Electronic excitation and transient defects in As_2S_3 glass

Uchino, Takashi

Elliott, S.R.

(Citation)
Physical Review B,67(17):174201-174201

(Issue Date)
2003-05

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90000244

Electronic excitation and transient defects in As_2S_3 glass

T. Uchino
Department of Chemistry, Kobe University, Nada-ku, Kobe 657-8501, Japan

S. R. Elliott
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

(Received 5 September 2002; revised manuscript received 13 March 2003; published 5 May 2003)

We have carried out *ab initio* quantum-chemical calculations on clusters of atoms modeling the structure of As_2S_3 glass in its electronically excited states. In the spin-singlet excited state, one of the As-S bonds in the model cluster is preferentially elongated, but the resultant elongated bond still has a substantial bonding character. When the excited state undergoes a spin flip to give a triplet state, the elongated As-S bond is almost completely broken, resulting in a self-trapped triplet exciton. The photoinduced structural changes observed in As_2S_3 glass can be interpreted in terms of this singlet-to-triplet exciton conversion and the concomitant electron-hole recombination, allowing further atomic rearrangements in the glass network.

DOI: 10.1103/PhysRevB.67.174201 PACS number(s): 61.43.Dq, 71.55.Jv, 73.61.Jc

I. INTRODUCTION

When band-gap or subband-gap light is used to irradiate chalcogenide glasses, e.g., As_xS_{1-x} and As_xSe_{1-x} glasses, atomic configurations, not only in the short-range length scale, but also in the intermediate-range length scale, are changed, resulting in various interesting photoinduced phenomena such as photodarkening, photopolymerization, and photochromism and photodegradation.[1–3] Since such photoinduced phenomena are often observed in other amorphous insulators as well, it is probable that these phenomena are characteristic of solids without long-range order. However, detailed knowledge about the electronic excitation processes following the formation of transient and/or metastable defects in such glassy materials is still missing.

Since exposure to band-gap light generates photoinduced electrons and holes in the conduction and valence bands respectively, it is quite likely that the electronic excitation and resultant recombination processes play a vital role in producing the observed photostructural changes. These photoexcited electrons and holes will migrate through the network in glasses and will finally localize, recombine, or be converted to metastable defects. The following two processes can then be envisaged as the transient processes of photoexcited charge carriers[1]: one is the process in which a photoexcited electron and a hole are spatially well separated in the structure of the material of interest, and the other is the process in which the two oppositely charged 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 (polarons). In previous papers,[4,5] we calculated the equilibrium geometry of the electron- and hole-trapping centers in As_2S_3 glass 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 allowed us to investigate how these charged defects change their atomic configurations on charge trapping and after the resulting recombination processes. From these previous calculations, we found the following. (1) The model cluster consisting of connected AsS_3 trigonal pyramids is likely to trap an electron, followed by the breaking of one of the As-S bonds in the 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 by $\sim$1 eV than the normal AsS_3 trigonal bipyramidal unit. It is hence quite likely that this defect center is responsible for the photodarkening effect in As_2S_3 glass: namely, a shift of the absorption edge to lower energies upon near-band-gap illumination.[6] (4) Another form of metastable defect (a valence-alternation pair), which comprises a fourfold-coordinated As unit and a nonbridging S atom [see Fig. 1(b)], can also exist. This fourfold-coordinated As center yields much lower excitation energies by $\sim$0.8 eV than the fivefold-coordinated As center, explaining the observed photoinduced midgap absorption below $\sim$2 eV.[7] Thus we have shown that localization of charge carriers is a reasonable model accounting for possible photostructural changes in As_2S_3 glass.

In this paper, we investigate another process of photoexcitation of charge carriers in As_2S_3 glass: i.e., the formation of an exciton, in which an electron and a hole coexist in an electronically excited state. Li and Drabold[8] recently investigated photostructural changes of As_2Se_3 glass with excited electron dynamics within first-principles molecular dynamics. They showed that the so-called ''valence-alternation pairs'' associated with band-tail states become involved in photoinduced reactions; that is, a homopolar-to-heteropolar bond transformation has been shown to occur around such overcoordinated defect sites at the onset of illumination. However, it is also interesting to investigate how normally bonded atoms or heteropolar bonds in chalcogenide glasses can be transformed into coordination defects having homopolar bonds upon electronic excitation. In the present paper, therefore, we concentrate our interest on the electronic excitation of As_2S_3 glass with normal bonding configurations, and the consecutive transient and relaxation processes are investigated on the basis of the quantum-chemical cluster method.

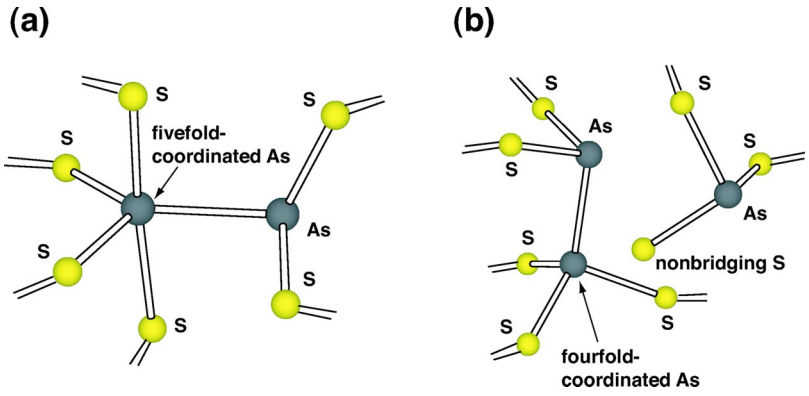

FIG. 1. Models of metastable coordination defects proposed in Refs. 4 and 5: (a) fivefold-coordinated As defect and (b) fourfold-coordinated As defect.

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 is rather a difficult problem. One promising method to obtain excited-state electronic structures is the so-called configuration-interaction- (CI-) singles approximation,[9] modeling 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. 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. The CI-singles approximation 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, yielding qualitatively correct restslts.[9,10] Another advantage of the CI-singles method is that it considerably reduces the computational time, as compared with other more accurate excited-state calculations—e.g., a complete active-space multiconfiguration self-consistent field (CASSCF) method—and hence can be applied to very large systems consisting of more than ~500 basis functions. In this work, we therefore obtain the equilibrium structure of the first singlet excited state (S_1) of clusters of atoms modeling the local structure of As_2S_3 glass using the CI-singles method. We then discuss how the atomic configurations in the excited state can be relaxed into a triplet state or other metastable structures.

II. MODELS AND CALCULATIONAL PROCEDURES

To begin with, we calculate the geometry in the electronic ground state (S_0) of As_2S_3 glass. For this purpose, we employ a cluster of atoms having seven AsS_3 units [model I: see Fig. 2(a)]. This cluster was also used in our previous paper[5] and was shown to have structural parameters that are comparable to those of the well-annealed network of As_2S_3 glass.[11,12] Thus model I can be regarded as having normal bonding configurations in the corresponding glassy material. Model I consists of two subunits having four and three connected AsS_3 units, respectively, that interact with each other through weak nonbonding interactions or van der Waals forces. Model I hence 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 in eliminating the unsaturated bonds of clusters modeling the local structure of the corresponding amorphous system.[13,14] In our previous paper,[5] the geometry of model I was optimized at the HF level with the 6-31G(d) basis set. In this work, we have also carried out geometry optimization at the density functional theory (DFT) level with Becke's B3LYP hybrid exchange-correlation functional[15,16] to include the possible effect of electron correlation.

Next, the geometry of model I was reoptimized by the CI-singles technique using the analytic CI-singles gradients with the 6-31G(d) basis [model II: see Fig. 2(b)]. Furthermore, we investigated the process of a singlet-to-triplet exciton conversion. Singlet-to-triplet exciton conversion has indeed been observed on the subpicosecond time scale in several materials, such as amorphous silica[21] and polydiacetylene,[17] leading to the formation of self-trapped excitons. We hence calculated the geometry of the model cluster in the spin-triplet excited state (T_1) using unrestricted HF (UHF) and unrestricted density functional theory (UDFT) wave functions with the 6-31G(d) basis set. It has recently been demonstrated that the UDFT approach is quite robust against spin contamination of the wave function in the T_1 state.[18] The optimized geometry of the cluster in the T_1 state [model III: see Fig. 2(c)] was calculated using the atomic configurations of model II as the initial geometry.

Since the UHF and UDFT calculations do not require a large amount of memory, as compared with the CI-singles method, we further employed a larger cluster of atoms than in model III to obtain the T_1-state geometry within the limitation of the present computer facility. It is interesting to consider such a larger cluster in terms of a possible size effect of the resultant T_1 geometry. Thus we used an $As_{14}S_{26}H_{10}$ cluster, and its S_0 [model IV: see Fig. 3(a)] and T_1 [model V: see Fig. 3(b)] geometries were calculated at the (U)HF/6-31G(d) and (U)DFT-B3LYP/6-31G(d) levels of theory.

All *ab initio* molecular orbital calculations in this work were performed with the 6-31G(d) basis set[19] using the GAUSSIAN 98 computer program.[20]

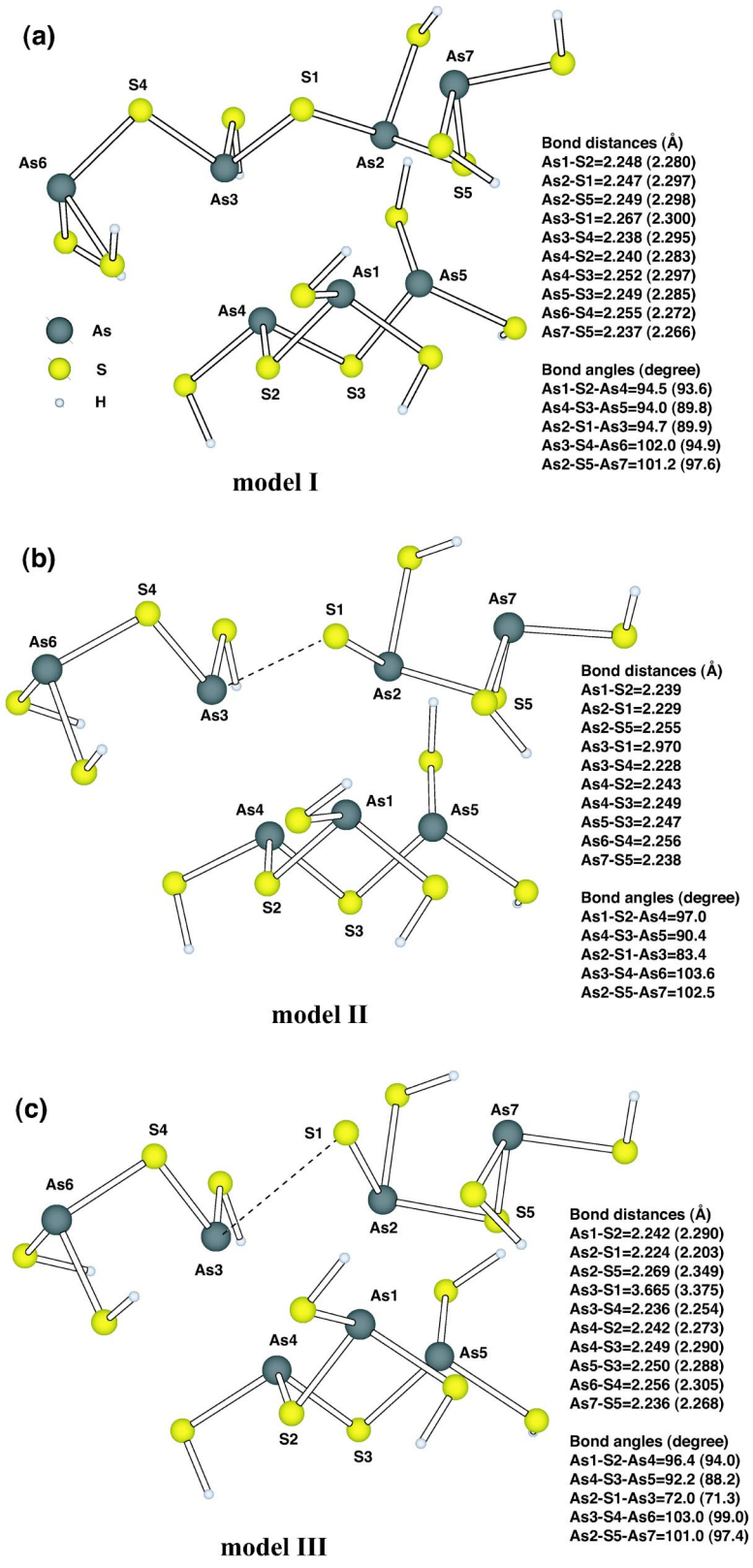

FIG. 2. Optimized geometries of the $As_7S_{16}H_{11}$ cluster in (a) the ground state (S_0, model I), (b) a spin-singlet excited state (S_1, model II), and (c) a spin-triplet excited state (T_1, model III). The optimized parameters for the S_0 and T_1 states were obtained at the levels of (U)HF/6-31G(d) and (U)DFT-B3LYP/6-31G(d) (see values in parentheses). The S_1 state was optimized at the CI-singles/6-31G(d) level.

III. RESULTS

The structural parameters of model I calculated at the HF/6-31G(d) and DFT-B3LYP/6-31G(d) levels are shown in Fig. 2(a). The average As-S bond distance and the average As-S-As bond angle calculated for model I are listed in Table I. We see from Fig. 2(a) and Table I that the structural parameters at the HF/6-31G(d) and DFT-B3LYP/6-31G(d) levels are basically similar, although the latter tend to give slightly longer As-S bond distances and smaller As-S-As bond angles.

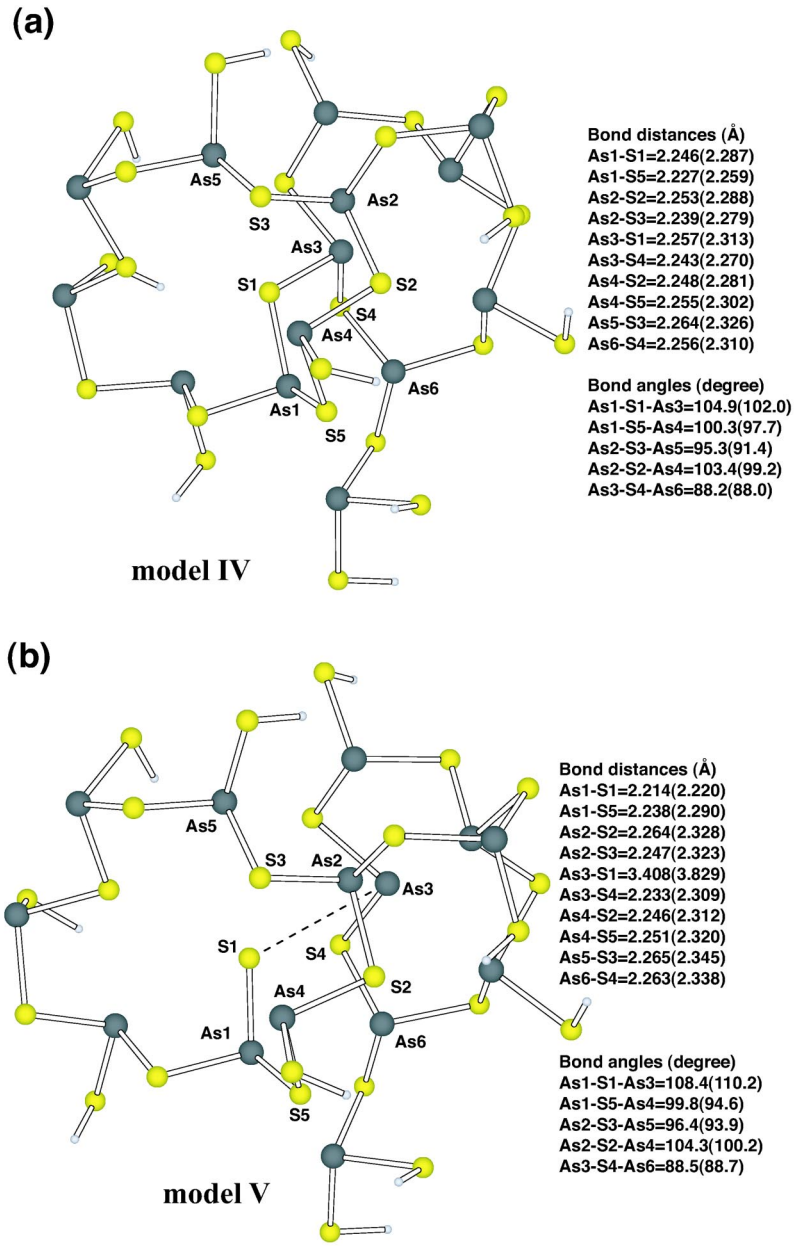

FIG. 3. Optimized geometries of the $As_{14}S_{26}H_{10}$ cluster in (a) the ground state (S_0, model IV) and (b) a spin-triplet excited state (T_1, model V). The optimized parameters at the S_0 and T_1 states were obtained at the levels of (U)HF/6-31G(*d*) and (U)DFT-B3LYP/6-31G(*d*) (see values in parentheses).

The optimized cluster in the S_1 state calculated at the CI-singles/6-31G(*d*) level, termed model II, is depicted in Fig. 2(b). 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 on going from model I to model II (see also Table I). 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, thereby forming a longer As-S bond such 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 normal As-S bonds (~0.4) in the same cluster. It is hence quite likely that, in such an S_1 state, the elongated As-S bond still has a considerable bonding character and that an electron and a hole will not be localized at particular atoms, but will be delocalized over the constituent atoms in model II, which is certainly a typical characteristic of a free electron-hole pair (singlet exciton).[21]

We next turn to the singlet-to-triplet exciton conversion process. One sees from Fig. 2(c) that the structural change occurring in model III (triplet-exciton state) is similar to that in model II (singlet-exciton state); that is, one of the As-S bonds is elongated in the respective excited states. However, the degree of elongation in model III is much greater than that in model II. The separations between the atoms As3 and S1 in model III are 3.665 and 3.375 Å at the UHF and UDFT levels, respectively, whereas the corresponding interatomic separation in model II is only 2.970 Å (see Table I). Such a considerable elongation in one of the As-S bonds in the T_1 state can also be seen even in the larger cluster [model V; see Fig. 3(b)], although the length of the elongated bond depends on the calculated level of theory (see also Table I).[22]

TABLE I. Average As-S bond distances (in Å), average As-S-As bond angles (in degree), and the interatomic distances between atoms As3 and S1 (in Å) obtained for the present model clusters.[a]

	Model I (S_0)	Model II (S_1)	Model III (T_1)	Model IV (S_0)	Model V (T_1)
Avg. As-S	2.242[b]	2.240[d]	2.240[b]	2.244[b]	2.245[b]
	2.285[c]		2.282[c]	2.285[c]	2.312[c]
Avg. As-S-As	97.3[b]	98.4[d]	98.2[b]	98.4[b]	98.4[b]
	93.1[c]		94.8[c]	95.5[c]	94.9[c]
As3-S1	2.267[b]	2.970[d]	3.665[b]	2.257[b]	3.408[b]
	2.300[c]		3.375[c]	2.313[c]	3.829[c]

[a]The elongated As3-S1 bonds in the S_1 an T_1 states were excluded to obtain average As-S bond distances and As-S-As bond angles.

[b]Calculated values at the (U)HF/6-31G(d) level.

[c]Calculated values at the (U)DFT-B3LYP/6-31G(d) level.

[d]Calculated values at the CI-singles/6-31G(d) level.

IV. DISCUSSION

Thus we have shown that one of the As-S bonds in the As_2S_3 network can be preferentially elongated during the electronic excitation processes. It should be noted, however, that, in the S_1 state, the elongated bond is not completely broken, but still has a considerable bonding character in terms of its bond overlap population. The subsequent singlet-to-triplet exciton conversion will induce further modification of its bonding character, accompanied by a considerable elongation of the As-S bond more than ~3.3 Å as mentioned just above. The bond-overlap populations of the elongated bond in the T_1 state have small negative values (see Table II), implying a repulsive rather than an attractive force between the two atoms. These results suggest that, in the spin-triplet excited state, the elongated bond is broken to form initially a twofold-coordinated As and a nonbridging S. Accordingly, an electron and a hole are localized, respectively, on these two types of undercoordinated atoms, yielding substantial spin densities on atoms As3 and S1 (see also Table II). It has previously been proposed that the formation of excitons and the resultant self-trapping process are responsible for the observed photostructural changes in chalcogenide glasses[1,23,24]; that is, the formation of such a self-trapped exciton, accompanied by the breaking of an As-S bond, has been suggested to occur in the photoinduced process of As_2S_3 glass. 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 As_2S_3 glass.

We[4,5] have already demonstrated that, when the As and S atoms in one of the As-S bonds are separated beyond 3.4 Å, the As and S atoms do not return to the original atomic configurations, but reorganize to form coordination defects consisting of fivefold-coordinated As and fourfold-coordinated As units, as mentioned previously. Considering that the As-S bond distance increases from ~2.2 to ~(3.4–3.8) Å upon self-trapping of an exciton, we suggest that the present self-trapped exciton in the network structure of As_2S_3 glass 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 the self-trapping of single carriers proposed in our previous papers,[4,5] induces substantial atomic rearrangements. These atomic rearrangements, accompanied by the breaking of As-S bonds, will result in the formation of the coordination defects that are most likely responsible for the observed photoinduced effects in As_2S_3 glass.

TABLE II. Mulliken bond-overlap populations n and spin densities ρ related to the atoms As3 and S1 in the model clusters in their spin-triplet state.

	Model III		Model V	
	UHF	UDFT-B3LYP	UHF	UDFT-B3LYP
n(As3-S1)	−0.026	−0.029	−0.089	−0.116
ρ(As3)	0.971	0.760	0.978	0.710
ρ(S1)	1.006	0.796	0.999	0.672

V. CONCLUSIONS

We have carried out *ab initio* quantum-chemical calculations on clusters of atoms modeling the network of As_2S_3 glass 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 an As-S bond distance of 2.970 Å in CI-singles calculations. In such an excited state, however, the elongated As-S bond still has considerable bonding character; an electron and a hole are delocalized over several As and S atoms. If, during the relaxation process of the free exciton, it undergoes a spin flip, then, as a result, the S atom moves away from one of the As atoms to which it was bonded; 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 As_2S_3 network, leading to the breaking of the As-S bond. These results suggest that singlet-to-triplet exciton conversion plays a role in inducing the photoinduced effects observed in As_2S_3 glass.

ACKNOWLEDGMENT

We would like to thank the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University, for providing the computer time.

[1] K. Shimakawa, A. Kolobov, and S. R. Elliott, Adv. Phys. **44**, 475 (1995).
[2] H. Fritzsche, in *Insulating and Semiconducting Glasses*, edited by P. Boolchand (World Scientific, Singapore, 2000).
[3] M. A. Popescu, *Non-Crystalline Chalcogenides* (Kluwer Academic, Dordrecht, 2000).
[4] T. Uchino, D. C. Clary, and S. R. Elliott, Phys. Rev. Lett. **85**, 3305 (2000).
[5] T. Uchino, D. C. Clary, and S. R. Elliott, Phys. Rev. B **65**, 174204 (2002).
[6] S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. **34**, 1346 (1975).
[7] K. Tanaka, in *Structure and Excitation of Amorphous Solids*, edited by G. Lucovsky and F. L. Galeener, AIP Conf. Proc. No. **31** (AIP, New York, 1976).
[8] J. Li and D. A. Drabold, Phys. Rev. Lett. **85**, 2785 (2000).
[9] J. B. Foresman, H. Head-Gordon, J. A. Pople, and M. J. Frisch, J. Phys. Chem. **96**, 135 (1992).
[10] J. B. Foresman and H. B. Schlegel, in *Molecular Spectroscopy: Recent Experimental and Computational Advances*, Vol. 406 of *NATO Advanced Study Institute, Series C*, edited by R. Fausto (Kluwer Academic, Dordrecht, 1993).
[11] C. Y. Yang, M. A. Paesler, and D. E. Sayers, Phys. Rev. B **36**, 9160 (1987).
[12] Y. Iwadate, T. Hattori, S. Nishiyama, K. Fukushima, Y. Mochizuki, M. Misawa, and T. Fukunaga, J. Phys. Chem. Solids **60**, 1447 (1999).
[13] M. O'Keeffe and G. V. Gibbs, J. Chem. Phys. **81**, 876 (1984).
[14] T. Uchino and T. Yoko, J. Chem. Phys. **108**, 8130 (1998).
[15] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[16] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[17] B. I. Greene, J. Orenstein, R. R. Millard, and L. R. Williams, in *Ultrafast Phenomena V*, edited by G. R. Fleming and A. E. Siegman (Springer-Verlag, Berlin, 1986).
[18] X.-Y. Cui, I. Morrison, and J.-G. Han, J. Chem. Phys. **117**, 1077 (2002).
[19] P. C. Hariharan and J. A. Pople, Mol. Phys. **27**, 209 (1974), and references therein. For As atoms, we used the $(14s\ 11p\ 5d)$ basis set reported in T. H. Dunning, Jr., J. Chem. Phys. **66**, 1382 (1977).
[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Computer code GAUSSIAN 98, revision A7, Gaussian Inc., Pittsburgh, 1998.
[21] P. N. Saeta and B. I. Greene, Phys. Rev. Lett. **70**, 3588 (1993).
[22] As shown in Table I, the separation between the atoms As3 and S1 in model III calculated at the UHF level is longer than that at the UDFT level, whereas the corresponding separation in model V gives the opposite tendency. This result indicates that, as far as the elongated As-S bond in the T_1 state is concerned, the length of separation depends strongly on the size of the cluster employed, as well as the calculated level of theory, ranging from $\sim$3.4 to $\sim$3.8 Å.
[23] R. A. Street, Solid State Commun. **24**, 363 (1977).
[24] K. Shimakawa and S. R. Elliott, Phys. Rev. B **38**, 12 479 (1988).