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

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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 recently become available from ion-exchange mass spectroscopy, but only limited information on atom ratios can be obtained using this method.13 Additional Raman spectral data has recently become available from ion-exchange mass spectrometry, but only limited information on atom ratios can be obtained using this method.13 Additional Raman spectral data has recently become available from ion-exchange mass spectrometry, but only limited information on atom ratios can be obtained using this method.13

We had previously calculated structures, energetics and spectra for various Sb(n) monomers and oligomers,10 assigning the spectra of Wood3 to a more protonated Sb(n) 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(n) 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$_2$S$^{14}$ and then for As(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 As(OH)$_3$ and AsO(OH)$_2^{-}$, and showed a 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 energetics7 for the formation of such oxidized dimer species which are in good agreement with the experimental data of Helz et al.8

We recently showed that visible-UV spectra in aqueous solution can be accurately calculated for arsenic (III) bisulfides, such as As(SH)$_3$, As(SH)$_2$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$_{n}$H$_2$, $n$ = 2–6, the bisulfide anion, SH$^-$, hydrogen sulfide, H$_2$S and the sulfanes, S$_n$H$_2$, $n$ = 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$_2$S. As and Sb(v) species, both monomers and dimers, also absorb at characteristically higher energies than do the analogous As and Sb(n) 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$_6$ with SH$^-$ to produce the polysulfides, S$_n$H$_2^-$, $n$ = 2–6. Our results are in excellent agreement with available experimental data, and support the existence of a S$_6$ species.
difference of around 0.5 eV. We calculated the UV absorption spectra for both bare gas-phase As(OH)3, its conjugate base and these same species microsolvated with water.16 The calculations were also extended to some of the oligomers of As(OH)3 and to related species derived from thioarsenious acid As(SH)2. 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 metalloid 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 sulfides it is important to understand both the speciation of As and Sb sulfides and the characteristics of the mineral surfaces. Helz et al. have noted that the m,ν and v,ν 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 Sb₂S₄ 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 or the time-averaged 22H₂O, we have calculated geometrically at the second order of Møller–Plesset perturbation theory (MP2) using the polarized SBK basis set.20 Our previous studies on As(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 S₄²⁻—4H₂O (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 method23 (CIS), the time-dependent Hartree–Fock method24 (TD HF), the CIS(D) method25 or the time-dependent density functional method25,27 (TD DFT) method. The DFT studies have been done mainly with the hybrid B3LYP potential and then immersing this species in a polarizable continuum. We have tried to approach the problem of 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.

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employed the ONIOM method\textsuperscript{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\textsuperscript{*} basis for the surrounding waters in the CIS ONIOM calculations.

The calculations were performed using the software packages GAMESS,\textsuperscript{35} GAUSSIAN94\textsuperscript{36} and GAUSSIAN98\textsuperscript{37} 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 \( \text{H}_2\text{S} \) and \( \text{S}_2\text{H}_2 \).\textsuperscript{38} Experimental energies where available are given in the last column. The experimental values are taken from ref. \textsuperscript{39–42} for \( \text{H}_2\text{S}, \text{SH}^+ \), 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. \textsuperscript{9}, in which we calculated gas-phase deprotonation energies at the polarized SBK MP2 level, and hydration energies at the 6–31G\textsuperscript{*} HF level using

\[
\begin{align*}
\text{S}_4\text{H}_2 & \quad 5.2 \quad 4.2 \\
\text{S}_2\text{H}_2 & \quad 5.4 \quad 5.4 \quad 3.0 \\
\text{S}_4\text{H}_2 & \quad 5.2 \quad 4.2 \\
\text{S}_2\text{H}_2 & \quad 3.6 \quad 3.6 \\
\end{align*}
\]

Table 1

| Molecule       | \( \Delta E \) CIS | \( \Delta E \) CIS COSMO | \( \Delta E \) exp. |
|----------------|---------------------|--------------------------|-------------------|
| \( \text{H}_2\text{S} \) | 6.2, 6.7            | 6.4, 6.9                  | 6.4, 6.7          |
| \( \text{SH}^- \) | 5.9, 5.9             | 6.4, 6.9                  | 6.4, 6.7          |
| \( \text{SH}^- \cdots 6\text{H}_2\text{O} \) | 5.6                 | 5.8                       | 5.4               |
| \( \text{S}_2\text{H}_2^- \) | 4.3                |                           |                   |
| \( \text{S}_2\text{H}_2^- \cdots 4\text{H}_2\text{O} \) | 2.4                | 3.3 (0.023)               | 3.5               |
| \( \text{S}_2\text{H}_2^- \cdots 6\text{H}_2\text{O} \) | 2.4                | 3.3 (0.023)               | 3.5               |
| \( \text{S}_3\text{H}_2^- \) | 3.0                | 3.6                       |                   |
| \( \text{S}_3\text{H}_2^- \cdots 4\text{H}_2\text{O} \) | 3.4                | 3.75 (0.027)              | 3.4               |
| \( \text{S}_3\text{H}_2^- \cdots 6\text{H}_2\text{O} \) | 3.4                | 3.75 (0.027)              | 3.4               |
| \( \text{S}_4\text{H}_2^- \) | 3.6                | 3.7                       |                   |
| \( \text{S}_4\text{H}_2^- \cdots 4\text{H}_2\text{O} \) | 3.4                | 3.7                       |                   |
| \( \text{S}_4\text{H}_2^- \cdots 6\text{H}_2\text{O} \) | 3.4                | 3.7                       |                   |

\(*\) The calculations give essentially the same absorption energies using 6-311+G(2d,p) basis on \( \text{S}_4\text{H}_2 \) and aug-cc-pVDZ bases, respectively. \( ^{1} \) ONIOM calculation, with 6-311+G(2d,p) basis on \( \text{S}_4\text{H}_2 \) and 6-31G\textsuperscript{*} basis on waters.

Table 2

| Molecule       | \( \Delta E \) CIS | \( \Delta E \) CIS COSMO | \( \Delta E \) exp. |
|----------------|---------------------|--------------------------|-------------------|
| \( \text{AsS}_3 \cdots 4\text{H}_2\text{O} \) | 2.7                | 4.0                       |                   |
| \( \text{AsS}_3 \cdots 6\text{H}_2\text{O} \) | 4.1                | 4.4                       |                   |
| \( \text{SbS}_3 \cdots 6\text{H}_2\text{O} \) | 4.0                | 4.6                       |                   |
| \( \text{SbS}_3 \cdots 4\text{H}_2\text{O} \) | 4.1                | 4.7                       |                   |
| \( \text{SbS}_3 \cdots 8\text{H}_2\text{O} \) | 4.3                | 4.5                       |                   |
| \( \text{SbS}_3 \cdots 6\text{H}_2\text{O} \) | 4.7                | 4.8 (0.064)               | 4.35              |
| \( \text{AsS}_3 \cdots 4\text{H}_2\text{O} \) | 3.2 (0)            |                           |                   |
| \( \text{SbS}_3 \cdots 8\text{H}_2\text{O} \) | 4.0 (0.0074)       |                           |                   |
| \( \text{SbS}_3 \cdots 6\text{H}_2\text{O} \) | 4.1 (0.030)        |                           |                   |
| \( \text{SbS}_3 \cdots 4\text{H}_2\text{O} \) | 4.6 (0.028)        |                           |                   |
| \( \text{SbS}_3 \cdots 6\text{H}_2\text{O} \) | 4.7 (0.022)        |                           |                   |
| \( \text{AsS}_5 \cdots 6\text{H}_2\text{O} \) | 3.0                |                           |                   |

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

\[ pK_a = 0.323 \Delta G_{\text{aq}} - 87.3 \]

The \( \Delta G_{\text{aq}} \) values obtained for \( \text{S}_4\text{H}_2 \), \( \text{SbS}_3\text{(SH)}_2^- \) and \( \text{SbS}_3\text{(SH)}_2^- \) are 288.1, 287.1 and 298.4 kcal mol\textsuperscript{-1}, respectively, which yield predicted \( pK_a(s) \) of 5.8, 5.4 and 9.1. This indicates that \( \text{S}_4\text{H}_2 \) and \( \text{SbS}_3\text{(SH)}_2^- \) will be fully deprotonated at neutral pH. \( \text{Sb}(\text{m}) \) species like \( \text{SbS}_3\text{(SH)}_2^- \) will be fully deprotonated above pH 9. These compounds are representative of all the polysulfides, and of all the As and Sb 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 \( \text{H}_2\text{S} \) and \( \text{S}_2\text{H}_2 \) our values agree almost as well with experiment as do those from the other, more traditional methods (such as multireference CI), used in ref. 37. The best previous calculated values are 6.37 and 4.98 eV for \( \text{H}_2\text{S} \) and \( \text{S}_2\text{H}_2 \), respectively, while we calculate 6.4 and 5.4 eV, which yield predicted \( pK_a(s) \) of 5.8 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 diatomic than for the monooanions and neutrals.

(6) The general experimental trend in visible-UV absorption energies of: polysulfides < bisulfide < \( \text{H}_2\text{S} \) is correctly reproduced.

(7) The calculations give essentially the same absorption
energies for $S_2^{2-}$ and $S_2H^-$, 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 $S_2^{2-}$ explicitly hydrated by a 22 water molecules are quite similar to the CIS COSMO results for $S_2^{2-}\cdots4H_2O$, 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 twice the computer time of CIS). For example, for $S_2^{2-}\cdots4H_2O$ 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 have also done a few calculations using the CIS(D) method, for $H_2S, S_2^{2-}$ and $S_2H_2$. The changes from the CIS results are small but apparently in the direction to better match experimental data. 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 $S_2^{2-}$ 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 $S_2^{2-}\cdots4H_2O$, 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 $S_2^{2-}\cdots4H_2O$ 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 SBDHF, polarized SBDMP2, 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 SBDMP2 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 species).16

(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 $AsS_3^{2-}$ by about 1 eV (in our 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 $e$ are only slightly, but consistently, higher than those for oxidation state $m$.

(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 $SbS_2^{2-}$ (which restriction would be relaxed away from the equilibrium geometry).

(7) The lowest energy absorption for a mixed bisulfide, polysulfide cluster $As(S_2)SH$ lies between that for $S_2^{2-}$ 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, including COSMO hydration) and CIS energies (all energies in eV).

| Table 3 | Analysis of changes in UV energies (in eV) between CIS, CIS COSMO and CIS IPCM for $S_2^{2-}$ (using the 6-311G(2d,p) basis) |
|--------|-----------------------------------------------------------|
| Method | CIS | CIS COSMO | CIS IPCM |
| $\Delta E_{CIS}^{c}$ | 3.02 | 3.54 | 3.35 |
| $\epsilon_{\text{HOMO}}^{c}$ | 0.82 | $-7.35$ | $-6.91$ |
| $\epsilon_{\text{LUMO}}^{c}$ | 7.94 | 1.80 | 1.69 |
| $\Delta\epsilon^{c}$ | 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 | $\Delta E_{\text{CIS COSMO}}$ |
|---------|-----------------------------------------------------------|
| SH$^-$ | 7.8 | 4.4 | 5.6 |
| SH$^-$ $\cdots$4H$_2$O | 4.6 | 4.3 | 5.8 |
| S$_2^{2-}$ | 4.5 | 2.9 | 3.6 |
| S$_2^{2-}$ $\cdots$4H$_2$O | 3.1 | 2.0 | 3.8 |

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course, the close similarity of CIS COSMO results for the bare and the explicitly hydrated SH and S\(^\text{2-}\) 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 \(S_n\) and SH\(^{n-}\) 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 \(\Delta G\), the hydration contributions to \(\Delta G\), the total \(\Delta G\) in solution and the experimental value of \(\Delta G\). 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.\(^{4,4}\) 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\(^{n-}\) and \(S_n\) rather than the rhombic sulfur mentioned in Giggenbach's paper. Since rhombic sulfur and \(S_n\) differ in standard enthalpy of formation by almost 25 kcal (mol of \(S_n\))\(^{-1}\), changing the reactant to rhombic sulfur would destroy the present agreement of absolute energetics (although trends in free energies in the \(S_n\) series would be unaffected). There is some controversy about the existence of the \(S_n\) polysulfides, which is disfavored by Giggenbach but used in one of the models developed by Teder.\(^{4,6}\) Our calculations indicate a degree of stability for \(S_n\) 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 the reactants and also eliminates the need to calculate a hydration energy contribution to the reaction energy. This reaction is

\[ \frac{3}{8} S_8(g) + H_2S(g) \rightarrow S_4H(g) \]

and all the necessary heat of formation data is available in the tabulations of Wagman et al.\(^{4,7}\) This is clearly the neutral gas-phase analog of the second equation in Table 6. The experimental value of \(\Delta H\) is 6.3 kcal mol\(^{-1}\), while the value calculated at the polarized SBK MP2 level for \(\Delta H\) 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 \(\Delta G\) value is 7.6 kcal mol\(^{-1}\) (more positive than the \(\Delta H\) since the \(-T\Delta S\) term is positive because of the reduction in number of moles of gas). This indicates that the energetics for reaction of \(S_n\) to form polysulfide-like species are not greatly changed in going from neutral molecules in the gas-phase to ions in solution, with \(\Delta G\) values around +5 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 \(H_2S\), sulfane systems\(^{4,8}\) 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 properties\(^{4,9}\) 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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