Results of Previous DOE Support (Theoretical Studies on Heavy Metal Sulfides in Solution):
DE-FG02-94ER14467, Nov. 1, 2003 – Oct. 31, 2006 (with a no cost extension from Nov. 1, 2006 to Oct. 31, 2007) Total amount awarded; $276,919, one postdoc and two graduate students supported
Published papers:

(1)"Calculation of the energetics for oxidation of gas-phase elemental Hg by Br and BrO", J. A. Tossell, J. Phys. Chem.A.107, 7804-7808(2003).

(2) "Calculation of the energetics for the oxidation of Sb(III) sulfides by elemental S and polysulfides in aqueous solution". J. A. Tossell, Geochim. Cosmochim. Acta, 67, 3347-3354 (2003)

(3) "Possible Al-F bonding environment in F-bearing Na-aluminosilicates glasses: from calculation of ^{19}F NMR shifts", Y. Liu and J. Tossell, , J. Phys. Chem B. 107, 11280-11289 (2003)

(4) "Calculation of the visible-UV absorption spectra of hydrogen sulfide, bisulfide , polysulfides and As and Sb sulfies, in aqueous solution", J. A. Tossell, Geochem. Trans. 4, 28-33 (2003)

(5) "Using quantum calculations of NMR properties to elucidate local and mid-range structures in amorphous oxides, nitrides and aluminosilicates", J. A. Tossell, in Computational Materials Chemistry: Methods and Applications, ed. M. S. Gordon and L. A. Curtiss, Kluwer (2004)

(6) "Calculation of ^{17}O NMR shieldings in molecular models for crystalline MO, M=Mg, Ca, Sr and in models for alkaline earth silicates", J. A. Tossell , Phys. Chem. Mineral. 31, 41-44 (2004)

(7) "Theoretical study on structural factors correlated with ^{23}Na NMR parameters", Y. Liu, J. Tossell and H. Nekvasil, Amer. Mineral., 89, 1314-1322. (2004)

(8) "Calculation of ^{19}F and ^{27}Al NMR parameters for rosenbergite, AlF[F0.5(H2O)0.5]4.H2O, a possible model for Al hydroxyfluorides in solution, J. A. Tossell and Y. Liu, Magn. Reson. Chem., 42, S34-40 (2004)

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(10) "Explaining the effects of T-O-T bond angles on NMR chemical shifts in aluminosilicates: A natural bonding orbital (NBO) and natural chemical shielding (NCS) analysis, Y. Liu and J. A. Tossell, J. Phys. Chem. A, 109, 3060-3066 (2005)

(11) "Calculation of the interaction of bicarbonate ion with arsenites in aqueous solution and with the surfaces of Al hydroxide minerals". J. A. Tossell", in Advances in Arsenic Research, ACS Symposium Series 915, pp. 118-130, ed. P. O'Day, (2005)

(12) "Theoretical study on the dimerization of $Si(OH)_4$ in aqueous solution and its dependence on temperature and dielectric constant", J. A. Tossell Geochim. Cosmochim. Acta 69, 283-291 (2005)

(13) “Calculation of the UV-visible spectra and the stability of Mo and Re oxysulfides in aqueous solution”, J. A. Tossell, Geochim. Cosmochim. Acta, 69, 2497-2503 (2005)

(14) "Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution", J. A. Tossell, Geochim. Cosmochim. Acta, 69, 2981-2993 (2005)

(15) "Ab initio molecular orbital calculaions for boron isotope fractionations on boric acids and borates", Y. Liu and J. A. Tossell, Geochim. Cosmochim. Acta, 69, 3995-4006.(2005)

(16) "Boric acid, 'carbonic acid' and N-containing oxyacids in aqueous solution: Ab initio studies of structure, pKa, NMR shifts and isotopic fractionations". J. A.Tossell, Geochim. Cosmochim. Acta 69, 5647-5658.(2005)

(17) “Calculation of the energetics for the oligomerization of gas pbaser HgO and HgS and for the solvolysis of crystalline HgO and HgS”, J. A. Tossell, J. Phys. Chem. A 110, 2571-2578.(2006)

(18) “Experimental evaluation of the isotopic exchange equilibrium B-10$(OH)_3$ + B-11$(OH)_4^-$ = B11$(OH)_3$ + B10$(OH)_4^-$ in aqueous solution”, R. H. Byrne, W. S. Yao, K. Klochko, A. J. Kaufman and J. A. Tossell, Deep-Sea Research Part I, 53, 684-688. (2006)

(19) “Experimental measurement of boron isotope fractionation in sea water”, K .Klochko, A. J. Kaufman, W. S Yao, R. H. Byrne and J. A. Tossell, Earth Planet Sci. Lett. 248, 276-285 (2006)

(20) “Boric acid adsorption on humic acids: Ab initio calculation of structures, stabilities ,B-11 NMR and B-11,B-10 isotopic fractionations of surface complexes”, J. A. Tossell, Geochim. Cosmochim. Acta, 70, 5089-5103 (2006)

(21) “H_2CO_3 and its oligomers: Structures, stabilities, vibrational and NMR spectra, and acidities”, J. A. Tossell, Inorg. Chem. 45, 5961-5970 (2007)

Manuscripts in preparation:

“Calculating the stabilities, Raman and UV spectra and acidities of As sulfides in aqueous solution”, J. A. Tossell, M. D. Zimmermann and G. R. Helz

Some of the Raman spectra obtained by reacting aqueous $As(OH)_3$ with aqueous bisulfide are shown below,taken from Wood, et al. (2002). To interpret these spectra we have carried out an extensive series of calculations, detailed for the case of $AsS(SH)_2^-$ in Table 1 below. By employing state of the art quantum chemical techniques to determine gas-phase harmonic and anharmonic frequencies and solution phase corrections we can accurately match features in the experimental spectrum shown in the top figure. The $AsS(SH)_2$- …22 H_2O nanocluster employed is shown in the lower figure. For this species we have calculated the equilibrium structure and the harmonic vibrational spectrum at the CBSB7 B3LYP level. For the free solute species $AsS(SH)_2^-$ we have carried out a whole series of calculations, evaluating harmonic and anharmonic vibrational frequencies at a number of different quantum mechanical levels. In the spectra below, Fig. 3 and Fig. 5 from Wood, et al. (2002), the features around 700-800 cm^{-1} are attributed to As-O stretches and those around 350-450 cm^{-1} to As-S stretches. In the nanocluster an isolated vibrational feature is observed at 425 cm^{-1}, an As=S stretch, close to the value (415 cm^{-1})

determined by Wood, et al. (2002). Analysis of the calculated frequencies for $AsS(SH)_2^-$ within a polarizable continuum model yields a similar result. Taking the highest level harmonic results, obtained from a CCSD calculation, and adding anharmonic and PCM corrections at the B3LYP level (designated (3) + (5) – (1) in Table 1) gives a frequency for the intense high frequency As=S stretch within 15 cm^{-1} of experiment. Although there is still interesting work to be done on the stabilities and the Raman and UV spectra of As sulfides, most of the basic concepts have been worked out and we are therefore proposing to move to a new area, that of humic acids (while continuing our studies complexes formed by As oxides and sulfides, now applied to functional groups present in humic acids).

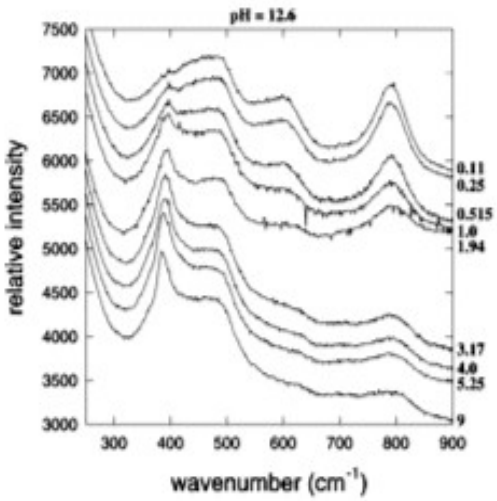


Fig. 3 Raman spectra of arsenic sulfide solutions at pH = 12.6 and $\Sigma As + \Sigma S = 0.1$ mol kg^{-1} H_2O as a function of $\Sigma S/\Sigma As$ ratio.

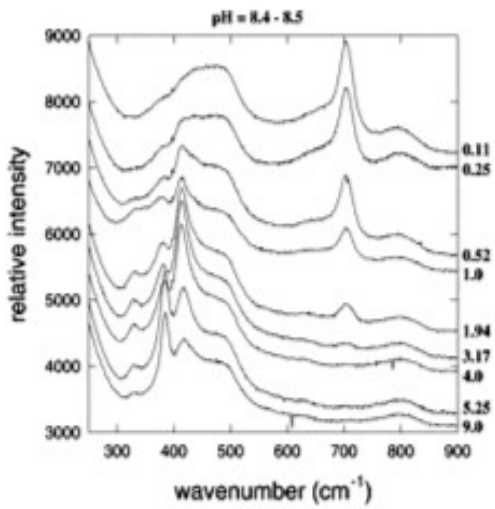
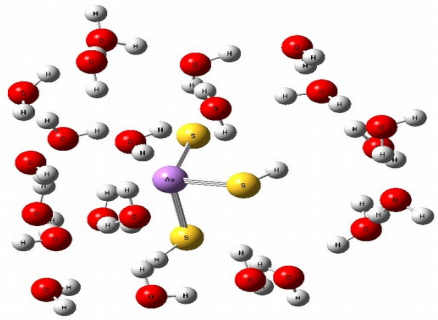


Fig. 5 Raman spectra of arsenic sulfide solutions at pH = 8.4–8.5 and $\Sigma As + \Sigma S = 0.1$ mol kg^{-1} H_2O as a function of $\Sigma S/\Sigma As$ ratio.



$AsS(SH)_2$-…$22H_2O$

Table 1. Calculated and experimental As-S and As-SH vibrational frequencies (cm^{-1}) for $AsS(SH)_2^{-1}$ (with relative Raman intensities given in parentheses for CBSB7 B3LYP harmonic frequencies

model	method	ν
free	CBSB7 B3LYP Harmonic	448 270 256 (20.9 24.4 19.1)
free	CBSB7 B3LYP anharmonic	448 258 228
free	6-311+G(2d,p) CCSD	452 303 299
in PCM	CBSB7 B3LYP harmonic	430 284 261
in PCM	CBSB7 B3LYP anharmonic	426 281 250
in $(H_2O)_{22}$	CBSB7 B3LYP extrapolated	av. As=S 425
(3) + (5) – (1)		430 314 293
exp.(aq)		415 330