Theoretical studies of the speciation of Sb in sulphidic solutions

J.A. Tossell

Dept. of Chemistry and Biochemistry University of Maryland
College Park, MD 20742, USA.

Introduction

In hydrothermal solutions arsenic and antimony are often present in appreciable concentration but the nature of the As and Sb species present is not generally well understood. In neutral to alkaline sulphidic waters at low temperature thio complexes are believed to predominate (Spycher and Reed, 1989). Solubility data for Sb_2S_3 have recently been obtained by Krupp (1988) and the Raman spectra of species formed by dissolving Sb_2S_3 in alkaline sulphidic solutions have been measured by Wood (1989).

Accurate first principles calculations of the structure and spectra of large molecules have recently been made possible by the development of faster computers and more efficient methods and by the accumulation of knowledge on the accuracy of different quantum chemical methods (Hehre, *et al.*, 1986). For species occurring in condensed phases the problem of matching calculation and experiment can be difficult since the perturbing effects of the medium may be significant. Techniques for simulating some aspects of the condensed phase environment have been discussed by Sauer (1989) and by Tossell and Vaughan (1992). To assist in identifying the Sb sulphide species present in alkaline sulphide solutions, we have used ab initio quantum mechanical methods to calculate the structures, stabilities and vibrational spectra of a number of monomeric and oligomeric Sb(III) sulphides.

Theoretical methods

We employ the conventional methods of ab initio self-consistent-field molecular orbital theory as described in quantum chemistry texts and monographs (Hehre, *et al.*, 1986) and as implemented in the program GAMESS (Schmidt, *et al.*, 1990). For each molecule we have determined the minimum energy or equilibrium geometry and have calculated the vibrational spectrum. The basis sets used to expand the molecular orbitals in our studies are of the relativistic effective core-potential valence double zeta type (Stevens, *et al.* 1992) with additional polarization functions of d type added on each of the atoms.

Results

Geometries and vibrational spectra of Sb sulphide species. Proposed assignments for the features in the Raman spectra of Wood (1989), based on the correspondence of experimental and calculated frequencies (after scaling by the standard correction factor 0.90), are shown in Table 1.

On the basis of dilution studies, Wood identified features at 314 and 350 cm^{-1} as arising from polymeric species and a major feature at 369 cm^{-1} as arising from a monomeric species. There was also a reproduceable shoulder at 380 cm^{-1} attributed to a monomeric species and a S-H stretching peak at about 2574 cm^{-1}.

TABLE 1. Suggested assignment of features in the experimental Raman spectra of sulphidic Sb solutions (Wood, 1989)

exp. υ	calc. υ scaled by 0.9
314	320 $Sb_2S_2(SH)_2$ Sb-SH
350	352 $Sb_2S_2(SH)_2$ Sb-S
369	351,347 $SbS_2(SH)^{-2}$ Sb-S
380	397 $SbS(SH)_2^{-1}$ Sb-S
2574	2499 hydrated SH^-; 2583-2612 SH^- stretch in Sb-SH groups

Based on our assignments of the Raman spectra we would propose that the main species present in the most concentrated solutions prepared by Wood (1989) are $SbS_2(SH)^{2-}$ and $Sb_2S_2(SH)_2$ and we would rewrite the reaction proposed by Wood to occur during dilution of this solution as:

$$Sb_2S_2(SH)_2 + 2\ SH^- + 2\ OH^- \rightarrow 2\ SbS_2(SH)^{2-} + 2\ H_2O \qquad (1)$$

Energetics of Sb sulphide species. We can also evaluate gas-phase electronic energies, zero-point vibrational energies, enthalpies and free energies

TABLE 2. Calculated gas-phase energetics (in kJ/mol) and entropies (in J/molK) for oligomerization and ligand exchange reactions

reaction	ΔE_{SCF}	ΔE_{ZP}	ΔH_{298}	ΔS_{298}	ΔG_{298}	
$2\ Sb(SH)_3 \rightarrow Sb_2S_2(SH)_2 + 2\ H_2S$	12.9	-11.5	2.5	110	-30.2	(2)
$3\ Sb_2S_2(SH)_2 \rightarrow 2\ Sb_3S_3(SH)_3$	-0.7	+6.7	21.1	-95.5	49.6	(3)
$Sb_2S_2(SH)_2 + 2\ H_2O \rightarrow Sb_2S_2(OH)_2 + 2\ H_2S$	37.4	-11.9	27.6	45.9	13.9	(4)

for oligomerization and ligand exchange reactions such as those shown in Table 2.

Edge-sharing dimerization (reaction (2)) is favorable while conversion of dimeric to trimeric structures (reaction (3)) is unfavorable, primarily due to the sign of the entropy changes, which are in turn dependent mainly on the numbers of molecules of reactants and products. Ligand exchange of -OH for -SH (reaction (4)) is unfavorable at 298 K but due to its positive entropy change becomes favorable at higher temperatures (above about 300°C). Krupp (1988) has presented evidence for the presence of dimeric species, like $Sb_2S_2(SH)_2$, in antimony sulphide solutions at low temperature and for the stability of mixed ligand species, like $Sb_2S_2(OH)_2$, at higher temperatures.

Conclusions

In agreement with the interpretation of Wood (1989), we assign a prominent feature observed at 369 cm^{-1} in the Raman spectrum of sulphidic Sb solutions to Sb-S stretching vibrations in a monomeric complex, $SbS_2(SH)^{2-}$. Raman features observed at 314 and 350 cm^{-1} are assigned to Sb-S(H) symmetric stretching vibrations of the dimeric species $Sb_2S_2(SH)_2$, which is calculated to be stable with respect to both the monomer $Sb(SH)_3$ and the trimer $Sb_3S_3(SH)_3$. The mixed-ligand complex $Sb_2S_2(OH)_2$ is calculated to become stable compared to $Sb_2S_2(SH)_2$ at high temperatures, in agreement with experimental solubility data.

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References

Hehre, W. J., Radom, L., Schleyer, P. v.R. and Pople, J. A. (1986) *Ab Initio Molecular Orbital Theory*, 548 pp., Wiley, New York.

Krupp, R. E. (1988) *Geochim. Cosmochim. Acta*, **52**, 3005–15.

Sauer, J. (1989) *Chem. Rev.*, **89**, 199–255.

Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Jensen, J. H., Koseki, S. and Gordon, M. S. (1990) GAMESS, *Quantum Chem. Prog. Exchange Bulletin*, **10**, 52–4.

Spycher, N. F. and Reed, M. H. (1989) *Geochim. Cosmochim. Acta*, **53**, 2185–94.

Stevens, W. J., Krauss, M., Basch, H. and Jansen, P. G. (1992) *Can. J. Chem.*, **70**, 612–30.

Tossell, J. A. and Vaughan, D. J. (1992) *Theoretical Geochemistry: Applications of Quantum Mechanics in the Earth and Mineral Sciences*, Oxford, New York, 514 pp.

Wood, S. A. (1989) *Geochim. Cosmochim. Acta*, **53**, 237–44.