

Calculating the stability, Raman and UV spectra and acidity of As sulfides in aqueous solution

J. A. TOSSELL, M. D. ZIMMERMANN AND G. R. HELZ

¹Dept. of Chemistry and Biochemistry, Univ. of Maryland,
College Park, MD 20742 USA tossell@umd.edu

Since the chemical and biological reactivity of As sulfides depends strongly upon their speciation, it is important to determine exactly what species are present within a given environment. Spectral probes such as Raman and UV can give partial information about speciation, but uncertainties and ambiguities generally remain. We are engaged in a program to perform state-of-the-art quantum mechanical studies of the structures, stabilities, spectra (Raman and UV) and acidity of As sulfide species in aqueous solution. We typically use very high level methods, such as CCSD with triple zeta, doubly polarized basis sets for the gas phase part of the calculation, and a lower-level polarizable continuum or nanocluster approach to simulate the effect of hydration. Anharmonic vibrational effects are calculated using 2nd order perturbation theory within a HF – DFT hybrid method. Using this approach we can accurately reproduce the Raman spectra of thioarsenious acid, As(SH)₃ and its conjugate bases. The Raman spectra of As(OH)₃ is also reproduced with errors of less than 10 cm⁻¹ and the As-O(H) distances with errors of only 0.02 Å. Such calculations establish that the neutral species in arsenious acid solutions is indeed As(OH)₃ rather than HAsO₂. This assignment is also supported by our calculated UV spectra. However, accurate calculation of the Raman spectra of the conjugate bases of As(OH)₃ requires the inclusion of both explicit waters and counterions. Trends in the acidity of As acids with changing oxidation state, ligand and degree of protonation are well reproduced, but accurate absolute values for the oxidic species are elusive. Possible reasons for the overestimation of pK_as for the oxidic species are presented. We have established computationally that the conjugate bases of As(OH)₃ are susceptible to sulfidation by H₂S, while As(III) sulfides such as AsS(SH)₂ are susceptible to oxidation to As(V) by elemental sulfur or polysulfides. By contrast the addition of H₂S to AsS(SH)₂⁻ to form As(SH)₄⁻ is calculated to be unfavorable. We can thus generate a comprehensive picture of speciation based upon direct quantum mechanical calculation of a number of properties for possible candidate species.