

Calculation of the visible-UV absorption spectra of hydrogen sulfide, bisulfide, polysulfides, and As and Sb sulfides, in aqueous solution

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Recently we showed that visible-UV spectra in aqueous solution can be accurately calculated for arsenic (III) bisulfides, such as $\text{As}(\text{SH})_3$, $\text{As}(\text{SH})_2\text{S}^-$ and their oligomers. The calculated lowest energy transitions for these species were diagnostic of their protonation and oligomerization state. We here extend these studies to As and Sb oxidation state III and V sulfides and to polysulfides S_n^{2-} , $n = 2-6$, the bisulfide anion, SH^- , hydrogen sulfide, H_2S and the sulfanes, S_nH_2 , $n = 2-5$. Many of these calculations are more difficult than those performed for the As(III) bisulfides, since the As and Sb(V) species are more acidic and therefore exist as highly charged anions in neutral and basic solutions. In general, small and/or highly charged anions are more difficult to describe computationally than larger, monovalent anions or neutral molecules. We have used both Hartree-Fock based (CI Singles and Time-Dependent HF) and density functional based (TD B3LYP) techniques for the calculations of absorption energy and intensity and have used both explicit water molecules and a polarizable continuum to describe the effects of hydration. We correctly reproduce the general trends observed experimentally, with absorption energies increasing from polysulfides to As, Sb sulfides to SH^- to H_2S . As and Sb(V) species, both monomers and dimers, also absorb at characteristically higher energies than do the analogous As and Sb(III) species. There is also a small reduction in absorption energy from monomeric to dimeric species, for both As and Sb III and V. The polysulfides, on the other hand, show no simple systematic changes in UV spectra with chain length, n , or with protonation state. Our results indicate that for the As and Sb sulfides, the oxidation state, degree of protonation and degree of oligomerization can all be determined from the visible-UV absorption spectrum. We have also calculated the aqueous phase energetics for the reaction of S_8 with SH^- to produce the polysulfides, S_nH^- , $n = 2-6$. Our results are in excellent agreement with available experimental data, and support the existence of a S_6 species.

Introduction

In hydrothermal solutions, As and Sb are often present in appreciable concentration,¹ often occurring in association with Ag, Au and Hg, but the identities of the As and Sb species present are not well understood. In neutral to alkaline sulfidic waters at low temperature, thio- species are believed to predominate.² The speciation of Sb in sulfidic solutions has been studied for some time, but new results are still emerging. The main questions concern the oxidation state (III or V), the coordination number and the degree of oligomerization of the species. Typically Sb(III) compounds, which essentially have a $5s^2$ lone pair orbital, will be trigonal three-coordinate, while Sb(V) compounds, without the lone pair, will be tetrahedral four-coordinate. By 1990 a consensus seemed to emerge that in alkaline sulfidic solutions Sb existed as Sb(III), based on numerous solubility studies²⁻⁴ and Raman studies.⁵

However, recent EXAFS studies^{6,7} have presented evidence for the presence of Sb(V) species in such solutions. The Sb-S distances determined by EXAFS were more consistent with those for model compounds with four-coordinate Sb(V) than for those with three-coordinate Sb(III) and the coordination numbers from the model fits to the data were close to 4. Recently Helz and coworkers⁸ reported the results of a solubility study for stibnite, Sb_2S_3 , and elemental S in equilibrium with alkaline sulfidic solutions, which could be best interpreted in terms of a number of dimeric species, including the mixed Sb(III,V) and the Sb(V,V) dimers, $\text{Sb}_2\text{S}_5^{2-}$ and $\text{Sb}_2\text{S}_6^{2-}$, which were new species, not previously

considered. They also presented visible-UV absorption spectra which showed a broad peak around 4.4 eV, consistent with the limited experimental data available on Sb(V) sulfides. In recent work we have calculated energetics⁹ for the formation of such oxidized dimer species which are in good agreement with the experimental data of Helz *et al.*⁸

We had previously calculated structures, energetics and spectra for various Sb(III) monomers and oligomers,¹⁰ assigning the spectra of Wood⁵ to a more protonated Sb(III) dimer than in the original work. At that time procedures recently developed to calculate pK_a s for such species¹¹ were not yet available. We also noted in ref. 10 that three-coordinate Sb(III) and four-coordinate Sb(V) had very similar Sb-S stretching frequencies so that information in addition to the Raman spectra was necessary to exclude the presence of Sb(V) species in the solutions studied. Additional Raman spectral data has since been presented for the As-S system,¹² but the spectra seem so complex that assigning species based just on the Raman seems very difficult. Additional information has also recently become available from ion-exchange mass spectrometry, but only limited information on atom ratios can be obtained using this method.¹³

Recently, UV spectroscopy has been used to study acid dissociation in solution, first for H_2S ¹⁴ and then for $\text{As}(\text{OH})_3$.¹⁵ Although the concentrations of the different species were determined primarily through changes in spectral intensities at energies lower than the absorption maximum (on the low energy side of the band), the maxima themselves were determined for $\text{As}(\text{OH})_3$ and $\text{AsO}(\text{OH})_2^-$, and showed a

difference of around 0.5 eV. We calculated the UV absorption spectra for both bare gas-phase $\text{As}(\text{OH})_3$, its conjugate base and these same species microsolvated with water.¹⁶ The calculations were also extended to some of the oligomers of $\text{As}(\text{OH})_3$ and to related species derived from thioarsenious acid $\text{As}(\text{SH})_3$. The calculated energies were in good agreement with experiment and it was clear that both protonation state and degree of oligomerization had observable effects upon the spectrum. This indicated that visible-UV spectroscopy could be a useful new technique for assessing speciation in solutions containing metalloids sulfides, and perhaps for polysulfides as well. It therefore became important to establish whether visible-UV spectra could be accurately calculated for a range of such anionic sulfide species in aqueous solution and whether simple recognizable trends in spectral energy were present, which could be used to determine speciation. Although visible-UV spectra have not been extensively studied for As sulfides, the instruments needed to perform such measurements are readily available. The main impediment to such experimental studies is the paucity of studies calculating and interpreting such data using accurate quantum chemical techniques. This paper represents part of our effort to remedy this deficiency.

A detailed knowledge of As and Sb speciation is important for a number of reasons. First, although several different speciation models may be able to explain a limited set of experimental solubility data, extrapolating into new regimes of concentration, P and T can reveal significant differences in both species concentrations and total element concentrations. Second, thermodynamic models for mineral stability and solubility can only be accurately constructed from experimental data if correct speciations are known. Third, the speciation of an element also influences the interaction of that element with mineral surfaces. For example, to understand the well known association between Au and the As and Sb sulfides¹⁶ it is important to understand both the speciation of As and Sb sulfides and the characteristics of the mineral surfaces. Helz *et al.*⁸ have noted that the III,V and V,V Sb sulfide dimers they have characterized will be anionic, rather than neutral as for As hydroxides, and that they will interact unfavorably with mineral surfaces carrying negative charges, leading to desorption of Sb. This is important since Sb_2S_3 in the presence of S is soluble enough to exceed the drinking water standards for total Sb concentration.

As discussed in more detail in ref. 10 determination of speciation from solubility data alone is often ambiguous. Even if spectral data such as EXAFS or Raman is also available, determining speciation based on comparison with model compound data is often difficult. Using quantum mechanical methods we can evaluate a number of different properties, including structure, energy and spectral properties for a number of candidate species, and search for the best overall fit to the available experimental data. In this case our primary goal is to determine if the visible-UV spectra of polysulfide and metalloid sulfide species show changes with oxidation state, protonation state or degree and type of oligomerization which are diagnostic of their structure.

Computational methods

We use the methods of Hartree–Fock theory and density functional theory.¹⁸ For all the species considered we have calculated geometries at the second order of Møller–Plesset perturbation theory¹⁹ (MP2) using the polarized SBK basis set.²⁰ Our previous studies¹⁶ on $\text{As}(\text{OH})_3$ and related molecules indicated that the effect of geometry on the visible-UV energies was fairly small. In addition, polarized SBK MP2 is an efficient, medium level correlated method which normally gives very accurate geometries at modest computational cost. We have also directly established the small effect of the method of

geometry optimization for the important species $\text{S}_4^{2-} \cdots 4\text{H}_2\text{O}$ (*vide infra*). For the calculation of the visible-UV energies we used both all-electron 6-311+G(2d,p) bases²¹ and the polarized SBK bases and employed both HF and DFT type methods. In a few cases we also have also utilized the large “correlation consistent” basis sets from Dunning’s group²² at the aug-cc-pVDZ and aug-cc-pVTZ (augmented correlation-consistent polarized valence double and triple zeta levels). In evaluating excitation energies we used either the configuration-interaction singles method^{23a} (CIS), the time-dependent Hartree–Fock method²⁴ (TD HF), the CIS(D) method^{23b} or the time-dependent density functional method^{25–27} (TD DFT) method. The DFT studies have been done mainly with the hybrid B3LYP potential.²⁸ Analyses of these different methods for calculating excitation energies are given in ref. 25 and 26. Basically, CIS describes the excited state wavefunction at a level comparable to Hartree–Fock, using single excitations from the HF determinant. The TD HF method (also called the random phase approximation, RPA) includes some double excitations, giving a slightly correlated description of both ground and excited states. The CIS(D) method also incorporates some double substitution corrections to the CIS energies, in a size-consistent way. TD DFT includes additional electron correlation through the exchange correlation potential. In ref. 25 it was found for several different molecules that TD DFT using the hybrid B3LYP potential gave the best agreement with experiment, consistently giving excitation energies intermediate between those from TD HF and TD DFT with pure DFT potentials. In our studies¹⁶ on $\text{As}(\text{OH})_3$ and related molecules we found the TD HF and TD B3LYP results appeared to bracket the experimental values, with TD B3LYP a few tenths of an eV closer to experiment, but consistently a little too low.

To describe the species in aqueous solution we use both an explicit supermolecule or microhydration approach, in which several water molecules (typically 4–6) are coordinated to the solute at the optimized geometry of the supermolecule, and a polarizable continuum approach. These geometries are similar to those we previously reported²⁹ for $\text{AsO}(\text{OH})_2^- \cdots 4\text{H}_2\text{O}$, a supermolecule which was used to calculate the vibrational spectrum of the arsenite anion in solution. The geometries of all the supermolecules in the present study were obtained by a similar approach, but utilizing the polarized SBK basis set at the MP2 level. The geometries have been verified to be local energy minima by frequency analysis, but are not necessarily the global minima. These species are in fact just simple approximations to the real hydrated species. We have not systematically studied the effect of varying the number of water molecules in the supermolecule, although we have employed a very large supermolecule with 22 water molecules for S_4^{2-} (with the geometry optimized at the polarized SBK HF level, not MP2).

Generally better results are obtained for solutes in aqueous environments if the solute is immersed in a polarizable continuum. For the most recent and complete such approach applied to spectral properties see ref. 30. It is also possible to use a “mixed” approach, employing both microhydration and a polarizable continuum. However, in many of the studies done so far with this approach the number of water molecules used has been very small, usually only one or two coordinating to the chromophoric group of the molecule, *e.g.* the C=O in a study of acetone.³¹ We have tried to approach the problem fairly simply yet systematically for the present species, using several waters of hydration (4–6) in the microhydrated species and then immersing this species in a polarizable continuum. We have utilized primarily the COSMO or CPCM version³² of the polarizable continuum model, although we have also tested the computationally less stable isodensity polarized continuum model.³³ The COSMO solvation approach has been applied both to bare anionic solutes and to the microhydrated species. For the very largest species considered, $\text{S}_4^{2-} \cdots 22\text{H}_2\text{O}$, we have

employed the ONIOM method,³⁴ in which different parts of the supermolecule can be treated at different levels of accuracy, using different basis sets or even different quantum methods. We employed the 6-311+G(2d,p) basis for the S atoms and the 6-31G* basis for the surrounding waters in the CIS ONIOM calculations.

The calculations were performed using the software packages GAMESS,³⁵ GAUSSIAN94^{36a} and GAUSSIAN98,^{36b} on two different clusters of COMPAQ DECStations.

Results and discussion

The main results of our spectral calculations are given in Tables 1 and 2. Table 1 gives results for hydrogen sulfide, bisulfide anion, polysulfide anions and gas-phase sulfanes. Results for As and Sb sulfide monomers and dimers are given in Table 2. Most of the results are obtained using the CIS and CIS COSMO methods with the 6-311+G(2d,p) basis set. Some results using the TD B3LYP method are given in italics. Both free anions and explicitly hydrated anions are considered. We can compare with previous calculations of excitation energies using (and referring to) a number of different methods for H₂S and S₂H₂.³⁷ Experimental energies where available are given in the last column. The experimental values are taken from ref. 38–42 for H₂S, SH⁻, polysulfides, Sb sulfides and sulfanes, respectively. Calculated oscillator strengths are given in parentheses for some of the compounds, particularly the more symmetric ones, where some transitions are forbidden at the equilibrium geometry.

To establish the protonation state expected for the polysulfides and As and Sb sulfides in the solutions of interest, we employ the procedure of ref. 9, in which we calculated gas-phase deprotonation energies at the polarized SBK MP2 level, and hydration energies at the 6–31G* HF level using

Table 1 Calculated and experimental values of the lowest energy optical transitions (eV) for hydrogen sulfide, bisulfide anion, polysulfide anions and sulfanes, using the 6-311+G(2d,p) basis (TD B3LYP results in italics, CIS oscillator strengths in parentheses)

Molecule	<i>ΔE</i> CIS <i>TD B3LYP</i>	<i>ΔE</i> CIS COSMO	<i>ΔE</i> exp.
H ₂ S	6.2, 6.7 <i>5.9, 5.9</i>	6.4, 6.9	6.4, 6.7
SH ⁻	4.6 <i>3.9</i>	5.6	
SH ⁻ ⋯6H ₂ O	5.6 <i>4.3</i>	5.8	5.4
S ₂ ²⁻	1.9	3.3	
S ₂ ²⁻ ⋯4H ₂ O	2.4	3.37 (0.023) 3.56 (0.025) 4.94 (0.060)	3.5
S ₃ ²⁻	2.4	3.2	
S ₃ ²⁻ ⋯4H ₂ O	2.8	3.22 (0.064) 4.23 (0.053)	3.0
S ₄ ²⁻	3.0	3.6	
S ₄ ²⁻ ⋯4H ₂ O	3.4	3.75 ^a (0.027) <i>1.9</i> 3.80 (0.006) 4.54 (0.027)	3.4
S ₄ ²⁻ ⋯22H ₂ O ^b	3.6	—	
S ₄ H ⁻	3.4	3.7	
S ₄ H ⁻ ⋯4H ₂ O	3.7	3.8	
S ₅ ²⁻	3.17	3.55	3.3
S ₆ ²⁻	3.25	3.54	—
S ₂ H ₂	5.4	5.4	5.0
S ₃ H ₂	5.2 <i>4.2</i>		4.5
S ₄ H ₂	5.2		4.2
S ₅ H ₂	5.1		4.1

^a 3.64 and 3.62 eV for TD COSMO with 6-311+G(2d,p) and aug-cc-pVDZ bases, respectively. ^b ONIOM calculation, with 6-311+G(2d,p) basis on S₄ unit and 6-31G* basis on waters.

Table 2 Calculated and experimental lowest energy optical transitions in As and Sb III and V sulfide monomers and dimers (TD B3LYP results in italics, CIS oscillator strengths in parentheses)

Molecule	<i>ΔE</i> CIS	<i>ΔE</i> CIS COSMO	<i>ΔE</i> exp. ^b
AsS ₃ ³⁻ ⋯4H ₂ O			
6-311+G(2d,p)	2.7	4.0	
6-311G(2d,p)	4.1	4.4	
SBK+As, S, O d	4.3	4.5	
As(SH) ₃ ⋯4H ₂ O			
6-311+G(2d,p)	5.3	5.3	
AsS ₄ ³⁻ ⋯6H ₂ O			
6-311+G(2d,p)	4.0	4.6	
6-311G(2d,p)	4.1	4.7	
SBK+As, S, O d	4.6	4.7	
SbS ₃ ³⁻ ⋯4H ₂ O			
SBK+Sb, S, O d	4.3	4.5	
SbS ₄ ³⁻ ⋯6H ₂ O			
SBK+Sb, S, O d	4.7	4.8 ^a	4.35
		3.3	
Sb ₂ S ₄ ²⁻ ⋯4H ₂ O		3.2 (0)	
SBK+Sb, S, O d		4.0 (0)	
		4.5 (0.074)	
Sb ₂ S ₅ ²⁻ ⋯5H ₂ O		4.1 (0.030)	
SBK+Sb, S, O d		4.6 (0.028)	
Sb ₂ S ₆ ²⁻ ⋯6H ₂ O			
SBK+Sb, S, O d	4.6	4.7 (0.022)	
As(S ₄)(SH)			
6-311+G(2d,p)	4.0	4.1	

^a 4.74 eV with TD COSMO method. ^b ref. 41 (see also ref. 8).

COSMO. This allows us to calculate an approximate aqueous deprotonation energy, called ΔG_{aq} in ref. 9, which we could then correlate with $\text{p}K_{\text{a}}$ s (of any order for polyprotic acids) using the equation:

$$\text{p}K_{\text{a}} = 0.323 \Delta G_{\text{aq}} - 87.3$$

The ΔG_{aq} values obtained for S₄H⁻, SbS₃(SH)²⁻ and SbS₂(SH)²⁻ are 288.1, 287.1 and 298.4 kcal mol⁻¹, respectively, which yield predicted $\text{p}K_{\text{a}}$ s of 5.8, 5.4 and 9.1. This indicates that S₄H⁻ and SbS₃(SH)²⁻ will be fully deprotonated at neutral pH. Sb(III) species like SbS₂(SH)²⁻ will be fully deprotonated above pH 9. These compounds are representative of all the polysulfides, and of all the As and Sb III and V species. Thus, we carried out our absorption energy calculations for the fully deprotonated species.

There are several conclusions which can be drawn based on the data in Table 1:

(1) For H₂S and S₂H₂ our values agree almost as well with experiment as do those from the older, more traditional methods (such as multireference CI), used in ref. 37. The best previous calculated values are 6.37 and 4.98 eV for H₂S and S₂H₂, respectively, while we calculate 6.4 and 5.4 eV, respectively, and the experimental values are 6.4 and 5.0 eV, respectively.

(2) The CIS COSMO results for explicitly hydrated anions are in the best agreement with experiment, although the calculated values tend to be too high by a few tenths of an eV.

(3) The TD B3LYP COSMO results are systematically around 1 eV too low.

(4) Employing COSMO and CIS together always increases the calculated absorption energies compared to CIS alone, but the change is much larger for bare anions than for explicitly hydrated anions.

(5) The effect of either COSMO or explicit hydration is larger for the dianions than for monoanions and neutrals.

(6) The general experimental trend in visible-UV absorption energies of: polysulfides < bisulfide < H₂S is correctly reproduced.

(7) The calculations give essentially the same absorption

energies for S_4^{2-} and S_4H^- , so that distinguishing protonation state in the polysulfides may not be possible.

(8) The nonlinear variation in lowest absorption energy with n for the polysulfide series, S_n^{2-} , seems to be qualitatively reproduced.

(9) For the sulfane series, S_nH_2 , the calculated effect of n on the absorption energy is very small, inconsistent with the values tabulated in ref. 42 (although the spectra are very broad and do not seem to necessarily support the tabulated energy values).

(10) CIS (ONIOM) results for S_4^{2-} explicitly hydrated by a 22 water molecules are quite similar to the CIS COSMO results for $S_4^{2-} \cdots 4H_2O$, so that larger explicitly solvated clusters could be used to replace continuum solvation (although at considerable additional computational cost).

We also find that the TD COSMO and CIS COSMO results are very similar (although TD requires about twice the computer time of CIS). For example, for $S_4^{2-} \cdots 4H_2O$ the lowest excitation energy calculated with TD COSMO is 3.64 eV, only about 0.1 eV lower than with CIS COSMO. Similar close agreement of CIS and TD HF results was seen in our previous study of As(III) oxo and thio acids.¹⁶ We also find that 6-311+G(2d,p), aug-cc-pVDZ and aug-cc-pVTZ bases also give very similar results (to within 0.1 eV) for $S_4^{2-} \cdots 4H_2O$ with the CIS TD method as a test case. Since the aug-cc-pVTZ calculations employ a basis set about twice as large and require about 2^4 times more computer time than those for aug-cc-pVDZ or 6-311+G(2d,p) bases we therefore have used only the 6-311+G(2d,p) basis for the other species. Therefore, we will from now on quote only the CIS results with the 6-311+G(2d,p) basis for polysulfides.

We have also done a few calculations using the CIS(D) method, for H_2S , S_3^{2-} and S_2H_2 . The changes from the CIS results are small but apparently in the direction to better match experiment. For example the lowest excitation energy in H_2S changes from 6.2 to 6.3 eV (exp. 6.4 eV) while that in S_2H_2 changes from 5.4 to 5.1 eV (exp. 5.0 eV). For S_3^{2-} the CIS(D) result is 2.7 eV, compared to 3.2 eV with CIS. A more relevant calculation to compare with experimental polysulfide spectra would be CIS(D) with COSMO solvation for $S_3^{2-} \cdots 4H_2O$, but this calculation is presently a bit too demanding of computer time (for S_2H_2 CIS(D) takes twice as much computer time as CIS).

For $S_4^{2-} \cdots 4H_2O$ we have also performed CIS COSMO calculations using the 6-311+G(2d,p) basis set at four different sets of optimized geometries, obtained using polarized SBK HF, polarized SBK MP2, 6-31G* MP2 and 6-31G* B3LYP methods. The lowest energy transitions calculated for these four different optimized geometries were 3.75, 3.74, 3.70 and 3.65 eV, respectively, indicating that the effect of geometry upon the absorption energy is fairly small and/or that these different methods give very similar optimized geometries.

Based on the data on As and Sb sulfides in Table 2, some additional conclusions can be drawn:

(1) For the As and Sb sulfides, the CIS COSMO results still seem the most reliable, but CIS COSMO and TD B3LYP COSMO results now appear to straddle the very limited experimental data, with CIS COSMO too high and TD B3LYP COSMO too low.

(2) The polarized SBK and the 6-311G(2d,p) bases give very similar results, while the bases with diffuse functions (e.g. 6-311+G(2d,p)) have a tendency to give energies which are too low, even when explicitly hydrated and stabilized within the polarizable continuum (a similar difficulty with diffuse functions was encountered previously by Tossell for $As(OH)_3$ anionic species¹⁶).

(3) The effects of explicit hydration and COSMO solvation are larger than seen for the polysulfides in Table 1, probably because of the larger charges on the anions.

(4) The neutral acid molecule $As(SH)_3$ shows absorption at higher energy than its anion AsS_3^{3-} by about 1 eV (in our

Table 3 Analysis of changes in UV energies (in eV) between CIS, CIS COSMO and CIS IPCM for S_4^{2-} (using the 6-311+G(2d) basis)

Method	CIS	CIS COSMO	CIS IPCM
$\Delta E_{CIS^{***}}$	3.02	3.54	3.35
ϵ_{HOMO}	0.82	-7.35	-6.91
ϵ_{LUMO}	7.94	1.80	1.69
$\Delta\epsilon$	7.13	9.14	8.60

Table 4 Comparison of calculated ionization energies and singlet-triplet excitation energies (evaluated at HF level, including COSMO hydration) and CIS energies (all energies in eV)

Molecule	Ionization energy	S \rightarrow T excitation energy	$\Delta E_{CIS \text{ COSMO}}$
SH^-	7.8	4.4	5.6
$SH^- \cdots 6H_2O$	4.6	4.3	5.8
S_4^{2-}	4.5	2.9	3.6
$S_4^{2-} \cdots 4H_2O$	3.1	2.0	3.8

earlier study $As(SH)_3$ and $AsS(SH)_2^-$ showed a difference of about half an eV).

(5) For the monomeric species, the calculated energies for oxidation state v are only slightly, but consistently, higher than those for oxidation state III.

(6) The dimeric species have slightly lower absorption energies than the monomers, particularly if we ignore the symmetry forbidden character of the lowest energy transition in $Sb_2S_4^{2-}$ (which restriction would be relaxed away from the equilibrium geometry).

(7) The lowest energy absorption for a mixed bisulfide, polysulfide cluster $As(S_4)(SH)$ lies between that for S_4^{2-} and $As(SH)_3$.

As suggested by many researchers, such mixed bisulfide, polysulfide clusters are quite possible and it would probably be worthwhile to investigate their properties more systematically.

We can gain some understanding of the effect that polarizable continuum hydration has on the calculated absorption energies by examining the data in Table 3 for S_4^{2-} , where we give calculated HOMO and LUMO energies, along with absorption energies calculated with CIS, COSMO and CIS IPCM methods. We see that using COSMO or IPCM increases the HOMO–LUMO gap, $\Delta\epsilon$, by on the order of 2 eV, since the HOMO is stabilized more than the LUMO by the charge distribution induced in the polarizable continuum. This increase in the HOMO–LUMO gap increases the absorption energy. Note that although the lowest energy transition has a large contribution from the HOMO to LUMO excitation, as discussed in detail in ref. 16 for the As(III) compounds, there are also other sizable orbital contributions, so that the change in the CIS transition energy is less than the change in the HOMO–LUMO gap.

As shown in Table 4, we can also establish the independence of our CIS COSMO energies from other energies that would be associated with charge-transfer-to-solvent (CTTS) type transitions (such as the ionization energies of the species) and their resemblance to singlet–triplet excitation energies calculated at the HF level, as discussed in a recent study of the CTTS spectra of I^- in water.⁴³ These are essentially test calculations to establish that the CIS COSMO results are a reflection of the electronic structure of the solute and are not describing ionization coupled with acceptance of electrons into an empty orbital of the solvent. That is, the spectra we are considering are not really CTTS spectra. It is sometimes assumed that any solution spectrum which changes as a function of polarity of the solvent is of CTTS nature. This is definitely not the case: transitions which are essentially internal to the solute will be modified to some extent by changing polarity in the solvent. Of

Table 5 Calculated effect of varying the dielectric constant on the lowest optical transition energies (in eV) for H₂S, SH⁻, S₄²⁻⋯4H₂O and SbS₃³⁻⋯4H₂O, using the CIS and CIS COSMO methods and the 6-311+G(2d,p) basis unless otherwise noted (*D* = dielectric constant)

Method/molecule	Free (CIS only)	<i>D</i> = 38.2	<i>D</i> = 78.5
H ₂ S	6.22	6.29	6.36
SH ⁻	4.57	5.14	5.62
S ₄ ²⁻ ⋯4H ₂ O	3.42	3.64	3.75
SbS ₃ ³⁻ ⋯4H ₂ O ^a	4.29	4.44	4.54

^a SBK+Sb, S, O d.

course, the close similarity of CIS COSMO results for the bare and the explicitly hydrated SH⁻ and S₄²⁻ anions in Table 4 (and for others in the previous tables) also supports this interpretation.

It is also clear from the effect of the COSMO solvation on the spectral energies that we can in fact model changes in the absorption spectra which are associated with changes in the dielectric constant of the solvent, which may occur as a result of temperature variation. In Table 5 we show calculated absorption energies for several different species, both free (*i.e.* dielectric constant of zero) and for continuum solvation with dielectric constants of 38.2 and 78.5 (appropriate to water at 25 °C). The value of 38.2 is selected somewhat arbitrarily as a value intermediate between 0 and 75.8 (this is also the value for nitromethane, a common organic solvent) but similar values of water dielectric constants are in fact found for supercritical conditions. It is clear that the absorption energies increases systematically with dielectric constant and that the effect becomes larger for both larger charge magnitudes and smaller sizes of the anions. Thus, this general method could be used to study changes in absorption energy with *T* in aqueous solution, although it is not yet clear whether the explicit hydration of the species would also need to be modified, along with the dielectric constant.

It would also be desirable to at least put some constraints on the thermodynamic stabilities of the species present in solutions in equilibrium with sulfide, sulfur and metalloid sulfides. We have previously done this for the Sb sulfide species in ref. 9. For this reason we have also directly calculated quantum mechanically the energetics for the formation of various polysulfides, starting from S₈ and SH⁻ as reactants, and have compared them with experiment in Table 6. We tabulate gas-phase reaction energies, gas-phase vibrational, translational and rotational contributions to Δ*G*, the hydration contributions to Δ*G*, the total Δ*G* in solution and the experimental value of Δ*G*. The calculated free energies are based on polarized SBK MP2 energies and vibrational frequencies for the species involved, with hydration energies evaluated using COSMO. The experimental free energies at 25 °C are obtained from the equilibrium constants tabulated by Shea and Helz,⁴⁴ based on polysulfide equilibria from Giggenbach.⁴⁵ We see that experimental and calculated free energies are in very good agreement, with discrepancies less than 1 kcal mol⁻¹, so long as we describe the reactants as SH⁻ and S₈, rather than the rhombic sulfur mentioned in Giggenbach's paper. Since rhombic sulfur and S₈ differ in standard enthalpy of formation by almost 25 kcal (mol of S₈)⁻¹, changing the reactant to rhombic sulfur would destroy the present agreement of absolute energetics (although trends in free energies in the S_{*n*}H⁻ series would be unaffected). There is some controversy about the existence of the S₆ polyspecies, which is disfavored by Giggenbach but used in one of the models developed by Teder.⁴⁶ Our calculations indicate a degree of stability for S₆H⁻ similar to that of the earlier members of the polysulfide series.

We have also evaluated the energy for a related reaction of gas-phase molecules, which eliminates the problem of defining

Table 6 Calculated energetics for the reaction of S₈ with SH⁻ to produce polysulfides, with gas-phase energies and vibrational corrections evaluated at the polarized SBK MP2 level, and with COSMO solvation

Reaction	Δ <i>E</i> _g	Δ <i>G</i> _{VRT}	ΔΔ <i>G</i> _{COSMO}	Δ <i>G</i> _{aq}	Δ <i>G</i> _{exp}
1/4 S ₈ +SH ⁻ → S ₃ H ⁻	-14.6	+0.5	+18.9	+4.8	+4.9
3/8 S ₈ +SH ⁻ → S ₄ H ⁻	-19.2	+1.4	+21.6	+3.8	+3.7
1/2 S ₈ +SH ⁻ → S ₅ H ⁻	-21.8	+2.4	+23.6	+4.3	+4.8
5/8 S ₈ +SH ⁻ → S ₆ H ⁻	-23.7	+3.3	+25.3	+4.9	na

^a na = not available.

the reactants and also eliminates the need to calculate a hydration energy contribution to the reaction energy. This reaction is



and all the necessary heat of formation data is available in the tabulations of Wagman *et al.*⁴⁷ This is clearly the neutral gas-phase analog of the second equation in Table 6. The experimental value of Δ*H* is 6.3 kcal mol⁻¹, while the value calculated at the polarized SBK MP2 level for Δ*H* is 5.8 kcal mol⁻¹, the same excellent level of agreement as for the solution reactions in Table 6. For this gas-phase reaction the calculated Δ*G* value is 7.6 kcal mol⁻¹ (more positive than the Δ*H* since the -*T*Δ*S* term is positive because of the reduction in number of moles of gas). This indicates that the energetics for reaction of S₈ to form polysulfide-like species are not greatly changed in going from neutral molecules in the gas-phase to ions in solution, with Δ*G* values around +8 in the gas-phase for the formation of the *n* = 4 sulfane and +4 in solution for formation of the *n* = 4 polysulfide. The good agreement of calculation and experimental for this sulfane reaction indicates that the equilibrium properties of H₂S, sulfane systems⁴⁸ could also be determined using such methods.

Conclusion

A method has been developed to calculate visible-UV absorption energies for anionic species in aqueous solution which gives both absolute energies and energy trends which are consistent with experiment. The method involves standard CIS calculations with standard large, polarized basis sets on microhydrated species within a polarizable continuum. It is anticipated that the new, more complete polarizable continuum approaches to spectral properties³⁰ may yield even better results. The basic trends in absorption energy for the different types of species expected in metalloid sulfidic solutions, such as bisulfide, polysulfide and metalloid sulfides, are described correctly. The calculations also predict observable changes in spectral energy for the metalloid sulfides as a function of oxidation state, protonation state and degree of oligomerization, which will provide an additional spectral tool for determining speciation.

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