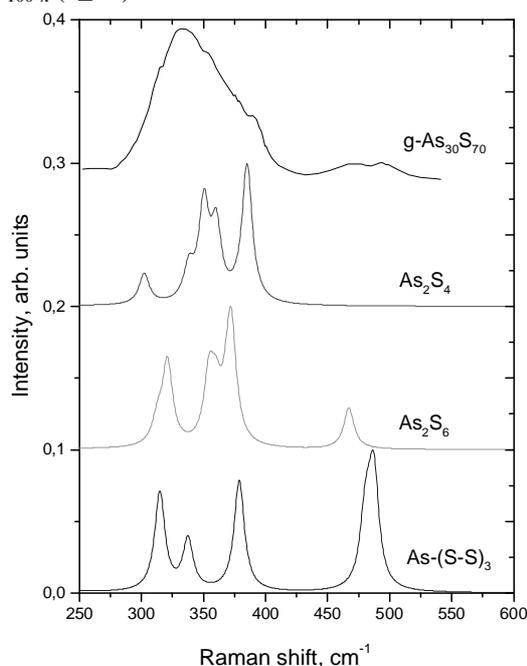


Fig. 4. Raman spectra of $g\text{-As}_{30}\text{S}_{70}$ and evolution of Raman spectra of defect As_nS_m clusters (See Fig. 1, b).

In the spectra of sulfur excess glass ($g\text{-As}_{30}\text{S}_{70}$) three peaks centered at 317, 356, and 392 cm^{-1} are observed. According to our calculations the first can be attributed to the $\text{As}-(\text{S}-\text{S})_3$

and/or As_2S_6 clusters. As can be seen from Fig. 4, both of these clusters in their integrated Raman spectra has peak ($\sim 320\text{ cm}^{-1}$ for As_2S_6 cluster, and $\sim 315\text{ cm}^{-1}$ for $\text{As}-(\text{S}-\text{S})_3$). The two second experimental peaks at 356 cm^{-1} and 392 cm^{-1} can be connected with As-S stretching vibrations in As_2S_4 ($\sim 350\text{ cm}^{-1}$, and $\sim 385\text{ cm}^{-1}$ respectively) but As-S stretching vibrations in As_2S_6 ($\sim 357\text{ cm}^{-1}$, $\sim 372\text{ cm}^{-1}$) and in $\text{As}-(\text{S}-\text{S})_3$ ($\sim 379\text{ cm}^{-1}$) can also have influence.

With increasing As content in As-S glasses we can see the main changes in Raman spectra (Fig. 5).

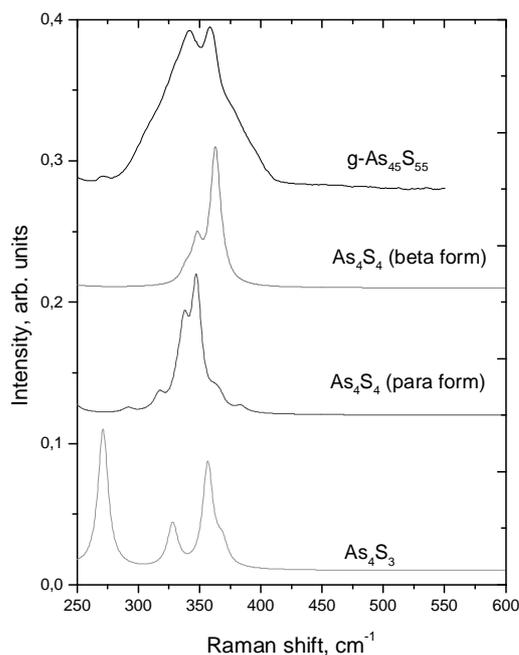


Fig. 5. Raman spectra of $g\text{-As}_{45}\text{S}_{55}$ and evolution of Raman spectra of defect As_nS_m clusters (See Fig. 1, c).

There are three independent peaks in the Raman spectra of $g\text{-As}_{45}\text{S}_{55}$ centered at 270, 340, and 360 cm^{-1} . Our calculated data shown that first of them can be attributed to vibrations in As_4S_3 molecule. This cluster have peak in the integrated Raman spectra at 271 cm^{-1} what is best accordance with experiment. The last experimental Raman mode of $g\text{-As}_{45}\text{S}_{55}$, 340 cm^{-1} , are the same in nature as in $g\text{-As}_2\text{S}_3$. The third peak (360 cm^{-1}) is unique and by resulting of calculations are shown the presence of As_4S_4 clusters in the glass network. There are three forms of As_4S_4 molecules: i) alpha and beta form and ii) para form (realised in alpha, beta- and para- realgar crystals respectively). As can be seen from Fig. 1, they have different structures and furthermore vibrational spectra. Beta form of As_4S_4 cluster have peak in the Raman spectra at 363 cm^{-1} by the calculations that is good accordance with experimental Raman spectra of $g\text{As}_{45}\text{S}_{55}$.

6. Conclusions

We have used first principles calculations and molecular cluster model to study the SRO and the MRO in chalcogenide glasses. The stretching type vibrations in the Raman spectra of As-S glasses having different compositions have been determined.

There was shown the evolution of vibrational spectra of differently sized As_nS_m clusters, that is very important for understanding broadening-effect of the glasses' Raman spectra. The calculations have shown that for S-rich As-S glasses the $\text{As}-(\text{S}-\text{S})_3$, As_2S_6 , and As_2S_4 clusters play important role in their structure. Finally, it is possible to conclude that in the structure of As-rich As-S glasses As_4S_3 and As_4S_4 (beta form) clusters are present.

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