

STRUCTURE OF As_2S_3 GLASS IN ELECTRONICALLY EXCITED STATES

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Using clusters of atoms that model the local structure of amorphous As_2S_3 ($a\text{-As}_2\text{S}_3$), we present a model of the structure of $a\text{-As}_2\text{S}_3$ in its electronically excited states. We have shown that in the spin-singlet excited state the one of the As-S bonds in the model cluster is elongated, but the elongated bond still has a substantial bonding character. As the excited state undergoes a spin flip, the complete breaking of the As-S bond occurs, generating the self-trapped triplet exciton. This singlet-to-triplet exciton conversion and the concomitant electron-hole recombination will induce the photoinduced phenomena observed for $a\text{-As}_2\text{S}_3$.

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1. Introduction

Photoinduced effects, e.g. photochromism, photopolymerization, and photo-degradation, in amorphous semiconductors have attracted much attention since they can offer the basis for various electronic switching and memory devices, optical memories, and imaging applications [1,2,3]. Such photoinduced phenomena are observed in many amorphous insulators as well, suggesting that these phenomena are characteristics of solids without long-range order. It is quite likely that photoexcitation of charge carriers plays a vital role in exhibiting such interesting effects in amorphous materials. However, a detailed knowledge about the photoexcitation processes along with concomitant photoinduced structural and chemical changes is still missing.

The photoexcitation process will be launched by creating pairs of free electrons and holes when the energies of photons are greater than that of the band gap of the material. As for the fate of free photoexcited charge carriers, the following two processes can be envisaged [2]: one is the process in which a photoexcited electron and a hole are spatially well separated in the lattice of the material of interest, and the other is the process in which the two oppositely charge carriers behave as a pair. The former process will be promoted by self-trapping of single carriers, i.e. self-trapping of holes or electrons. In previous papers [4,5], we calculated equilibrium geometry of the electron- and hole-trapping centers in amorphous As_2S_3 ($a\text{-As}_2\text{S}_3$) on the basis of the *ab initio* molecular orbital method using clusters of atoms that model the localization of the respective charge carriers. These calculations allow us to investigate how these charged defects change their atomic configurations on charge-trapping and resulting recombination processes. From these previous calculations, we found the following: (1) The model cluster consisting of connected AsS_3 trigonal pyramids is apt to trap an electron, followed by breaking of one of the As-S bond in AsS_3 units. (2) A metastable fivefold-coordinated As site, having four As-S bonds and one As-As bond, is formed after recombination of the negatively charged defect [see Fig. 1(a)]. (3) This fivefold-coordinated As center is an unprecedented coordination defect, which exhibits a lower electronic excitation energy than the normal AsS_3 trigonal bipyramidal unit by ~ 1 eV. It is hence quite likely that this defect center is responsible for the photodarkening effect $a\text{-As}_2\text{S}_3$, namely, a shift of the absorption edge to lower energies upon near-band-gap illumination [6]. (4) Another form of metastable defects, which comprises a fourfold-coordinated As unit and a nonbridging S atom [see Fig. 1(b)], is also possible to exist. This fourfold-coordinated As center yields much lower excitation energies by ~ 0.8 eV than the fivefold-coordinated As center, explaining the observed photoinduced midgap absorption below

~ 2 eV [7]. Thus, we have shown that localization of charge carriers is a reasonable model accounting for possible photostructural changes in a -As₂S₃.

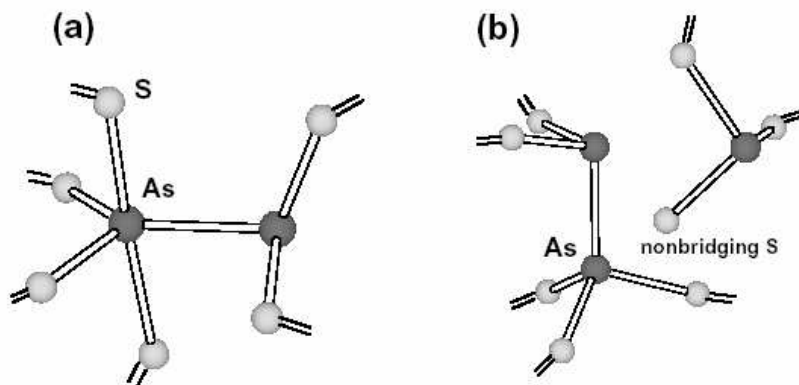


Fig. 1. Models of metastable coordination defects proposed in Refs. 4 and 5. (a) a fivefold-coordinated As defect; (b) a fourfold-coordinated As defect.

In this paper, we investigate the other process of photoexcitation of charge carriers in a -As₂S₃, i.e. the formation of an exciton, in which an electron and a hole coexist in an electronically excited state. In comparison to ground state electronic states, *ab initio* molecular orbital methods for determining the wave functions and energies of atoms and molecules in excited states are challenging, and modeling excited states and predicting their properties are rather a difficult problem. One promising method to obtain excited-state electronic structures is the so-called configuration interaction (CI)-singles approximation [8], where modeling of excited states as a linear combination of all determinants formed by replacing a single occupied orbital of a Hartree-Fock (HF) ground state with a virtual orbital is performed. This is the simplest level of theory which can be used to include some of the effects of electron correlation via the mixing of excited determinants. CI-singles is hence regarded as an adequate zeroth-order treatment for many of the excited states of atoms and molecules. It has been shown that the “CI-singles” wave functions can be used to compute efficiently the analytic first derivative of the energy in order to obtain optimized geometries for a wide range of molecules in their excited states [8,9]. In this work, we therefore obtain the equilibrium structure of the first singlet excited state of clusters of atoms modeling the local structure of a -As₂S₃ using the CI-singles theory. We then discuss how the atomic configurations in the excited state can be relaxed into a metastable or a stable structure.

2. Models and calculational procedures

A cluster of atoms having seven AsS₃ units is used as a model of the ideally well-annealed network of a -As₂S₃ (model I). As shown in Fig. 2(a), model I consists of two subunits having four and three connected AsS₃ units, respectively, that interact with each other through weak nonbonding interactions or van der Waals forces. Thus, model I takes account of both intralayer and interlayer interactions. The outermost S atoms in the cluster were terminated by H atoms. Such H termination is employed to suppress the “surface” effect arising from the dangling bonds of the outermost atoms and has been shown to be useful to eliminate the unsaturated bonds of clusters modeling the local structure of the corresponding amorphous system. In order to calculate the geometry in the ground electronic state, we first optimized the geometry of model I at the Hartree-Fock (HF) level with the 6-31G(d) basis set. Next, the geometry of model I was reoptimized by the CI-singles technique using the 6-31G(d) basis set to obtain information about the geometry of the cluster in its electronically excited state. In this work, we calculated the geometry of the first singlet excited state by the use of analytic CI-singles gradients. The resultant optimized cluster in the spin-singlet excited state is referred to as model II.

3. Results

The optimized structure of model I, which models the local structure of a -As₂S₃ in its ground state, is depicted in Fig. 2(a). It has been found that the average As–S distance calculated for model I is 2.242 Å, in reasonable agreement with the average As–S bond distance observed for annealed a -As₂S₃

film (2.280 Å [10]). It should also be noted that the average As–S–As bond angle (97.3°) calculated for model I agrees well with the corresponding observed value (~100° [10,11]). These results strongly suggest that the present HF/6-31G(d) geometry of model I reasonably represents the actual well-annealed network of *a*-As₂S₃.

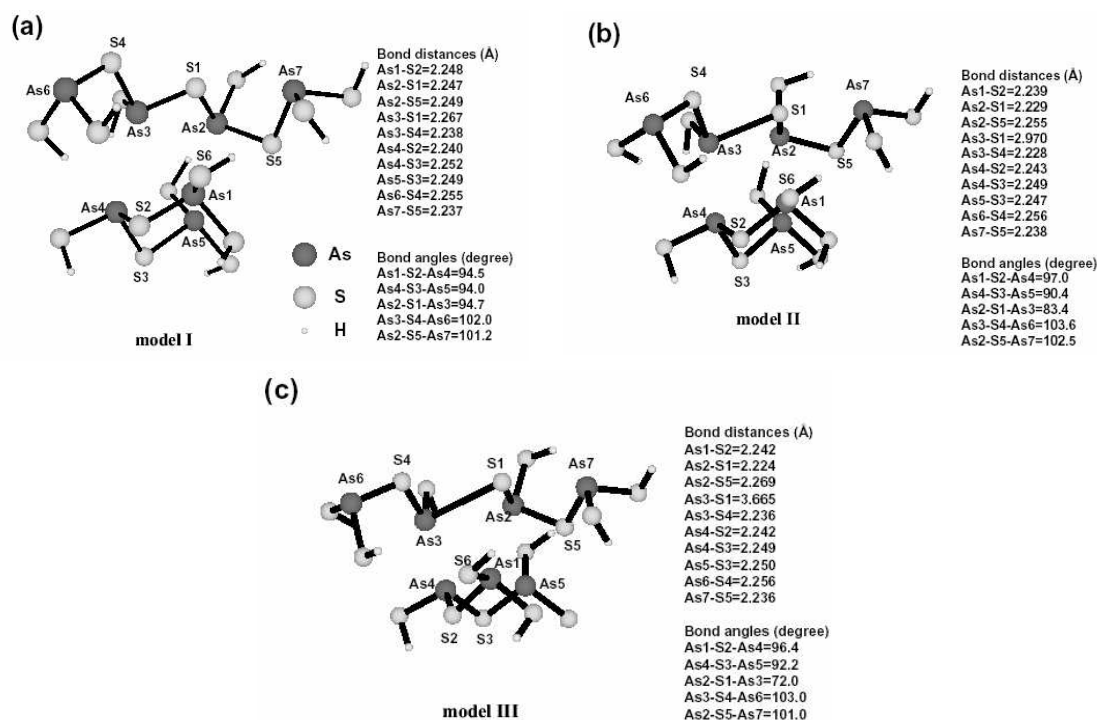


Fig. 2. Optimized geometries of the As₇S₁₆H₁₁ cluster in its ground and excited states. (a) a ground-state configuration optimized at the HF/6-31G(d) level; (b) a spin-singlet excited state optimized at the CI-singles/6-31G(d) level; (c) a spin-triplet excited state optimized at the unrestricted HF/6-31G(d) level.

We next turn to the CI-singles geometry of the model cluster [see Fig. 2(b)] to investigate possible structural changes resulting from the transition between a ground state and a spin-singlet excited state. It is clear from Fig. 2(b) that one (As3–S1) of the As–S bonds in the cluster becomes longer by ~0.7 Å as we go from model I to model II. This implies that after absorption of a photon and subsequent excitation of an electron into the conduction band, the attractive interaction between As and S atoms in one of the As–S bonds decreases, forming such a longer As–S bond as shown in Fig. 2(b). It should be noted, however, that the bond overlap population for the elongated As3–S1 bond is calculated to be 0.413, which is comparable to that of the other usual As–S bonds (~0.42) in the same cluster. It is hence quite likely that in such a spin-singlet excited state, an electron and a hole will not be localized at particular atoms but will be delocalized over the As3 and S1 atoms in model II, which is certainly a typical characteristic of a bound electron-hole pair (singlet exciton) [12].

4. Discussion

We have shown that the creation of a singlet exciton induces elongation of one of the As–S bonds in the network of *a*-As₂S₃, although the elongated bond is not expected to be broken in terms of its bond overlap population. It is hence interesting to investigate whether such a spin-singlet excited state will induce further structural rearrangements after the subsequent electron-hole recombination or will lead to the formation of metastable defects. To investigate a possible relaxation process of the spin-singlet excited state, we further optimized the structure of model II using the conventional HF wave function in its spin-singlet state. That is, we optimized the geometry of the cluster using the configuration of model II as an initial geometry at the HF/6-31G(d) level by assuming that the total

charge and multiplicity are 0 and 1, respectively.

As a result of the geometry optimization, it has been found that the geometry of model II returns to the geometry that is very similar to the ground state configuration, namely, model I. This suggests that the structural change seen in the spin-singlet excited state (model II) is not large enough to allow further structural reorganizations during the electron-hole recombination process. It can hence be concluded that the formation of the singlet exciton and its resulting singlet-to-singlet decay process may not induce any photoinduced changes in the structure of *a*-As₂S₃.

Another possible fate of the singlet exciton is a single-to-triplet exciton conversion, which has been observed on the subpicosecond time scale in several materials such as amorphous silica [12] and polydiacetylene [13]. To investigate the effect of a spin flip on the excited state structure of *a*-As₂S₃, we then calculated the geometry of the model cluster in the spin-triplet excited state using a conventional Unrestricted HF (UHF) wave function with the 6-31G(d) basis set. The optimized geometry of the cluster in the triplet state (model III) was calculated using the atomic configurations of model II as an initial geometry, and the resultant optimized structure is shown in Fig. 2(c).

One sees from Fig. 2(c) that the structural change seen in model III is similar to that in model II; that is, one of the As-S bond is elongated in the respective excited states. However, the degree of elongation in model III is much greater than that in model II. The separation between As₃ and S1 atoms in model III is 3.665 Å, whereas the corresponding interatomic separation in model II is 2.970 Å. It should also be worth mentioning that in model III the spin densities of the As₃ and S1 atoms are calculated to be 0.971 and 1.006, respectively, and the bond overlap population between these two atoms is -0.026. These results indicate that in the spin-triplet excited state, the bond between As₃ and S1 is almost completely broken to form a twofold-coordinated As and a nonbridging S and that two unpaired electrons are localized respectively on these two types of undercoordinated atoms. Thus, it can safely be said that in model III the exciton is self-trapped to break one of the As-S bonds in the network of *a*-As₂S₃. Previously, the formation of such a self-trapped exciton accompanied by breaking of an As-S bond has been suggested to occur in the photoinduced process of *a*-As₂S₃ [2,14,15]. To our knowledge, however, this is the first theoretical work showing the creation of the self-trapped exciton and its effect on the network structure of *a*-As₂S₃.

We [4,5] have already demonstrated that when As and S atoms in one of the As-S bonds in the *a*-As₂S₃ network are separated over 3.4 Å, the As and S atoms do not return to the original atomic configurations but to reorganization such to form coordination defects fivefold-coordinated As and fourfold-coordinated As units as mentioned in the Introduction. Considering that the As-S bond distance increases from ~2.2 to ~3.7 Å upon self-trapping of an exciton, we suggest that the presence of self-trapped exciton in the network structure of *a*-As₂S₃ leads to the formation of similar fivefold- and/or fourfold-coordinated As defects during the subsequent electron-hole recombination processes. It is hence probable that the single-to-triplet exciton conversion as well as self-trapping of single carriers induces substantial atomic rearrangements. These atomic rearrangements accompanied by the breaking of the As-S bond will result in the formation of the coordination defects that are most likely responsible for the observed photoinduced effects in *a*-As₂S₃.

5. Conclusions

We have carried out ab initio quantum chemical calculations on clusters of atoms modeling the network of *a*-As₂S₃ to investigate the structure in its electronically excited states. We have found that in the spin-singlet excited state one of the As-S bonds in the cluster is elongated, resulting in the As-S bond distance of 2.970 Å. In such an excited state, however, the elongated As-S bond still has a considerable bonding character; an electron and a hole are delocalized over several As and S atoms. It has further been found that as the exciton undergoes a spin flip the S atom moves away from one of the As atoms to which it was bonded and that the associated electron (hole) becomes localized on that As (S) atom, generating the spin-triplet excited state. Thus, the exciton is self-trapped in the *a*-As₂S₃ network, leading to the breaking of the As-S bond. These results suggest that the singlet-to-triplet exciton conversion plays a role in inducing the photoinduced effects observed in *a*-As₂S₃.

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