

Theoretical studies on As and Sb sulfide molecules

J. A. TOSSELL

Department of Chemistry and Biochemistry
University of Maryland, College Park, MD 20742, U.S.A.

Abstract—Dimorphite (As_4S_3) and realgar and pararealgar (As_4S_4) occur as crystalline solids containing As_4S_3 and As_4S_4 molecules, respectively. Crystalline As_2S_3 (orpiment) has a layered structure composed of rings of AsS_3 triangles, rather than one composed of discrete As_4S_6 molecules. When orpiment dissolves in concentrated sulfidic solutions the species produced, as characterized by IR and EXAFS, are mononuclear, *e.g.* AsS_3H_2^- , but solubility studies suggest trimeric species in some concentration regimes. Of the antimony sulfides only Sb_2S_3 (stibnite) has been characterized and its crystal structure does not contain Sb_4S_6 molecular units. We have used molecular quantum mechanical techniques to calculate the structures, stabilities, vibrational spectra and other properties of As_4S_3 , As_4S_4 , As_4S_6 , As_4S_{10} , Sb_4S_3 , Sb_4S_4 , Sb_4S_6 and Sb_4S_{10} (as well as S_8 and P_4S_3 , for comparison with previous calculations). The calculated structures and vibrational spectra are in good agreement with experiment (after scaling the vibrational frequencies by the standard correction factor of 0.893 for polarized split valence Hartree-Fock self-consistent-field calculations). The calculated geometry of the As_4S_4 isomer recently characterized in pararealgar crystals also agrees well with experiment and is calculated to be about 2.9 kcal/mole less stable than the As_4S_4 isomer found in realgar. The calculated heats of formation of the arsenic sulfide gas-phase molecules, compared to the elemental cluster molecules As_4 , Sb_4 and S_8 , are smaller than the experimental heats of formation for the solid arsenic sulfides, but shown the same trend with oxidation state. As(III) sulfides, like As_4S_6 , are calculated to be stable toward disproportionation to a mixture of As(II) and As(V) sulfides and As_4S_4 does not disproportionate to As(III) and elemental As. As_4S_6 reacts exothermically with H_2S to give $\text{As}_2\text{S}_3(\text{SH})_3$. Calculated electric field gradients at the As atoms in the arsenic sulfides are found to be determined by the As coordination number and by the number of As—As bonds within the first coordination sphere. UV spectral energies and intensities and polarizabilities are calculated for the isomers of As_4S_4 using the random-phase-approximation. Based on a comparison with the spectral properties of S_8 we project an excitation energy of about 3.3 eV to the lowest energy singlet and 2.2 eV to the lowest energy triplet state of realgar. The optimized geometry of the triplet state shows breaking of one of the As—As bonds, allowing a facile rearrangement to the pararealgar form.

INTRODUCTION

ALTHOUGH MOST minerals crystallize in ionic or covalent structures without discrete “molecules”, elemental S and the sulfides of As and Sb sometimes adopt “molecular” structures, in which ring or cage molecules of moderate size are held together in the solid by weak van der Waals forces. Such molecular units may also exist in amorphous forms of such materials or in solution. We have recently begun a program of study of sulfide species existing in solution and have characterized monomeric and small oligomeric sulfide species of Sb (TOSSELL, 1994) and As (HELZ *et al.*, 1995). It is important to know whether larger oligomeric species, *e.g.* As_4S_4 , which exist in both realgar (MULLEN and NOWACKI, 1972) and pararealgar (BONAZZI, 1995), in amorphous films of As_2S_3 (NEMANICH *et al.*, 1978) and in the gas phase (MARTIN, 1984) also exist in solution and/or react to produce other solution species. As a first step in such a study we here present calculations of the structural, energetic and spectral properties of a number of As and Sb sulfide molecules.

Studies of speciation in solution typically employ solubility methods in which the variation of total metal concentration with pH and ligand concentration is used to develop a model of the species present (*e.g.*, KRUPP, 1988). In most cases it is not possible to significantly vary the activities of the metal sulfide component, making it difficult to identify oligomeric species. In the Cu-S system THOMPSON and HELZ (1994) were able to vary CuS activity to some extent and to develop a model with multinuclear Cu species. A powerful tool for determining speciation is vibrational spectroscopy, particularly Raman spectroscopy, (*e.g.*, WOOD, 1989) which yields spectral signatures for the different species (although identifying a particular peak with a given species can be quite difficult). EXAFS can also be used to determine local geometry about metal centers, which can help in identifying the species present (*e.g.*, HELZ, *et al.*, 1993) but for highly insoluble sulfides obtaining high enough solution concentrations to yield usable EXAFS spectra can be difficult.

To assist in determining speciation quantum mechanical calculations can be very valuable (Tos-

SELL and VAUGHAN, 1993; TOSSELL, 1994; HELZ *et al.*, 1995). For small gas-phase molecules quantum mechanical techniques exist which can determine heats of formation to within a few kcal/mol of experiment (CURTISS *et al.*, 1991). Other properties, *e.g.* structures and vibrational spectra, can also be calculated to high accuracy for small molecules. Even for relatively large gas-phase molecules Hartree-Fock level quantum calculations combined with standard correction factors can give good agreement with experiment. For condensed phase species such calculations are more difficult although enormous progress has been made in the calculation of the properties of crystalline materials using both Hartree-Fock (PISANI *et al.*, 1988) and density-functional based theories. Calculating the electronic structure of crystalline realgar at the *ab initio* Hartree-Fock level would presently be a very formidable task, since the unit cell contains 4 As_4S_4 molecules. In addition, a correct description of the van der Waals forces which hold such a solid together requires a method which incorporates electron correlation, making the computational problem even more difficult. For the present we will apply molecular quantum mechanical methods to a study of the discrete molecules, such as As_4S_4 , which exist in such phases.

A considerable number of quantum mechanical computations have been performed on various neutral (HOHL *et al.*, 1988; RAGHAVACHARI *et al.*, 1990) and anionic (GANTEFOR *et al.*, 1995) oligomers of elemental sulfur. Fewer calculations have been done on As species, although YSTENES *et al.* (1993, 1994) have carried very complete studies of the vibrational spectra of P_4S_3 and P_4S_4 and have used their calculated force fields, after rescaling, to interpret the vibrational spectrum of As_4S_3 and As_4S_4 (realgar). SUNDARARAJAN and KUMAR (1995) have recently used the *ab initio* molecular dynamics density functional approach to study Sb clusters, up to Sb_{12} . As_4S_4 and As_2S_3 crystals have been studied using a non-self-consistent LCAO approach by BULLETT (1976), who concentrated on their density of states and photoemission spectra and BABIC *et al.* (1989) have treated the As_4S_4 and As_4S_6 molecules using density functional theory. They employed an *s,p* orbital only basis and did only a partial geometry optimization, although they obtained equilibrium As—As and As—S distances fairly close to experiment.

COMPUTATIONAL METHODS

We employ the conventional methods of *ab initio* Hartree-Fock self-consistent-field molecular orbital theory as described in quantum chemistry texts (SZABO and

OSTLUND, 1989) and monographs (HEHRE *et al.*, 1986) and as implemented in the program GAMESS (SCHMIDT *et al.*, 1993). All the calculations were done on a cluster of DEC Alpha workstations and were done in direct SCF mode, *i.e.* without disk storage of two-electron repulsion integrals. TOSSELL and VAUGHAN (1992) have reviewed the applications of quantum chemical calculations to a number of mineralogical and geochemical problems and SIMONS (1991) has written a brief experimentalist's guide to the use of *ab initio* quantum chemical techniques and the interpretation of the results. SAUER (1989) has reviewed the application of quantum mechanical methods to a number of condensed phase systems.

Although the *ab initio* Hartree-Fock MO techniques commonly applied to large molecules do not give exact agreement with experiment, the errors due to the use of a finite basis set for expansion of the MO's and the neglect of electron correlation are often quite systematic. For example, when studying neutral molecules at the polarized valence double zeta basis set self-consistent-field (SCF) level (*i.e.* Hartree-Fock *ab initio* MO theory with two functions to describe each valence atomic orbital plus additional functions with higher azimuthal quantum numbers, *e.g.* 3d on oxygen, to describe the polarization of the electron density which occurs upon bond formation), we expect calculated bond distances to be too short by a few hundredths of an angstrom and vibrational frequencies to be too high by about 10% (HEHRE *et al.*, 1986). The root-mean-square error in the vibrational frequencies for an extensive series of neutral gas-phase main-group molecules was found to be minimized when the calculated vibrational frequencies were scaled down by the factor 0.893 (POPLE *et al.*, 1993). This scaling factor appeared to be appropriate for all types of vibrations. The scaling factor, however, is somewhat larger for highly charged anions, as discussed in TOSSELL (1994) and YSTENES *et al.* (1993).

The basis sets used to expand the molecular orbitals in our studies of geometry, stability and vibrational spectra are of the relativistic compact effective core-potential valence double zeta type (STEVENS *et al.* 1992), with polarization functions of d type added on each of the non-H atoms. We shall refer to these as polarized SBK basis sets. For Sb the relativistic effective core potential replaces 46 core electrons so that only the $5s^25p^3$ electrons are explicitly treated, with the 5s and 5p shells each described by two contracted Gaussian functions. Although these basis functions are quite new they have already been successfully used to study a number of different problems, including Zn complexes as models for the enzyme carbonic anhydrase (GARMER and KRAUSS, 1992) and the Sb sulfides (TOSSELL, 1994). In all cases so far examined the calculated geometries and other properties were very similar to those obtained at the all-electron polarized valence double zeta SCF level. For these effective core potential basis set calculations we can then use the standard correction factors appropriate for polarized valence double zeta SCF calculations. The elimination of core electrons in the Sb sulfide calculations is very important since it reduces the number of orbitals in the basis set and consequently the computer time required, which scales as approximately the third to fourth power of the number of basis functions.

For calculation of the electric field gradients at the As nuclei we use all-electron basis sets of the 6-31G* type (HEHRE *et al.*, 1986), which are basically of single zeta quality for the core orbitals and double zeta quality for the

valence orbitals, with appropriate polarization functions added. We have also evaluated optical excitation energies and intensities as well as frequency dependent molecular dipole polarizabilities for the two isomers of As_4S_4 using the program RPAC (BOUMAN and HANSEN, 1991), interfaced to GAMESS. This approach evaluates excitation properties in terms of the random-phase approximation, or RPA (HANSEN and BOUMAN, 1985), which is a method that includes those first-order electron correlation effects that are important for electronic intensities and excitation energies.

For each molecule we have determined the minimum energy or equilibrium geometry and have calculated the vibrational spectrum, making sure that this spectrum has

no imaginary frequencies and that the geometry thus corresponds to (at least a local) minimum on the potential energy surface. For each of molecules studied we have also calculated the vibrational energy spectrum and have displayed the normal modes of vibration using the capabilities of GAMESS and its auxiliary graphics programs.

RESULTS

Calculated bond distances and angles for the As sulfides are collected in Table 1 and compared with experiment (the crystal structures of the Sb sulfides do not contain molecular units). Bond distances are

Table 1. Calculated bond distances and angles in As_4S_3 , the two isomers of As_4S_4 , As_4S_6 and As_4S_{10} compared with experimental data for alpha-dimorphite, realgar, pararealgar, gas-phase As_4S_4 and gas phase As_4S_6 (bond distances in Å and bond angles in degrees)

Molecule	Calc. geom.	Exp. geom.
As_4S_3 (assumed C_{3v})	R(As-S) = 2.217 R(As-As) = 2.442 <S-As-S = 109.5 <As-S-As = 91.6 <As-As-As = 60	R(As-S) = 2.200-2.220 R(As-As) = 2.445-2.450 <S-As-S = 97.8-98.0 <As-S-As = 105.7-106.1 <As-As-As = 60.2 (WHITFIELD, 1970)
As_4S_4 , realgar (assumed C_{2v})	R(As-S) = 2.238 R(As-As) = 2.563 <S-As-S = 95.3 <As-S-As = 100.4	R(As-S) = 2.228-2.247 R(As-As) = 2.566-2.571 <S-As-S = 94.5-95.1 <As-S-As = 100.8-101.2 (MULLEN and NOWACKI (1972), crystalline realgar) R(As-S) = 2.23 ± 0.02 R(As-As) = 2.49 ± 0.04 <S-As-S = 93 <As-S-As = 101 (LU and DONOHUE (1994), gas phase electron diffraction)
As_4S_4 , pararealgar (assumed C_s)	R(As-S) As1-S 2.248, 2.251 As2, As3-S 2.249, 2.263 As4-S4 2.212 As-As 2.492	R(As-S) As1-S1 2.254 As1-S3 2.238 As1-S4 2.261 As2-S1 2.251 As2-S2 2.252 As3-S2 2.244 As3-S3 2.228 As4-S4 2.190 As2-As4 2.484 As3-As4 2.534 (BONAZZI <i>et al.</i> (1995), crystalline solid)
As_4S_6 (assumed C_{3v})	R(As-S) = 2.250 <As-S-As = 116.5 <S-As-S = 105.7	R(As-S) = 2.25 ± 0.02 <As-S-As = 100 ± 2 <S-As-S = 114 ± 2 (LU and DONOHUE (1994), gas-phase electron diffraction)
As_4S_{10} (assumed C_{3v})	R(As-S) = 2.040 (terminal) 2.230 (bridging)	

satisfactorily reproduced in all cases although some bond angles deviate substantially from experiment. The apparent disagreement between gas-phase and solid state experimental results for As_4S_4 may not be real since the gas-phase results were from an early electron-diffraction study in which only the shorter As—S distance could be directly determined from the data. Note the considerably different structures for the realgar and pararealgar forms of As_4S_4 (Fig. 1). Each molecule can be described as the result of adding four S atoms to tetrahedral As_4 and has 8 As—S and 2 As—As bonds but they are arranged very differently. In realgar there are two As—As groups on opposite sides of the molecule while in pararealgar there is a group of three As atoms on one side. Both structures are minima on the potential energy surface for the singlet ground state with the realgar structure calculated to be more stable by 2.9 kcal/mole. Notice also that although As_4S_3 , realgar As_4S_4 and pararealgar As_4S_4 exhibit As—As single bonds the bond lengths are quite different, with the longest bond (2.563 Å) in realgar and the shortest (2.442 Å) in the As_3 grouping of As_4S_3 .

For the Sb compounds the calculated structures are very much like those for the As analogues. For

example, a realgar-like structure of Sb_4S_4 shows Sb—Sb distances of 2.93 Å and Sb—S distances of 2.42 Å. The pararealgar-like isomer is 4.2 kcal/mol higher in energy and shows a structure very much like the corresponding sulfide. Detailed geometries for the other Sb sulfides are available from the author. Although Sb_4S_4 and Sb_4S_6 molecules have not been characterized, the $\text{Sb}_4\text{S}_6^{-2}$ anion is known (MARTIN *et al.*, 1995), and shows an Sb—Sb bond distance of 2.86 Å and Sb—S_{bridging} distances of 2.44 – 2.48 Å.

In Table 2 we collect calculated formation energies for the As and Sb sulfides. These energies are obtained from SCF calculations of internal energies for these gas-phase molecules and for the most stable gas-phase forms of the elements, S_8 , As_8 and Sb_8 , at their optimized geometries. We can compare these with conventional heats of formation, *i.e.* enthalpy differences between the solid crystalline compounds and the stable (solid) forms of the elements. It should be noted that the newest values of the formation enthalpy of As_4S_4 and As_2S_3 (BRYNDZIA and KLEPPA, 1988 and JOHNSON *et al.* 1980) are much smaller (in absolute value) than earlier results such as those tabulated in MILLS (1974). One might suspect that the Sb sulfide for-

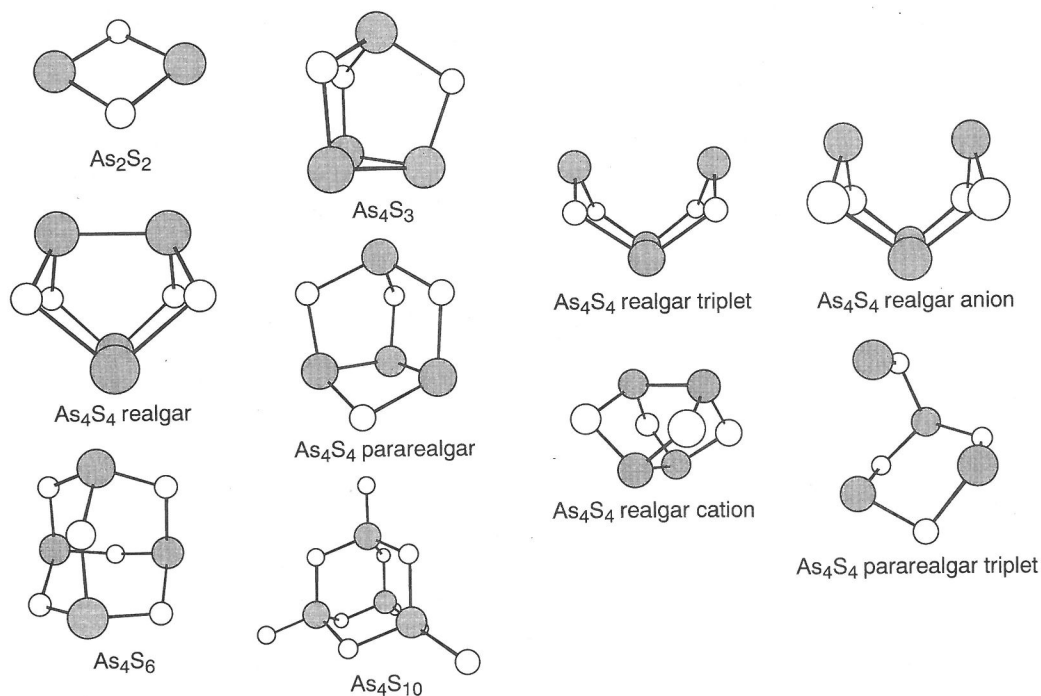


FIG. 1. Equilibrium geometries for various As sulfide species. As are shown as larger, solid spheres, S as smaller, open spheres.

Table 2. Calculated internal energies of formation of As and Sb sulfides from As_4 , Sb_4 and S_8 molecules, in kcal/mole (of formula shown)

Molecule	Calculated SCF formation energy
As_2S_2	+8
As_4S_3	-48
As_4S_4	-61 (realgar), -58 (pararealgar)
As_4S_6	-69
As_4S_{10}	-15
Sb_4S_3	-60
Sb_4S_4	-80
Sb_4S_6	-99
Sb_4S_{10}	-37

mation enthalpies reported in MILLS (1974) are also in error. Based on a As_4S_4 formation enthalpy of -26.9 kcal/mol (of As_4S_4) from BRYNDZIA and KLEPPA (1988) and sublimation energies of As(s) to As_4 and S(s) to S_8 reported in MILLS (1974) we obtain an experimental value of -74.5 kcal/mol. Our calculated values are -61 kcal/mol for the realgar form of As_4S_4 and -58 kcal/mol for the pararealgar form. A similar calculation for As_4S_6 using data from BRYNDZIA and KLEPPA (1988) and MILLS (1974) gives -93.2 kcal/mol (of As_4S_6) for the formation enthalpy of crystalline orpiment, As_2S_3 , while our calculated SCF value for the formation enthalpy of gas-phase As_4S_6 is -69 kcal/mol (of As_4S_6). We have also studied the formation of As_4S_4 and As_4S_6 from As_4 and S_8 (but not the analogous Sb sulfides) at a somewhat higher quantum mechanical level. Incorporating zero-point vibrational energy corrections makes the formation energy less negative by 0.7 kcal/mol for As_4S_4 and 0.6 kcal/mol for As_4S_6 while incorporating electron correlation at the level of second-order Moller-Plesset perturbation theory (MP2, see HEHRE *et al.*, 1986) makes the formation energy less negative by 4.8 kcal/mol for As_4S_4 and 9.8 kcal/mol for As_4S_6 . These corrections change the calculated formation energies to -56 kcal/mol for As_4S_4 and -59 kcal/mol for As_4S_6 , a substantial change from the SCF energies in Table 2. The difference between our best calculated value for the formation enthalpy of the As_4S_4 realgar molecule and the experimental value for As_4S_4 in the realgar crystal is about 18 kcal/mol, fairly close to the 24.5 kcal/mol sublimation enthalpy of S_8 (MILLS, 1974). It seems reasonable that since As_4S_4 and S_8 both form molecular solids and their basic structural units in both the solid and gas phases are very similar, they would have similar sublimation energies. For As_4S_6 the

difference between the calculated gas-phase formation enthalpy and the experimental formation enthalpy for orpiment is 34 kcal/mol, consistent with a greater stability for the non-molecular crystal structure of orpiment, compared to a hypothetical molecular solid with As_4S_6 units.

Based on the SCF formation energies we can establish that the most stable oxidation state for As and/or Sb in combination with S is the trivalent state, *i.e.* As_4S_6 (or As_2S_3). As(III) and Sb(III) sulfides would not be expected to disproportionate to mixtures of divalent and quintavalent states and the stability of the quintavalent sulfides will be very limited. It is not immediately clear how to reconcile this with the mass spectrometric data of MARTIN (1984) which showed As_4S_4 to be more abundant than As_4S_6 in the gas phase over either solid AsS or As_2S_3 . As noted by Martin it may be that some of the $As_4S_4^+$ cluster ions observed are actually decomposition products of As_4S_6 or other molecules. The highest energy occupied molecular orbitals (HOMO's) of As_4S_6 are As—S bonding while the lowest energy unoccupied orbitals (LUMO's) are As—S antibonding. Exciting electrons from HOMO to LUMO could then lead to fragmentation. It could also be that the As_4S_4 molecule is the first formed, even over (amorphous) As_2S_3 , and that the reaction of As_4S_4 with elemental S to give As_4S_6 is slow under the conditions of the experiment.

Based on our energies for As, S, As_4 , S_8 and As_4S_6 we can also evaluate energies of atomization and compare with experimental atomization enthalpies (see *e.g.* HUHEEY *et al.*, 1993, Table E.1). We calculate an atomization energy of 30.4 kcal/per As—As bond for As_4 (exp. 35 kcal) and 46.1 kcal for the atomization energy per S—S bond in S_8 (exp. 54 kcal). The calculated atomization energy of the As—S bond in As_4S_6 is 43.1 kcal.

We can qualitatively understand the transformations from As_4 (or Sb_4) to the various sulfides by recognizing that the HOMO's of twenty valence electron tetrahedral molecules like As_4 are p lone-pair orbitals directed out of the tetrahedron while the LUMO's are p sigma antibonding orbitals directed along the edges of the tetrahedra (BURDETT, 1980, p. 240). Attack by a nucleophile occurs through interreaction with these LUMO's. For example in As_4^{-2} one As—As bond will be broken to give a rhombus structure (TOSSELL, 1983). When the nucleophile is sulfur, a S atom can be inserted into the broken As—As bond. Insertion of three S atoms along three of the six As—As edges of As_4 gives the molecule As_4S_3 while four S insertions

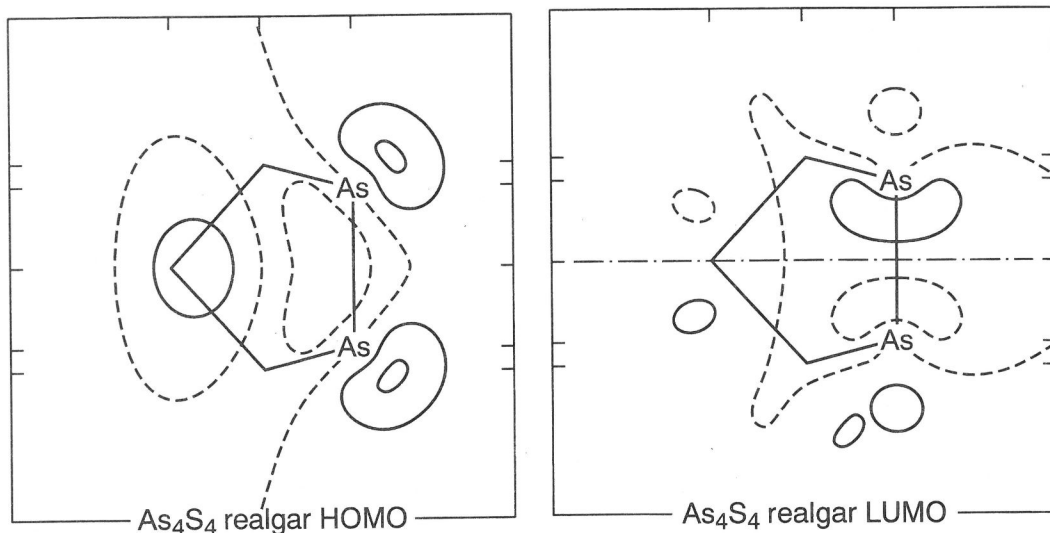


FIG. 2 Contour plots of the highest energy occupied MO and the lowest energy unoccupied MO for the ground state of As_4S_4 realgar. The plane shown contains one As—As bond and bisects the molecule. The positions of the As atoms are marked. Positive contours are shown as solid lines, negative contours as broken lines.

give As_4S_4 . The two different isomers of As_4S_4 seen in realgar and pararealgar result from addition of four S atoms to a different set of four As—As edges of a As_4 tetrahedron. In the realgar form of As_4S_4 the HOMO is a As 5p lone pair distributed over the atoms in the As—As bonds while the LUMO is an As—As sigma antibonding orbital, as shown in Fig. 2. Further addition of S breaks the final two As—As bonds to give As_4S_6 . To convert As_4S_6 to As_4S_{10} we must oxidize As by transferring its tangential lone-pair electrons to S.

In Table 3 we collect calculated vibrational energies for P_4S_3 , As_4S_3 and Sb_4S_3 and compare them

the calculations of YSTENES *et al.* (1993) for P_4S_3 and with experiment for P_4S_3 and As_4S_3 . We have scaled the calculated vibrational frequencies for P_4S_3 and As_4S_3 in Table 3 by the factor of 0.86 favored by YSTENES *et al.* (1993) (they report a scaling factor of 0.74 for the *force constants* which is equivalent to a scaling factor of 0.86 for the *frequencies*). If we had scaled the frequencies by the more standard factor of 0.893 the overall degree of agreement would have been very similar. Our results for P_4S_3 are very similar to those of YSTENES *et al.* (1993), with an identical order of frequencies and assignment of bands, and our calculations on

Table 3. Calculated vibrational frequencies for P_4S_3 , As_4S_3 , scaled by 0.86 and compared to experimental data from BUES *et al.* (1980) and the calculations of YSTENES *et al.* (1993) ($\times 2$ signifies a doubly degenerate vibration)

P_4S_3 6-31G* (YSTENES <i>et al.</i> , 1993)	Pol. SBK	Pol SBK, scaled by 0.86	Exp	As_4S_3 pol. SBK	Pol. SBK scaled by 0.86	Exp.	Sb_4S_3 pol. SBK	Pol. SBK scaled by 0.86
567	582	501	483	427	367	375	395	292
533×2	540×2	464	(none)	413×2	355	370	362×2	311
513×2	524×2	451	440	406	349	354	349	299
493	523	450	420	397×2	341	340	340×2	292
484	485	417	417	314	270	268	219	188
406×2	411×2	353	351	248	213	217	176	151
394	392	337	339	230×2	198	197	162×2	139
332×2	330×2	284	287	207×2	178	181	158×2	136
252×2	251×2	216	218	198×2	170	175	140×2	120
219	216	186	187	137	118	142	102	88

Table 4. Calculated vibrational frequencies in cm^{-1} (scaled by 0.893) for the two isomers of As_4S_4 and for As_4S_6 (with calculated relative IR intensities in parentheses), compared with experiment (FORNERIS, 1969) for realgar ($\times 2$ indicates a doubly degenerate vibration)

As_4S_4 realgar calculated frequencies scaled by 0.893	As_4S_4 realgar exp. frequencies	As_4S_4 pararealgar calculated frequencies scaled by 0.893	As_4S_6 calculated frequencies scaled by 0.893
104 (0)	47, 60	113 (.001)	106 (0) $\times 3$
153 (0)	141, 143	114 (.023)	121 (0) $\times 2$
168 (.088) $\times 2$	170	158 (.001)	151 (.073) $\times 3$
190 (0)	183	158 (.031)	214 (.253) $\times 3$
196 (.113)	194	178 (.085)	233 (.0004)
219 (.066) $\times 2$	225 (e)	185 (.134)	316 (.104) $\times 3$
225 (0)	222	208 (.031)	328 (.0004) $\times 2$
234 (.100)	—	232 (.038)	342 (0)
343 (0)	330	243 (.094)	355 (0) $\times 3$
359 (0)	343	244 (.0004)	408 (2.67) $\times 3$
360 (.881) $\times 2$	358	334 (.084)	
370 (0)	367 (e)	344 (.075)	
372 (.009) $\times 2$		345 (.181)	
382 (1.107)	373 (e)	353 (.357)	
		362 (.128)	
		375 (.271)	
		377 (1.25)	
		393 (1.92)	

As_4S_3 also agree well with their scaled force field results and with experiment. As expected, the calculated spectrum of Sb_4S_3 is qualitatively similar to that of P_4S_3 or As_4S_3 , with all the vibrations displaced to lower frequency.

The calculated frequencies for the two isomers of As_4S_4 and for As_4S_6 , scaled by the commonly used 0.893 factor, are listed in Table 4, along with calculated relative IR intensities, and are compared with the data of FORNERIS (1969) for realgar (WARD (1968) and others have published similar realgar spectra). The calculated vibrational normal modes for the two As_4S_4 isomers are shown in Fig. 3. The agreement of scaled calculated and experimental frequencies is quite good, except in the very low frequency region, in which the vibrational motions of one As_4S_4 molecule may be strongly coupled with those of others. Our results for As_4S_4 are also in good agreement with the scaled force field results of YSTENES *et al.* (1994). As noted by FORNERIS (1969), the As_4S_4 molecule will have 18 vibrational normal modes, of which 8 are expected to involve As—S stretching, 2 As—As stretching and 8 mainly bending motions. The As—S stretches are expected to occur at highest frequency and we indeed find them at scaled calculated frequencies of 343–382 cm^{-1} (Table 4 and Fig. 3), with corresponding experimental values from 330 to 373 cm^{-1} . In agreement with the analysis of YANG *et al.* (1987), based on the temperature de-

pendence of EXAFS, the calculated normal modes shown in Fig. 3 indicate that the Raman feature at a scaled calculated frequency of 225 cm^{-1} is mainly an As—As stretching mode. An IR active mode at a scaled calculated frequency of 234 cm^{-1} is partly As—As and partly As—S stretching. The modes calculated from 104–219 cm^{-1} are predominantly bending modes.

Our predicted spectrum for pararealgar is significantly different in detail from that of realgar. The stretching vibrations of the As_3 group in pararealgar occur at about 5–15 cm^{-1} higher frequency than the As—As stretch in realgar and the highest energy vibration in pararealgar is mostly a stretch of the S atoms vs. the “terminal”-type As and is about 10 cm^{-1} higher than the highest energy As—S stretch in realgar. Note that our calculated vibrational spectrum for As_4S_6 is not directly comparable to that measured for solid As_2S_3 since the crystalline material does not contain such molecular units. The calculated vibrational spectrum of As_4S_{10} is quite similar to that of As_4S_6 , the main difference being the presence of high energy As—S_{terminal} stretches in As_4S_{10} , at scaled energies of 472 cm^{-1} for the three-fold degenerate vibration and 481 cm^{-1} for the totally symmetric one.

We have also calculated a number of the electronic properties of the As_4S_4 isomers. The calculated ionization potentials (IP's) and electron affinities (EA's), both vertical and adiabatic, are given

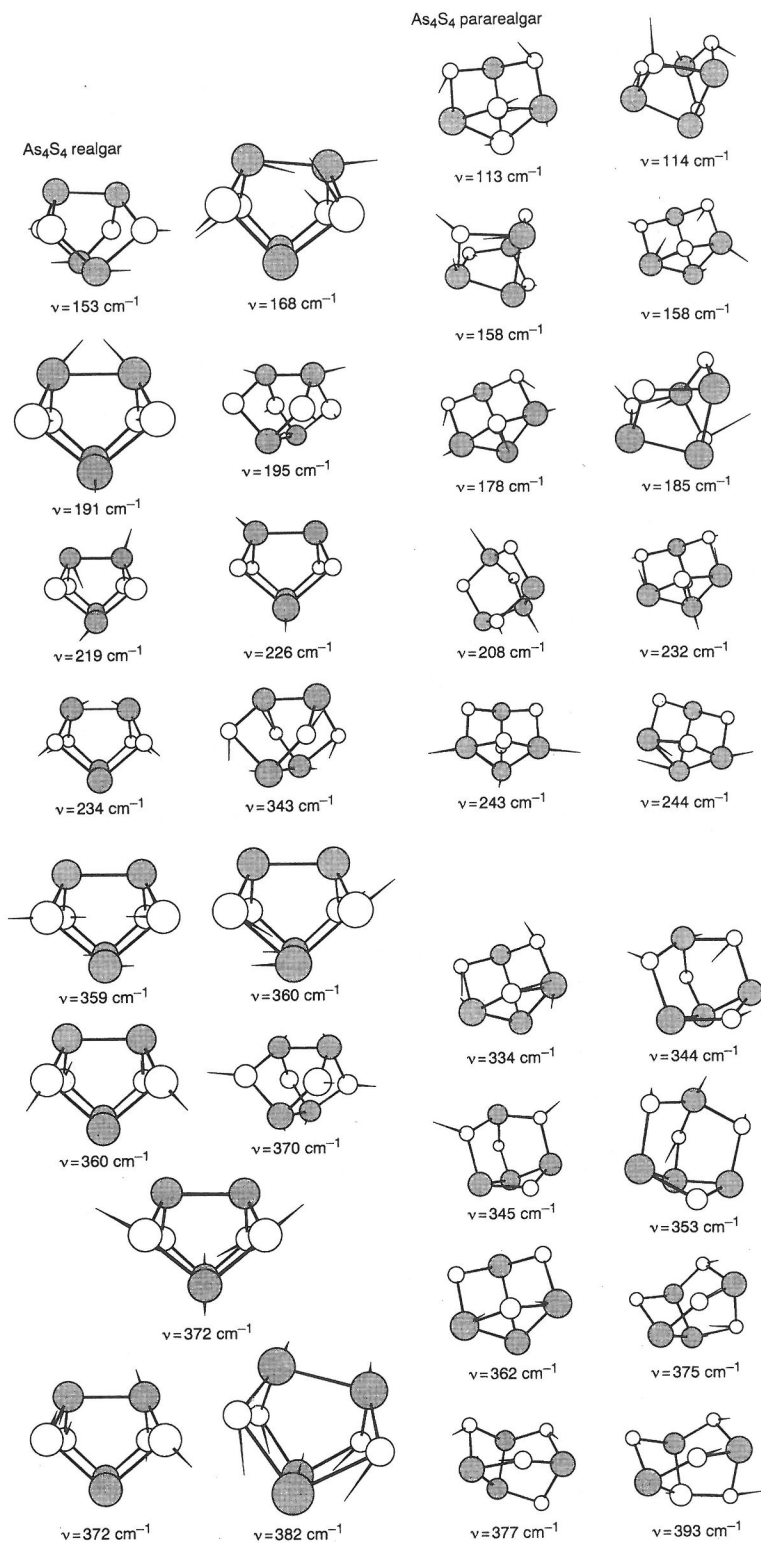


FIG. 3. Vibrational normal modes in the two isomers of As₄S₄. As are shown as larger, solid spheres, S as smaller, open spheres. The arrows are proportional to the nuclear displacements. The normal modes are identified by their scaled calculated frequencies.

Table 5. Calculated properties of different electronic and charge states of As_4S_4 , realgar isomer, in eV (IP = ionization potential, EA = electron affinity)

Vertical IP (ΔE_{SCF})	8.62
Adiabatic IP (reopt. geom.)	8.35
Vertical EA (ΔE_{SCF})	-0.45
Adiabatic EA (reopt. geom.)	0.73
Transition energy to triplet state:	
At ground singlet equilibrium geom.	3.69
At triplet equilibrium geom.	0.80
Transition energy to lowest singlet at ground state singlet geom.	4.83
Negatives of orbital eigenvalues for highest occupied orbitals in neutral singlet: 9.14, 9.68, 3×10.46 , 10.83, 11.25, 2×11.54 , 2×13.43 , 13.82, 14.02, 14.90	

for the realgar molecule in Table 5. We also list the negatives of the orbital eigenvalues, which according to Koopmans' theorem approximate the vertical ionization energies, for the highest energy occupied orbitals of the realgar isomer. These relative ionization energies match reasonably well against the UV photoemission data of TAKANASHI and HARADA (1980). Although the geometry of the relaxed As_4S_4 cation is not much different from that of the neutral, the relaxed anion shows a broken As—As bond. This change in geometry is consistent with the As—As antibonding character in the LUMO of neutral As_4S_4 . The optimized geometry of the triplet state (corresponding to a HOMO-LUMO excitation) is very close to that in the anion. The geometries calculated for the anion and the triplet state are like that observed for $\text{As}_4\text{S}_6^{-2}$ (PORTER and SHELDRIK, 1971), which may be seen as

the product of nucleophilic attack of S_2^{-2} on one of the As—As bonds of As_4S_4 .

In Table 6 we collect the calculated electric field gradients at the As nucleus in the various molecules. Since the electric field gradient is a property depending strongly on the electron density near the nucleus we utilize an all-electron basis, the polarized double zeta 6-31G* basis (HEHRE *et al.*, 1986), to calculate it. All the As sulfides except the As(V) compound As_4S_{10} show an electric field gradient slightly smaller than that for gas-phase AsCl_3 . To calculate quadrupole coupling constants from the electric field gradients we have used the value of 0.27 barns for the nuclear quadrupole moment of ^{75}As (SEMIN *et al.*, 1975), which is probably uncertain to at least 10%. Given this uncertainty our calculated coupling constant for AsCl_3 is in reasonable agreement with experiment. For crystalline and amorphous As_2S_3 quadrupole resonance frequencies of about 72–73 MHz are observed (RUBINSTEIN and TAYLOR, 1972). Assuming an asymmetry parameter reasonably close to zero (as must be exactly the case for a molecule with a three-fold rotation axis and consistent with the later results of SZEFTEL and ALLOUL (1979) for vitreous As_2S_3) this translates to a nuclear quadrupole coupling constant of 144–146 MHz, in reasonable agreement with our calculations for $\text{As}(\text{SH})_3$ or As_4S_6 . An interesting feature of the calculated electric field gradients is the small variation within the lower oxidation state As sulfides. Only for As_2 of As_4S_3 , which is bonded to two As atoms within a triangular geometry and only one S (see Table 1) is the field gradient significantly different from the average. Even As_4 in As_4S_4 pararealgar, which is bonded to two As atoms and only one S, has an

Table 6. Calculated principal axis components of the electric field gradient (in atomic units) and quadrupole coupling constant (in MHz) at the As nuclei in AsCl_3 , $\text{As}(\text{SH})_3$, As_4S_3 , As_4S_4 (realgar and pararealgar), As_4S_6 and As_4S_{10} (using the 6-31G* basis at the polarized SBK equilibrium geometry)

Molecule	q_{11}	q_{22}	q_{33}	e^2qQ/h
AsCl_3	-1.32	-1.32	2.63	168 (exp. value 173 ^a)
$\text{As}(\text{SH})_3$	-1.23	-1.23	2.46	156
As_4S_3 As1	-1.21	-1.21	2.42	154
As2	-1.67	0.28	1.39	106
As_4S_4 , realgar	-1.63	-0.84	2.47	157
As_4S_4 , pararealgar				
As1	-1.48	-1.02	2.50	159
As2, As3	-1.49	-1.02	2.50	159
As4	-1.52	-0.86	2.38	151
As_4S_6	-1.14	-1.14	2.29	146
As_4S_{10}	1.47	1.47	-2.94	187

^a SEMIN *et al.* (1975).

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As_4S_6	-1.14	-1.14	2.29	146
As_4S_{10}	1.47	1.47	-2.94	187

^a SEMIN *et al.* (1975).

electric field gradient very much like that in the other sulfides. For the As_4S_{10} molecule, containing four-coordinate As(V), the electric field gradient components are larger (and of opposite sign), indicating a higher quadrupole coupling constant.

Calculated HOMO-LUMO energy gaps for all the molecules studied are shown in Table 7. It is clear that As and S containing molecules have similar valence orbital energetics while Sb containing species have somewhat smaller energy gaps. For the As_4S_y and Sb_4S_y series the trends in HOMO-LUMO energy gaps are similar, with the gaps increasing from $y = 3$ through $y = 6$ and then decreasing for $y = 10$, in the same order as the heats of formation. The HOMO-LUMO gap is also smaller in the less stable pararealgar isomer of As_4S_4 . According to the principle recently formulated by PARR and CHATTARAJ (1991), the most stable molecules are those with a maximum "hardness". Although this "hardness" is actually defined in terms of second derivatives of the total energy with respect to the number of electrons, it can be approximated by the difference of LUMO and HOMO eigenvalues, or the energy gap. Consistent with this principle, realgar has a larger HOMO-LUMO gap than pararealgar and the largest gaps appear for the As(III) and Sb(III) sulfides, which have the most negative calculated formation energies.

For S_8 we calculate the lowest energy allowed dipole transition at 5.81 eV using the polarized SBK basis and the RPA method, compared to experimental values of 4.3 eV (COOK and SPEAR, 1969) and 4.4–4.7 eV (STEUDEL *et al.*, 1988). Calculations of the spectrum of S_3^- by JOHANSEN (1995) showed that basis set expansion and correlation decreased the calculated energy of the transitions near 4.5 eV. Modest expansion of our basis

set for the As_4S_4 calculation (using two 3d polarization functions on each atom instead of one) indeed reduces the calculated excitation energy from 4.83 to 4.63 eV. This suggests that we are overestimating the excitation energies by about 1.5 eV, leading to an estimated excitation energy to the lowest singlet state of about 3.3 eV in realgar and about 2.2 eV for excitation to the lowest triplet. Because of the very high absorption of realgar in the UV its full spectrum has not been characterized. Studies of its photoconductivity by STREET and GILL (1966) yielded an optical gap of about 2.4 eV and a photoconductivity peak at about 2.9 eV.

For the isomers of As_4S_4 molecular dipole polarizabilities have also been calculated for energies from 0 to 4.5 eV and are presented as well in Table 8. Based on an average dielectric constant of about 2.64 for realgar in sodium D light ($E = 2.1$ eV) from WINCHELL and WINCHELL (1964), the formulas of HARTSHORNE and STUART (1960) and a volume of 199.8 \AA^3 per molecule (MULLEN and NOWACKI, 1972) we obtain an experimental polarizability per molecule of 31.8 \AA^3 , compared to a calculated value of 25.1 \AA^3 with our best basis set. It is not immediately clear whether all the discrepancy with experiment for the excitation energies and polarizability can be attributed to basis set truncation and correlation effects or whether solid-state effects within the realgar crystal are also of some importance. Of course we are also using an effective core potential basis set which excludes any contribution from the core electrons of As and S.

CONCLUSIONS

It is apparent that quantum mechanical calculations at this level can satisfactorily reproduce many of the structural and energetic properties of As and Sb sulfide molecules. Using standard scaling factors we can also reproduce the vibrational spectra of these molecules and assign the normal modes. The vibrational spectra of the realgar and pararealgar forms of As_4S_4 are predicted to differ in significant and understandable ways. Calculating the UV spectra and polarizabilities of the arsenic sulfide molecules would seem to be a greater challenge, with both compromises in the quantum mechanical treatment and solid state effects potentially important in explaining the discrepancies with experiment. There is also evidence that the UV spectrum of realgar may depend significantly upon temperature, since the mineral's color changes from bright red at room temperature to green-yellow at -180°C (BERAN *et al.*, 1994).

Table 7. Calculated HOMO-LUMO gaps (in eV) for molecules studied

S_8	11.63
As_4	10.65
Sb_4	8.85
As_4S_3	9.06
As_4S_4	
realgar	9.93
pararealgar	9.64
As_4S_6	10.19
As_4S_{10}	7.71
Sb_4S_3	8.70
Sb_4S_4	8.85
Sb_4S_6	9.36
Sb_4S_{10}	9.20

Table 8. Calculated singlet and triplet excitation energies, ΔE_1 and ΔE_3 (in eV), oscillator strengths (in parentheses) and dynamic polarizabilities, $\alpha(E)$ (in \AA^3) for realgar and pararealgar (basis set a only) As_4S_4 molecules, using the random-phase-approximation and the specified basis sets (a: polarized SBK; b: polarized SBK + diffuse s,p; c: SBK + double 3d)

Realgar						Para-realgar	pol. SBK				
ΔE_1			ΔE_3			$\alpha(E)$			ΔE_1	ΔE_3	
a	b	c	a	b	c	E	a	b	c		
4.83 (0.002)	4.84 (0.002)	4.63 (0.005)	3.69	3.93	3.52	0.0	20.5	20.6	24.2	4.306 (0.001)	3.385
5.38 (0.0)	5.53 (0.0)	5.17 (0.0)	4.56	4.66	4.28	0.5	20.6	20.7	24.3	5.014 (0.005)	3.910
5.54 (0.0)	5.57 (0.0)	5.31 (0.0)	4.62	4.72	4.35	1.0	20.8	20.8	24.4	5.042 (0.007)	4.311
5.63 (0.082)	5.82 (0.138)	5.40 (0.049)	4.74	4.78	4.53	1.5	21.0	21.1	24.7	5.217 (0.011)	4.395
5.65 (0.00)	5.83 (0.00)	5.42 (0.00)	4.98	5.22	4.74	2.0	21.4	21.6	25.1	5.273 (0.011)	4.580
5.78 (0.123)	5.91 (0.0)	5.60 (0.097)	5.06	5.34	4.81	2.5	22.0	22.2	25.7	5.335 (0.011)	4.664
5.84 (0.00)			5.29	5.41	4.97	3.0	22.8	23.0	26.5	5.356 (0.011)	4.740
						3.5	23.8	24.1	27.6	5.456 (0.024)	4.780
						4.0	25.1	25.6	29.1	5.560 (0.002)	4.848
						4.5	27.2	28.0	32.1	5.814 (0.034)	4.900

Studies of the light-induced alteration of realgar to pararealgar (DOUGLAS *et al.*, 1992) indicate that light with energy around 2 eV is most effective in effecting the transformation and that there is an intermediate phase (labeled c) which gradually transforms to pararealgar. Based on the comparison of calculated S_8 and As_4S_4 spectra this may be a triplet state of the As_4S_4 molecule, which relaxes to break one of the As—As bonds. Formation of pararealgar from this triplet state can be accomplished by motion of one of the S atoms, without significant energy penalty. Alternatively it is possible that more than one As_4S_4 molecule is involved in the transformation step.

The next step in studying the solution chemistry of these compounds will be to evaluate the interaction of these molecules with species present in sulfidic solution. At the SCF level As_4S_6 reacts exothermically with H_2S to give solution species such as the trimer $\text{As}_3\text{S}_3(\text{SH})_3$ (see HELZ *et al.*, 1995 for a discussion of this species), but the reaction energy per mole of $\text{As}_3\text{S}_3(\text{SH})_3$ formed is only -3.3 kcal. As_4S_4 reacts exothermically with H_2S and S_8 to give the same product with a reaction energy of -9.4 kcal per mole of $\text{As}_3\text{S}_3(\text{SH})_3$ formed.

It is also clear that more work remains to be done in elucidating the molecular mechanism of the realgar-pararealgar conversion as well as the mechanism of thermal annealing of vapor-deposited As_2S_3 films. Also many questions remain concerning the effect of light on various amorphous As sulfides (LEE *et al.*, 1990).

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