

Calculation of the energetics for the oxidation of Sb(III) sulfides by elemental S and polysulfides in aqueous solution

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Recently Helz, et al. (2002) reported the existence of two new Sb sulfide species, $\text{Sb}_2\text{S}_5^{-2}$ and $\text{Sb}_2\text{S}_6^{-2}$, in alkaline sulfidic solutions in equilibrium with stibnite, Sb_2S_3 , and orthorhombic S. I have calculated from first principles of quantum mechanics the energetics for the oxidation of the Sb(III) sulfide dimer $\text{Sb}_2\text{S}_4^{-2}$ to the mixed Sb(III,V) dimer $\text{Sb}_2\text{S}_5^{-2}$ and then to the all Sb(V) dimer, $\text{Sb}_2\text{S}_6^{-2}$. Gas-phase reaction energies have been evaluated using polarized valence double zeta effective core potential basis sets and Moller-Plesset 2nd order treatments of electron correlation. Hydration energies have been obtained using the COSMO version of the self-consistent reaction field polarizable continuum method. Negative free energy changes are calculated for the oxidation of the dianion of the III,III dimer to the III,V dimer by both small polysulfides, like S_4H^{-1} , and elemental S, modeled as S_8 . For the further oxidation of the III,V dimer to the V,V dimer the reaction free energies are calculated to be close to zero. The partially protonated Sb III,III dimer monoanion $\text{HSb}_2\text{S}_4^{-1}$ can also be oxidized, but the reaction is not so favorable as for the dianion. Comparison of the calculated aqueous deprotonation energies of $\text{H}_2\text{Sb}_2\text{S}_4$, $\text{H}_2\text{Sb}_2\text{S}_5$ and $\text{H}_2\text{Sb}_2\text{S}_6$ and their dianions with values calculated for various oxyacids indicates that the III,V and V,V dimers will have pK_{a2} values below 5, so that their dianions will be the dominant species in alkaline solutions. These results are thus consistent with the recent identification of $\text{Sb}_2\text{S}_5^{-2}$ and $\text{Sb}_2\text{S}_6^{-2}$ species by Helz, et al. (2002). I have also calculated the Raman spectra of $\text{Sb}_2\text{S}_5^{-2}$ and $\text{Sb}_2\text{S}_6^{-2}$ to assist in their identification. The calculated vibrational frequencies of the III,V and V,V dimers are characteristically higher than those of the III,III dimer I previously studied. The III,V dimer may contribute shoulders to the Raman spectra previously obtained by Wood (1989).

Perturbing the tridecameric $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ polycation: Effects of substitution, deprotonation, dehydration and adsorption of arsenites and arsenates

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The aluminum tridecameric polyoxocation, $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ is a major component in partially hydrolyzed $\text{Al}^{+3}(\text{aq})$ solutions and has been extensively studied experimentally, mainly using vibrational and NMR spectroscopy. I recently calculated the equilibrium geometry and NMR properties of this $\text{Al}_{13}\dots$ polyoxocation using Hartree-Fock and density functional techniques. In the present work I carry out several different perturbations upon this polyoxocation and compute the resulting changes in its properties. Some of these perturbations have actually been carried out experimentally, while others are hypothetical. For example, one can experimentally replace the central $\text{Al}[4]$ with other atoms, such as Ga or Ge. Protons can be removed from the exterior $-\text{OH}_2$ or $-\text{OH}$ groups to reduce the cation charge and the geometry of the molecule reoptimized. This allows a computational determination of the acidity of the $\text{Al}_{13}\dots$ species. Waters can be removed from the original polyoxocation to produce 5-coordinate Al and the energy for this dehydration can be compared with that for other Al oxyhydroxide species. Such coordinatively unsaturated 5-coordinate sites resemble those on the surfaces of gibbsite and bayerite and small molecules and anions like $\text{AsO}(\text{OH})_3$ and $\text{AsO}_2(\text{OH})_2^{-1}$ can be adsorbed on them and their reaction energetics determined. Vibrational frequencies for these adsorbed species can then be compared with experimental studies on the adsorption of these anions on Al hydroxide surfaces. Al oxyhydroxide oligomers can also be studied to assess the mechanism of formation of the $\text{Al}_{13}\dots$ polyoxocation. Analogous computations for Ga^{+3} oxyhydroxide oligomers give bond distances which compare well with recent experimental studies using EXAFS. Ga NMR shieldings have also been calculated for a number of oligomers, to assist in their identification and to establish trends in shielding with deprotonation and oligomerization. Calculations on such large polyoxocations at the Hartree-Fock level are quite expensive, but the expense can be enormously reduced by using approximate semiempirical MO methods, like PM3, without too great a loss of accuracy in some cases