



# A Raman spectroscopic study of arsenite and thioarsenite species in aqueous solution at 25 °C

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The Raman spectra of thioarsenite and arsenite species in aqueous solution were obtained at room temperature. Solutions at constant  $\Sigma\text{As} + \Sigma\text{S}$  of 0.1 and 0.5 mol kg<sup>-1</sup> were prepared with various  $\Sigma\text{S}/\Sigma\text{As}$  ratios (0.1–9.0) and pH values (~7–13.2). Our data suggest that the speciation of As under the conditions investigated is more complicated than previously thought. The Raman measurements offer evidence for at least six separate S-bearing As species whose principal bands are centered near 365, 385, 390, 400, 415 and 420 cm<sup>-1</sup>. The data suggest that at least two different species may give rise to bands at 385 cm<sup>-1</sup>, bringing the probable minimum number of species to seven. Several additional species are possible but could not be resolved definitively. In general, the relative proportions of these species are dependent on total As concentration,  $\Sigma\text{S}/\Sigma\text{As}$  ratio and pH. At very low  $\Sigma\text{S}/\Sigma\text{As}$  ratios we also observe Raman bands attributable to the dissociation products of H<sub>3</sub>AsO<sub>3</sub>(aq). Although we were unable to assign precise stoichiometries for the various thioarsenite species, we were able to map out general pH and  $\Sigma\text{S}/\Sigma\text{As}$  conditions under which the various thioarsenite and arsenite species are predominant. This study provides a basis for more detailed Raman spectroscopic and other types of investigations of the nature of thioarsenite species.

## 1. Introduction

In moderately oxidizing to moderately reducing hydrothermal solutions the species H<sub>3</sub>AsO<sub>3</sub><sup>0</sup> or one of its deprotonated equivalents generally is considered to be the dominant form of dissolved arsenic.<sup>1–9</sup> The As(v) species H<sub>3</sub>AsO<sub>4</sub><sup>0</sup> or one of its dissociation products may be predominant under near-surface, oxidizing conditions.<sup>6,10</sup> Under extremely reducing conditions, dissolved arsine gas, AsH<sub>3</sub>(aq), may be an important species.<sup>5</sup> However, at low temperatures, in near-neutral to alkaline, sulfide-rich solutions, some form of thioarsenite [As(III)-sulfide] species is most likely responsible for the hydrothermal transport of As.<sup>2,7,11–24</sup>

The exact stoichiometry of the important thioarsenite complexes remains controversial even under standard conditions despite intense investigation. Spycher and Reed<sup>21,25,26</sup> proposed that the As(III)-sulfide species most consistent with the available literature at the time were the trimers H<sub>3</sub>As<sub>3</sub>S<sub>6</sub><sup>0</sup>, H<sub>2</sub>As<sub>3</sub>S<sub>6</sub><sup>-</sup> and HAs<sub>3</sub>S<sub>6</sub><sup>2-</sup>. Krupp<sup>27,28</sup> emphasized some of the drawbacks of the approach of Spycher and Reed<sup>21</sup> and favored, in analogy with Sb, some form of the dimer (H<sub>2</sub>As<sub>2</sub>S<sub>4</sub>, HAs<sub>2</sub>S<sub>4</sub><sup>-</sup>, or As<sub>2</sub>S<sub>4</sub><sup>2-</sup>). Subsequently, new experimental solubility studies have been interpreted both in terms of the trimer H<sub>2</sub>As<sub>3</sub>S<sub>6</sub><sup>-</sup><sup>7,22,23</sup> and the dimeric species.<sup>22</sup> Using EXAFS, Raman spectroscopy and *ab initio* molecular orbital calculations, Helz and coworkers<sup>24</sup> have concluded that, in solutions undersaturated with respect to either orpiment or amorphous As<sub>2</sub>S<sub>3</sub>, monomeric species (*i.e.*, H<sub>2</sub>AsS<sub>3</sub><sup>-</sup> and HAsS<sub>3</sub><sup>2-</sup>, actually formulated<sup>24</sup> as AsS(SH)<sub>2</sub><sup>-</sup> and AsS<sub>2</sub>(SH)<sub>2</sub><sup>2-</sup>) are predominant. However, Helz and coworkers<sup>24</sup> reinterpret previous solubility experiments<sup>7,22,23</sup> and suggest that, at saturation, the predominant species are the trimer As<sub>3</sub>S<sub>4</sub>(SH)<sub>2</sub><sup>-</sup> and the monomer AsS(OH)(SH)<sup>-</sup>. Thus, the results of Helz *et al.*<sup>24</sup> strongly support the possibility that the degree of polymerization of thioarsenite species depends on the total As concentration in solution and that there may be a progression from monomers through dimers to trimers (to possibly higher polymers) as

total As increases towards saturation with respect to an arsenic sulfide phase. Krupp<sup>29</sup> has suggested the possibility of a similar progression for thioantimony species.

It is apparent from this brief review of the literature that additional work is required to determine unambiguously the stoichiometries and thermodynamic stabilities of thioarsenite species. In this paper we present results of Raman spectroscopic measurements conducted on thioarsenite and arsenite species near 25 °C in near-neutral to alkaline solutions. These results are preliminary in nature but they do provide some additional constraints on the nature of thioarsenite species and the conditions under which they are transformed into arsenite species.

## 2. Experimental

All solution preparation and manipulation was conducted in a low-oxygen, nitrogen-filled glove bag in order to minimize oxidation. Solutions were prepared in which the total sulfur to total arsenic ratio ( $\Sigma\text{S}/\Sigma\text{As}$ ) varied but the sum of the total arsenic and sulfide concentrations was held constant. A NaHS stock solution was prepared by bubbling H<sub>2</sub>S gas through a solution of known NaOH concentration until measured pH was constant with time. A sodium arsenite solution was prepared by dissolving reagent-grade As<sub>2</sub>O<sub>3</sub>(s) in a NaOH solution. For a given set of experiments, the stock solutions of NaHS had the same sulfide concentration as the concentration of As in the stock sodium arsenite solutions. These two stock solutions were then mixed in various proportions to obtain solutions with  $\Sigma\text{S}/\Sigma\text{As}$  ratios of 9, 5.25, 4, 3.17, 1.94, 1.00, 0.515, 0.25 and 0.11. Two different sets of experiments were carried out: one in which  $\Sigma\text{As} + \Sigma\text{S} = 0.1$  mol kg<sup>-1</sup>, and one in which  $\Sigma\text{As} + \Sigma\text{S} = 0.5$  mol kg<sup>-1</sup>. In each set of experiments, the pH of each of the solutions was adjusted to a constant value using solutions of NaOH or HCl. A pH range from 13.2 to approximately 7 was investigated. More acidic solutions could

not be studied owing to precipitation of arsenic sulfide. Measurements of pH were conducted using an Orion Research Meter (Model SA250) with a Ross combination electrode, standardized against NIST pH buffers. An aliquot of each solution was placed in a glass NMR tube, and the tube was capped and sealed with Parafilm. The Raman spectrum of each solution was acquired at room temperature within 1–2 hours after being sealed in the NMR tube. Owing to the preliminary nature of the experiments, no internal standards were employed. Thus, the spectra could only be treated in a semi-quantitative manner.

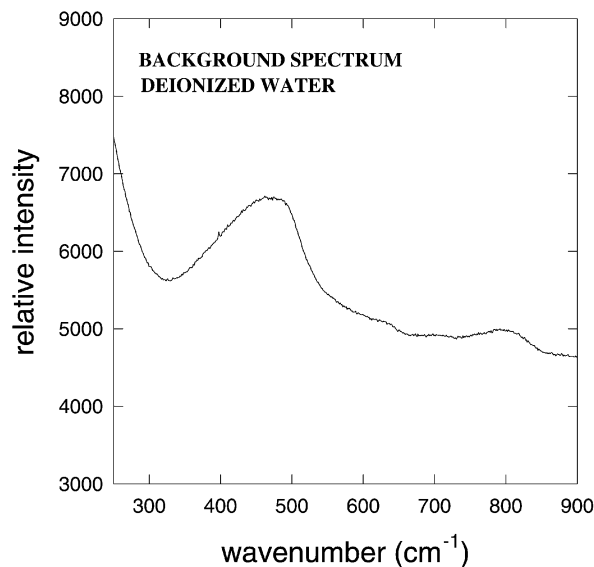
The Raman instrumentation has been described in detail previously.<sup>30,31</sup> Raman spectra were excited using the 514-nm line of a Spectra Physics Ar-ion laser (model 2025-05) focused onto the sample with a cylindrical lens to match the monochromator slit. The laser delivered approximately 400 mW of power to the sample. The Raman scattering was viewed in a 135° backscattering configuration, with the scattered light collimated with a fast plano-convex lens (f1 1.3, planar side toward focused spot on sample) and then subsequently focused onto the slit of the monochromator (SPEX Triplemate, f1 6.3 input optics) with a second plano-convex f-matching lens (f1 6.5, planar side towards monochromator). The first two stages of the monochromator were locked in an additive-subtractive mode and function as a tunable bandpass filter, especially against the Rayleigh-scattered photons. The final stage dispersed the inelastically scattered photons across a Princeton Applied Research model 1420 intensified silicon diode-array detector. The slit width of the monochromator was set at 140  $\mu\text{m}$ . In general, 10 scans, each with a 10 s integration time, were co-added to improve the signal-to-noise ratio. Spectra were calibrated against standard peaks of toluene in methanol and the emission lines of a neon lamp. Spectral data were saved as ascii files. Attempts to reduce the spectra in the manner described by Brooker *et al.*<sup>32</sup> or to use PeakFit (Jandel Scientific) to obtain quantitative band parameters (peak maxima, band widths, and band areas) were frustrated by the variable nature of the fluorescence of the NMR tube. Thus, only the raw spectra are presented here. However, PeakFit was employed to help identify the peaks of obvious Raman bands.

### 3. Results

Fig. 1 shows the background spectrum due to deionized water and the glass NMR tubes. The major features of the background are: (1) the Rayleigh wing descending from 250  $\text{cm}^{-1}$ ; (2) a broad, moderately intense, asymmetric band with a peak near 480  $\text{cm}^{-1}$ ; (3) a broad, weak band centered at 800  $\text{cm}^{-1}$ ; and (4) a very weak, broad band near 600  $\text{cm}^{-1}$ . Water has libration bands owing to hydrogen bonding at 450 and 789  $\text{cm}^{-1}$  which may contribute to the two most prominent broad bands.<sup>33</sup> However, the broad band near 480  $\text{cm}^{-1}$  is far more intense than usually observed in pure water, and probably is a result of fluorescence due to impurities in the glass NMR tube. The bands for thioarsenite species all fall on the low-wavenumber side of the broad band near 480  $\text{cm}^{-1}$  which, combined with the proximity of the Rayleigh wing, hindered quantitative band-fitting.

Fig. 2–6 contain spectra for solutions containing both S and As. Each figure shows the spectra for a given pH and  $\Sigma\text{S} + \Sigma\text{As}$  value as a function of  $\Sigma\text{S}/\Sigma\text{As}$  ratio. For the convenience of the reader, some of these spectra are replotted in a slightly different manner in Fig. 7–11. In the latter, each figure shows the spectra for  $\Sigma\text{S} + \Sigma\text{As} = 0.1$  and a given  $\Sigma\text{S}/\Sigma\text{As}$  ratio as a function of pH.

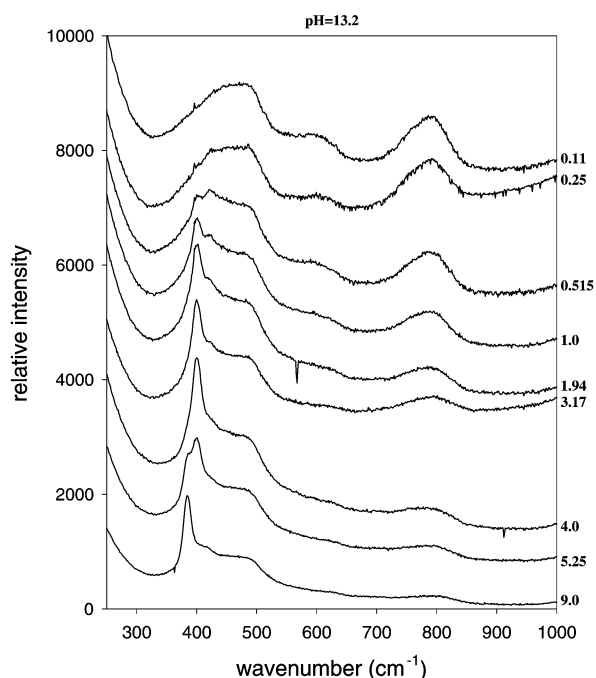
In our solutions with relatively high  $\Sigma\text{S}/\Sigma\text{As}$  ratios, significant bisulfide ( $\text{HS}^-$ ) is expected to be present. This species should yield a narrow band at about 2574  $\text{cm}^{-1}$ .<sup>34</sup> At an early stage of this study, we verified that this band is present in some



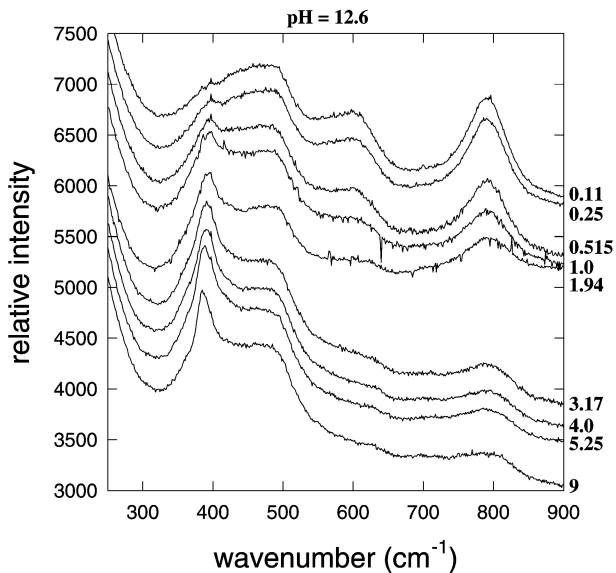
**Fig. 1** Raman spectrum of deionized water in a glass NMR tube. Note broad bands from approximately 335 to 550  $\text{cm}^{-1}$  and 750 to 850  $\text{cm}^{-1}$ . There may also be a less intense broad band near 600  $\text{cm}^{-1}$ .

of the solutions with higher  $\Sigma\text{S}/\Sigma\text{As}$  ratios, but we did not routinely monitor this area of the spectrum. Attention was focused on the wavenumber range from 250 to 900  $\text{cm}^{-1}$  where bands for thioarsenite and arsenite species occur.

Fig. 2 contains the spectra of solutions with  $\Sigma\text{S} + \Sigma\text{As} = 0.1 \text{ mol kg}^{-1}$  at pH = 13.2 for various  $\Sigma\text{S}/\Sigma\text{As}$  ratios. At a  $\Sigma\text{S}/\Sigma\text{As}$  ratio of 9, a prominent, narrow band centered at approximately 385  $\text{cm}^{-1}$  is evident, together with a low-intensity shoulder on its high-wavenumber side. Upon a decrease in  $\Sigma\text{S}/\Sigma\text{As}$  ratio to 5.25, another narrow band, centered near 400  $\text{cm}^{-1}$  can be seen to emerge at the expense of the band at 385  $\text{cm}^{-1}$ . The low-intensity shoulder on the high-wavenumber side does not appear to undergo much of a change as  $\Sigma\text{S}/\Sigma\text{As}$  decreases. By a  $\Sigma\text{S}/\Sigma\text{As}$  ratio of 4, the band at 385  $\text{cm}^{-1}$  has disappeared. Between  $\Sigma\text{S}/\Sigma\text{As} = 4$  and  $\Sigma\text{S}/\Sigma\text{As} = 0.25$ , the band at 400  $\text{cm}^{-1}$  loses intensity, while a band



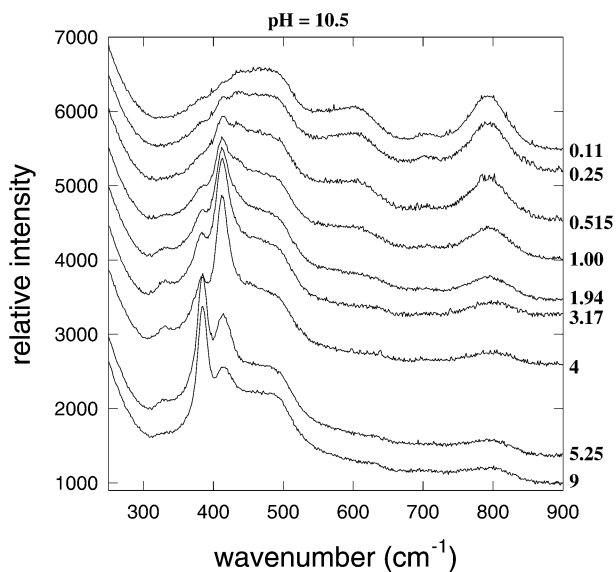
**Fig. 2** Raman spectra of arsenic sulfide solutions at pH = 13.2 and  $\Sigma\text{As} + \Sigma\text{S} = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of  $\Sigma\text{S}/\Sigma\text{As}$  ratio.



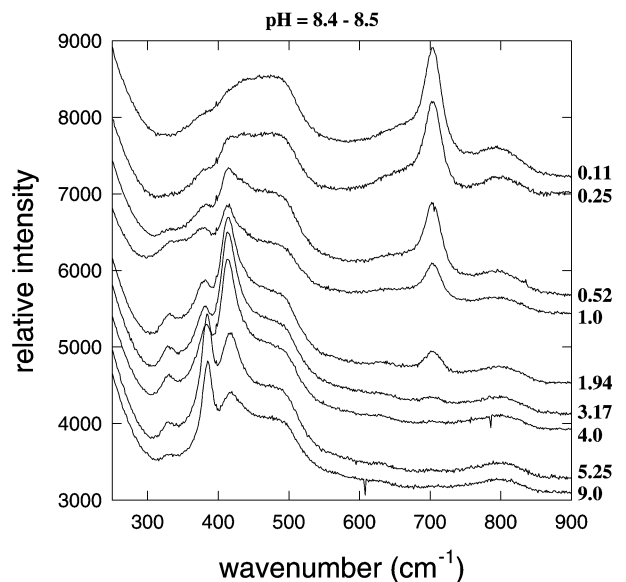
**Fig. 3** Raman spectra of arsenic sulfide solutions at pH = 12.6 and  $\Sigma\text{As} + \Sigma\text{S} = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of  $\Sigma\text{S}/\Sigma\text{As}$  ratio.

centered near  $420 \text{ cm}^{-1}$  becomes relatively more prominent (although it never becomes very intense), until it too loses intensity. Meanwhile broad bands near  $600$  and  $800 \text{ cm}^{-1}$  grow in intensity. At  $\Sigma\text{S}/\Sigma\text{As} = 0.11$ , the bands in the  $350\text{--}450 \text{ cm}^{-1}$  range have disappeared, leaving only the broad band observed in the background spectrum, and bands of increased intensity near  $600$  and  $800 \text{ cm}^{-1}$ . As indicated below, the increase in intensity of the latter bands can be attributed to the appearance of an arsenite species. It is possible that the shoulder observed on the high-wavenumber side of the bands at  $385$  and  $400 \text{ cm}^{-1}$  at higher  $\Sigma\text{S}/\Sigma\text{As}$  ratios is the same as the band at  $420 \text{ cm}^{-1}$  visible at lower  $\Sigma\text{S}/\Sigma\text{As}$  ratios, inasmuch as there continually appears to be some intensity at around  $420 \text{ cm}^{-1}$  throughout the entire range of  $\Sigma\text{S}/\Sigma\text{As}$  ratios investigated. The bands at  $385$ ,  $400$  and  $420 \text{ cm}^{-1}$  each appear to belong to separate species as their intensities do not change in a concerted manner as  $\Sigma\text{S}/\Sigma\text{As}$  is varied. Thus, at pH = 13.2 and  $\Sigma\text{S} + \Sigma\text{As} = 0.1 \text{ mol kg}^{-1}$  at least three separate species exist, in addition to that responsible for the bands at  $600$  and  $800 \text{ cm}^{-1}$ .

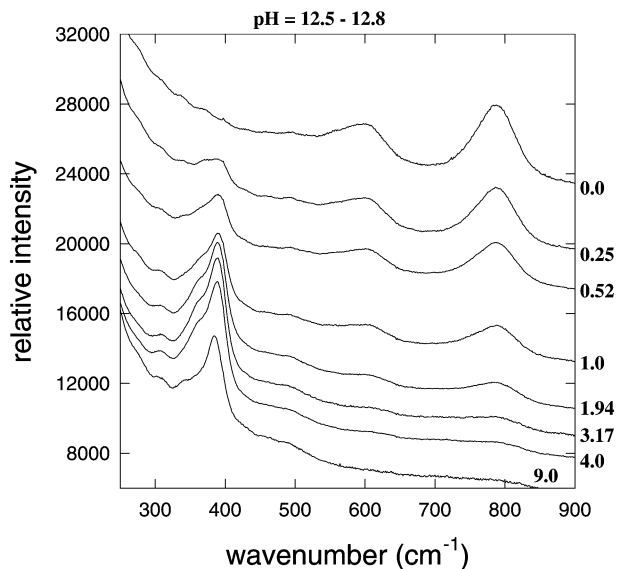
Raman spectra for solutions with  $\Sigma\text{S} + \Sigma\text{As} = 0.1 \text{ mol kg}^{-1}$



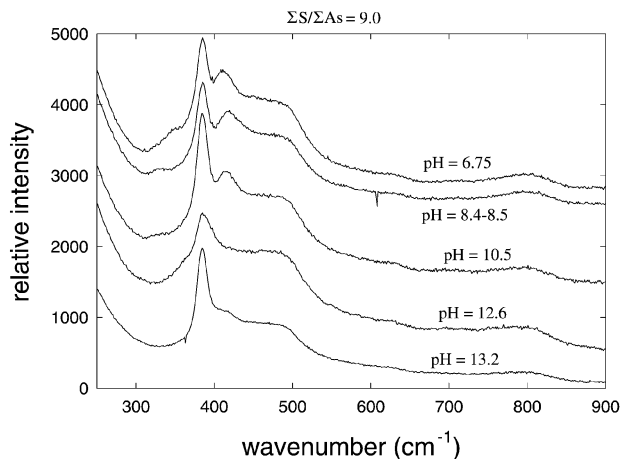
**Fig. 4** Raman spectra of arsenic sulfide solutions at pH = 10.5 and  $\Sigma\text{As} + \Sigma\text{S} = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of  $\Sigma\text{S}/\Sigma\text{As}$  ratio.



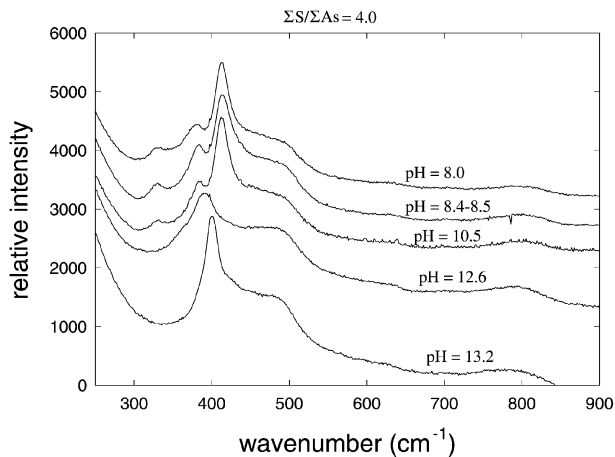
**Fig. 5** Raman spectra of arsenic sulfide solutions at pH = 8.4-8.5 and  $\Sigma\text{As} + \Sigma\text{S} = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of  $\Sigma\text{S}/\Sigma\text{As}$  ratio.



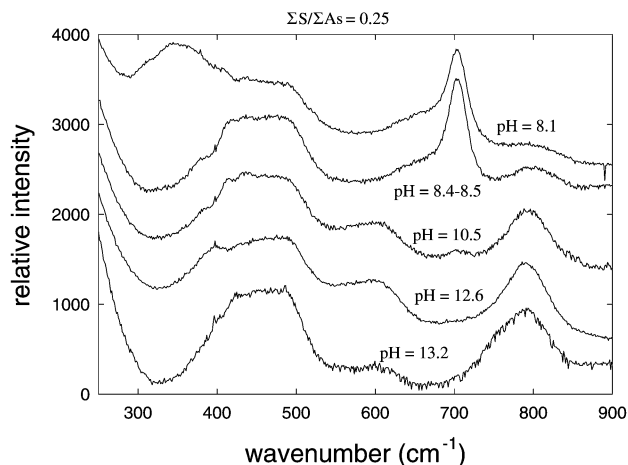
**Fig. 6** Raman spectra of arsenic sulfide solutions at pH = 12.6 and  $\Sigma\text{As} + \Sigma\text{S} = 0.5 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of  $\Sigma\text{S}/\Sigma\text{As}$  ratio.



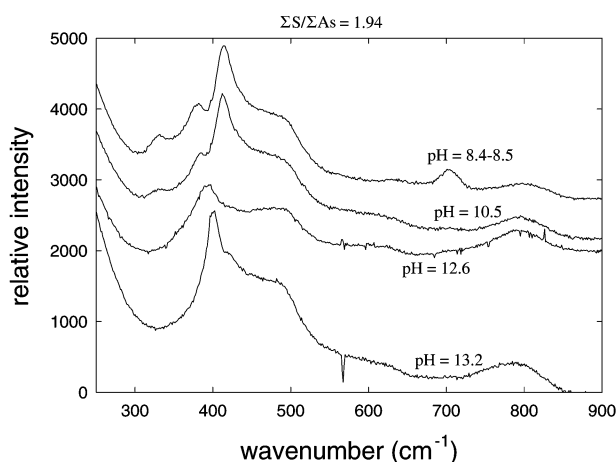
**Fig. 7** Raman spectra of arsenic sulfide solutions at  $\Sigma\text{S}/\Sigma\text{As} = 9.0$  and  $\Sigma\text{As} + \Sigma\text{S} = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of pH.



**Fig. 8** Raman spectra of arsenic sulfide solutions at  $\Sigma S/\Sigma As = 4.0$  and  $\Sigma As + \Sigma S = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of pH.

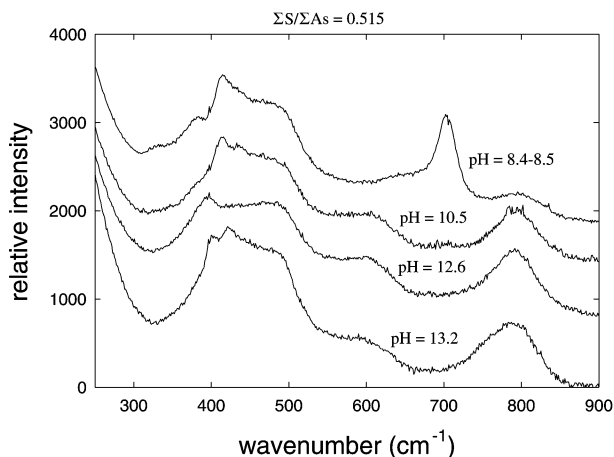


**Fig. 11** Raman spectra of arsenic sulfide solutions at  $\Sigma S/\Sigma As = 0.25$  and  $\Sigma As + \Sigma S = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of pH.



**Fig. 9** Raman spectra of arsenic sulfide solutions at  $\Sigma S/\Sigma As = 1.94$  and  $\Sigma As + \Sigma S = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of pH.

and pH = 12.6 are shown in Fig. 3. Only one prominent band is noted above background in the range 350–450  $\text{cm}^{-1}$ , but the maximum of this band appears to shift from about 385  $\text{cm}^{-1}$  to 397  $\text{cm}^{-1}$  as the  $\Sigma S/\Sigma As$  ratio varies from 9 to 0.25. The band is asymmetric to the high-wavenumber side, and there may also be some intensity above background on the low-wavenumber side. All of these observations suggest the presence of more



**Fig. 10** Raman spectra of arsenic sulfide solutions at  $\Sigma S/\Sigma As = 0.515$  and  $\Sigma As + \Sigma S = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  as a function of pH.

than one component to the band. We interpret these observations in terms of the presence of three strongly overlapping bands, the same ones at 385 and 400  $\text{cm}^{-1}$  observed at pH = 13.2, and an additional band at approximately 390  $\text{cm}^{-1}$ . The intensity of these bands varies with  $\Sigma S/\Sigma As$  in such a manner that the apparent peak of the band envelope shifts to higher wavenumbers. As at pH = 13.2, as the  $\Sigma S/\Sigma As$  ratio decreases, bands near 600 and 800  $\text{cm}^{-1}$  increase in relative intensity, suggesting the formation of arsenite species.

The band near 385  $\text{cm}^{-1}$ , observed in both Fig. 2 and 3, is also observed in solutions with high  $\Sigma S/\Sigma As$  at  $\Sigma S + \Sigma As = 0.1 \text{ mol kg}^{-1}$  and pH = 10.5 (Fig. 4). In addition, at low  $\Sigma S/\Sigma As$  ratios a band near 415  $\text{cm}^{-1}$  is present, and this band increases in intensity with respect to the band at 385  $\text{cm}^{-1}$  as  $\Sigma S/\Sigma As$  decreases. A broad, low-intensity band appears to be present at about 330  $\text{cm}^{-1}$  at  $\Sigma S/\Sigma As = 9$ . This band increases and then seems to remain constant in intensity from  $\Sigma S/\Sigma As = 5.25$  to  $\Sigma S/\Sigma As = 3.17$ , and then decreases in intensity and disappears by  $\Sigma S/\Sigma As = 0.52$ . The band near 385  $\text{cm}^{-1}$  remains visible until  $\Sigma S/\Sigma As = 1$ , after which it disappears. The band at 415  $\text{cm}^{-1}$  attains a maximum intensity at  $\Sigma S/\Sigma As = 4$ , and then decreases in intensity until it disappears completely at  $\Sigma S/\Sigma As < 0.25$ . The peak position of this band appears to change slightly from 415 to 412  $\text{cm}^{-1}$  with decreasing  $\Sigma S/\Sigma As$  ratio. A very low-intensity band appears at about 435  $\text{cm}^{-1}$  at  $\Sigma S/\Sigma As = 1.0$  but disappears at  $\Sigma S/\Sigma As < 0.25$ . At about  $\Sigma S/\Sigma As = 1.94$ , bands begin to appear at 600 and 790  $\text{cm}^{-1}$  and these grow in intensity to reach a maximum at the lowest  $\Sigma S/\Sigma As$  (0.11) value measured. At  $\Sigma S/\Sigma As < 0.515$ , a weak, broad band also appears near 700  $\text{cm}^{-1}$ . The band near 415  $\text{cm}^{-1}$  could possibly be interpreted to result from the same species responsible for the band observed at 420  $\text{cm}^{-1}$  at pH = 13.2. However, we reject this interpretation for the following reasons: (1) A difference of 5–8  $\text{cm}^{-1}$  is outside the uncertainty in identification of band peak positions for such a relatively narrow band; (2) the intensities of the bands at 330 and 415  $\text{cm}^{-1}$  appear to be correlated, yet no corresponding band at 330  $\text{cm}^{-1}$  was observed to occur with the band at 420  $\text{cm}^{-1}$  at pH = 13.2 (although admittedly the intensity of the latter band is low and so a band at 330  $\text{cm}^{-1}$  might not be detectable even if present); and (3) a band near 415–420  $\text{cm}^{-1}$  was not observed at pH = 12.6, and it is highly unlikely that a species present at pH = 13.2 would first disappear and then reappear as pH decreases. Thus, we conclude that the band at 415  $\text{cm}^{-1}$  represents a previously unidentified As species. The apparent shift of this band to lower wavenumbers with decreasing  $\Sigma S/\Sigma As$  ratios could be an indication of overlap of bands of two different species, the relative intensities of which vary with  $\Sigma S/\Sigma As$  ratio. The

apparent band at  $435\text{ cm}^{-1}$  may represent yet another As species, but we are less confident of its existence because of the very low observed intensity of this band. Thus, at least one, possibly more, new species appear as pH is decreased to 10.5.

The spectra at low wavenumbers for solutions with  $\Sigma\text{S} + \Sigma\text{As} = 0.1\text{ mol kg}^{-1}$  and  $\text{pH} = 8.4\text{--}8.5$  at high  $\Sigma\text{S}/\Sigma\text{As}$  (Fig. 5) are very similar to those in Fig. 4 ( $\text{pH} = 10.5$ ). Bands are observed near  $330$ ,  $385$  and  $415\text{ cm}^{-1}$ , and the relative intensities of these bands at a given value of  $\Sigma\text{S}/\Sigma\text{As}$  do not appear to be strongly dependent on pH. In fact, given the fact that pH differed by 2 units in the solutions the spectra of which are shown in Fig. 4 and 5, the lack of change in relative intensities of the bands in the region  $300\text{--}450\text{ cm}^{-1}$  is particularly striking. On the other hand, the peak of the band near  $415\text{ cm}^{-1}$  actually shifts from around  $419\text{ cm}^{-1}$  at  $\Sigma\text{S}/\Sigma\text{As} = 9.0$ , to a minimum of  $412\text{ cm}^{-1}$  at  $\Sigma\text{S}/\Sigma\text{As} = 1.0$ , and then back up to  $415\text{ cm}^{-1}$  at  $\Sigma\text{S}/\Sigma\text{As} = 0.52$ . Once again, these apparent shifts may be an indication of the presence of two or more species with overlapping bands. In the spectral region above  $500\text{ cm}^{-1}$  there are a number of changes that occur at low  $\Sigma\text{S}/\Sigma\text{As}$  on going from  $\text{pH} = 10.5$  to  $\text{pH} = 8.5$ . First, the intensity of the bands near  $600$  and  $790\text{ cm}^{-1}$  are substantially reduced at the lower pH values. Second, a rather sharp band appears near  $702\text{ cm}^{-1}$  and increases in intensity towards a maximum at  $\Sigma\text{S}/\Sigma\text{As} = 0.11$ . Finally, a low, broad shoulder appears on the low-wavenumber side of the latter peak at approximately  $650\text{ cm}^{-1}$ .

Finally, Fig. 6 shows the spectra obtained for solutions with  $\Sigma\text{As} + \Sigma\text{S} = 0.5\text{ mol kg}^{-1}$  and  $\text{pH} = 12.5\text{--}12.8$ . At  $\Sigma\text{S}/\Sigma\text{As} = 9.0$ , these solutions exhibit an intense band with a peak near  $384\text{ cm}^{-1}$  and asymmetric to the low-wavenumber side. Very weak peaks are also apparent at about  $308$  and  $344\text{ cm}^{-1}$ . With decreasing  $\Sigma\text{S}/\Sigma\text{As}$  ratio, the intense band near  $384\text{ cm}^{-1}$  appears to shift to  $389\text{ cm}^{-1}$ , and a prominent shoulder develops at  $\sim 365\text{ cm}^{-1}$ . The shoulder seems to maintain its intensity relative to the more intense band from  $\Sigma\text{S}/\Sigma\text{As} = 4.0$  to  $1.94$ . At lower  $\Sigma\text{S}/\Sigma\text{As}$  ratios, both the shoulder near  $365$  and the main peak near  $389\text{ cm}^{-1}$  decrease in intensity, but the intensity of the shoulder decreases faster than that of the main peak. At  $\Sigma\text{S}/\Sigma\text{As} = 0.52$  the shoulder has all but disappeared, but the main band remains markedly asymmetric. This main band is still present at  $\Sigma\text{S}/\Sigma\text{As} = 0.25$ , but disappears completely at  $\Sigma\text{S}/\Sigma\text{As} = 0$ . Thus, at this higher value of  $\Sigma\text{As} + \Sigma\text{S}$ , at least one new species, one with a band near  $365\text{ cm}^{-1}$ , has been identified. At this point is not clear whether the band near  $308\text{ cm}^{-1}$  represents a separate species or is a band attributable to the same species responsible for the band at  $365\text{ cm}^{-1}$ . However, the broadness of the spectral envelope in the region  $350\text{--}400\text{ cm}^{-1}$  is permissive of the existence of several additional species. Very broad bands near  $600$  and  $800\text{ cm}^{-1}$ , attributable to arsenite species, are clearly present at  $\Sigma\text{S}/\Sigma\text{As}$  ratios as high as  $1.94$ , and possibly  $3.17$ . These are essentially the same bands observed in solutions with  $\Sigma\text{S} + \Sigma\text{As} = 0.1\text{ mol kg}^{-1}$  and  $\text{pH} = 12.6$  at low  $\Sigma\text{S}/\Sigma\text{As}$ , indicating that the arsenite species do not form polynuclear species under the conditions investigated here. This conclusion is consistent with the Raman results of Pokrovski *et al.*<sup>9</sup> which showed that  $\text{H}_3\text{AsO}_3^0$  does not form polynuclear species until  $\Sigma\text{As} > 1\text{ mol kg}^{-1}$ .

Fig. 7 shows the spectra at  $\Sigma\text{S} + \Sigma\text{As} = 0.1$  and  $\Sigma\text{S}/\Sigma\text{As} = 9.0$  as a function of pH. This figure shows essentially the same data as seen in Fig. 2–6, with the addition of the spectrum of a solution with  $\text{pH} = 6.75$ , the only solution of this pH for which we were able to obtain a spectrum. As discussed above, a band near  $385\text{ cm}^{-1}$  persists at all pH values at the given values of  $\Sigma\text{S} + \Sigma\text{As}$  and  $\Sigma\text{S}/\Sigma\text{As}$ . Moreover, a band near  $415\text{ cm}^{-1}$  (accompanied by a band at  $330\text{ cm}^{-1}$ ) appears starting at  $\text{pH} = 10.5$  and persists to the lowest pH investigated.

Spectra for  $\Sigma\text{S} + \Sigma\text{As} = 0.1$  and  $\Sigma\text{S}/\Sigma\text{As} = 4.0$  as a function of pH are compiled in Fig. 8. Again, these data were depicted in previous figures, with the exception of an additional spectrum

collected at  $\text{pH} = 8.0$ . As noted previously, a band occurs at about  $400\text{ cm}^{-1}$  at  $\text{pH} = 13.2$ , but by  $\text{pH} = 12.6$ , the latter is replaced by a band at  $\sim 390\text{ cm}^{-1}$ . At pH values between  $10.5$  and  $8.0$ , bands occur at  $330$ ,  $385$  and  $413\text{ cm}^{-1}$ , the relative intensities of which do not change much over a range of  $2.5$  pH units. Fig. 9 shows similar spectral features at  $\Sigma\text{S}/\Sigma\text{As} = 1.94$  to those in Fig. 8, although at  $\text{pH} = 13.2$  the band near  $400\text{ cm}^{-1}$  seems to have a more prominent shoulder on its high-wavenumber side. Also, in Fig. 9 at  $\text{pH} = 8.4\text{--}8.5$ , a band appears at  $\sim 700\text{ cm}^{-1}$  as well.

At  $\Sigma\text{S} + \Sigma\text{As} = 0.1$  and  $\Sigma\text{S}/\Sigma\text{As} = 0.515$ , the spectral features between  $300$  and  $500\text{ cm}^{-1}$  (other than the background band) have very low intensities and are not very distinct (Fig. 10). Between  $\text{pH} = 10.5$  and  $\text{pH} = 8.4\text{--}8.5$ , there is a notable change above  $600\text{ cm}^{-1}$ , in which the broad band near  $800\text{ cm}^{-1}$  gives way to a sharper band near  $700\text{ cm}^{-1}$  that has a shoulder on the low-wavenumber side. At  $\Sigma\text{S} + \Sigma\text{As} = 0.1$  and  $\Sigma\text{S}/\Sigma\text{As} = 0.25$  (Fig. 11), the spectra are very similar to those in Fig. 10, except that there is almost no intensity above background from  $300$  and  $500\text{ cm}^{-1}$ . Also, at  $\text{pH} = 8.1$  a very broad band appears from about  $300$  to  $420\text{ cm}^{-1}$ . This band most likely represents scattering from solid particles precipitated on decrease of pH.

The Raman bands enumerated above are the minimum number of bands present. There may well be other bands representing additional species, that cannot be resolved without quantitative band fitting. Indeed, results of attempts to perform such band fitting support the likely presence of other species. However, owing primarily to the presence and variable intensity of the broad fluorescence band, we found it impossible to fit the observed spectral data with bands that exhibited systematic peak positions, intensities and peak widths as a function of pH and  $\Sigma\text{S}/\Sigma\text{As}$ . Nevertheless, our results do indicate the presence of at least 6–8 separate S-bearing As species. It seems clear that separate species are responsible for bands near  $365$ ,  $385$ ,  $390$ ,  $400$ ,  $415$  ( $330$ ) and  $420\text{ cm}^{-1}$ . In addition, more tentatively identified bands at  $308$ ,  $344$  and  $435\text{ cm}^{-1}$  may represent additional species (Table 1).

## 4. Discussion

### Arsenite species

At low  $\Sigma\text{S}/\Sigma\text{As}$  ratios, bands appear in the spectral region from  $600$  to  $800\text{ cm}^{-1}$  which may be attributed to S-free, As(III) species (*i.e.*, arsenites). Loehr and Plane<sup>35</sup> have assigned Raman bands to the various arsenite species, and these assignments are given in Table 2. In Fig. 12, the distribution of arsenite species as a function of pH at  $25\text{ }^\circ\text{C}$  and  $1\text{ bar}$  is illustrated.

The very broad bands observed near  $600$  and  $800\text{ cm}^{-1}$  at  $\text{pH} = 13.2$  (Fig. 2) are probably attributable to the species  $\text{HAsO}_3^{2-}$  and  $\text{AsO}_3^{3-}$ , which are present in nearly equal proportions at  $\text{pH} = 13.2$  (Fig. 12). The bands assigned by Loehr and Plane<sup>35</sup> to the first species are rather uncertain, but overall our observations are consistent with their band assignments for these two most deprotonated arsenite species.

At  $\text{pH} = 12.6$  (Fig. 3 and 11), the bands at  $600$  and  $800\text{ cm}^{-1}$  appear to be somewhat narrower than those at  $\text{pH} = 13.2$ , consistent with the predominance of a single species,  $\text{HAsO}_3^{2-}$ , at  $\text{pH} = 12.6$  (Fig. 12). The positions of the bands are consistent with those given by Loehr and Plane<sup>35</sup> for  $\text{HAsO}_3^{2-}$ . The species  $\text{H}_2\text{AsO}_3^-$  is expected to be predominant at  $\text{pH} = 10.5$  according to the speciation diagram in Fig. 12. The spectral assignment of Loehr and Plane<sup>35</sup> would suggest the most intense bands for this species to occur at  $790$ ,  $610$ , and  $570\text{ cm}^{-1}$ . We observe the most intense band at  $790\text{ cm}^{-1}$ , and a broad band that covers the region from  $570$  to  $610\text{ cm}^{-1}$ , consistent with the predominance of  $\text{H}_2\text{AsO}_3^-$  at this pH (Fig. 4 and 11). A weak band near  $700\text{ cm}^{-1}$  is apparent at low

**Table 1** Summary of observed Raman bands as a function of solution composition

$\Sigma S + \Sigma As / \text{mol kg}^{-1}$	pH	$\Sigma S / \Sigma As$	Peak positions/cm <sup>-1</sup>
0.1	13.2	9.0	385
		5.25	385, 400
		4.0	400
		3.17	400, 420, 600, 800
		1.94	400, 420, 600, 800
		1.0	400, 420, 600, 800
		0.52	400, 420, 600, 800
		0.25	420?, 600, 800
		0.11	600, 800
		0.1	12.6
5.25	389		
4.0	390		
3.17	391, 600, 800		
1.94	395, 600, 800		
1.0	395, 600, 800		
0.52	396, 600, 800		
0.25	397, 600, 800		
0.11	600, 800		
0.1	10.5		
		5.25	327, 385, 415
		4.0	331, 385, 412
		3.17	332, 384, 413
		1.94	329, 384, 412, 600, 790
		1.0	329, 384, 412, 435?, 600, 790
		0.52	413, 435?, 600, 790
		0.25	435?, 600, 700, 790
		0.11	600, 700, 790
		0.1	8.4–8.5
5.25	329, 384, 418		
4.0	331, 384, 413		
3.17	331, 383, 413, 700		
1.94	332, 382, 414, 701		
1.0	334, 380, 412, 702		
0.52	333, 384, 415, 702, 800?		
0.25	415, ~650sh, 702, 800		
0.11	~650sh, 702, 800		
0.1	6.75		
		8.0	331, 384, 413
		8.1	350, ~650sh, 702, 800
0.5	12.6	9.0	308, 344, 384
		4.0	308, 365sh, 389
		3.17	308, 365sh, 389
		1.94	308, 365sh, 389, 600, 800
		1.0	308, 365sh, 389, 600, 800
		0.52	308?, 390, 600, 800
		0.25	370?, 390, 600, 800
		0.11	600, 800

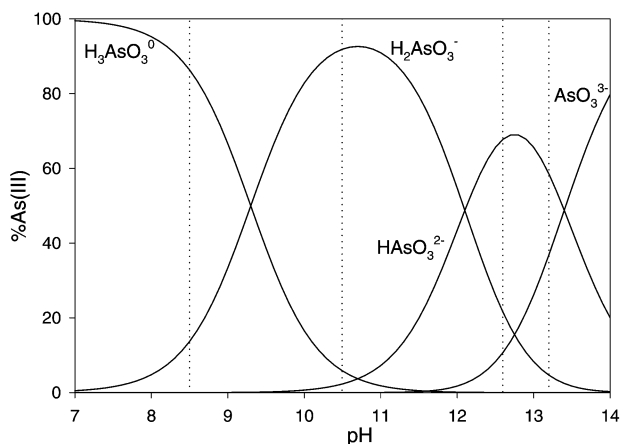
$\Sigma S / \Sigma As$  ratios in Fig. 4, which may be due to the presence of a small proportion of  $H_3AsO_3^0$  at pH = 10.5 (cf. Fig. 12).

Finally, at pH  $\leq$  8.5, the speciation diagram in Fig. 12 suggests that the completely protonated arsenite,  $H_3AsO_3^0$ , should be predominant. For this species, Loehr and Plane,<sup>35</sup> and also Pokrovski *et al.*,<sup>9</sup> observed a very distinctive intense

**Table 2** Compilation of Raman spectral assignments for arsenite species from Loehr and Plane.<sup>35</sup>

Species <sup>a</sup>	Observed bands/cm <sup>-1</sup>
$H_3AsO_3^0$ or $As(OH)_3^0$	710, 655
$H_2AsO_3^-$ or $AsO(OH)_2^-$	790, 610, 570, 370, 320
$HAsO_3^{2-}$ or $AsO_2(OH)^{2-}$	810?, 770?, 670-520?
$AsO_3^{3-}$	752, 680, 340

<sup>a</sup>Second formulations given are those preferred by Loehr and Plane.<sup>35</sup>

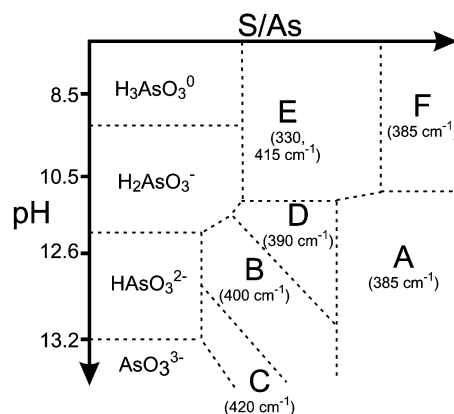


**Fig. 12** Distribution of arsenite species as a function of pH at 25 °C and 1 bar. Thermodynamic data used to construct this diagram ( $pK_1 = 9.3$ ;  $pK_2 = 12.1$ ;  $pK_3 = 13.4$ ) are from Akinfiev *et al.*<sup>8</sup>

peak near 710  $cm^{-1}$ , with a shoulder near 655  $cm^{-1}$ . These features are clearly observed in Fig. 5, 10 and 11. We also observe a broad, low-intensity band near 790  $cm^{-1}$  at pH = 8.5, which is consistent with the presence of a small proportion of  $H_2AsO_3^-$  at pH = 8.5 (Fig. 12).

### Thioarsenite species

The bands observed in the region 300–450  $cm^{-1}$  can be attributed to As–S bonds.<sup>24,36,37</sup> These species may be simple thioarsenites, or a mixed species such as  $AsO_2S^{3-}$ , for example. However, as all the bands in the region above 500  $cm^{-1}$  can be accounted for by known arsenite species, we will assume that simple thioarsenites are responsible for all the bands observed in the region 300–450  $cm^{-1}$ . The Raman spectra offer evidence of the existence of at least 6–8 separate thioarsenite species over the range of conditions investigated. To simplify discussion, each major species (as inferred from the existence of a Raman band exhibiting independent behavior as a function of pH and  $\Sigma S / \Sigma As$ ) has been assigned an alphabetic designation as enumerated in the caption to Fig. 13. Fig. 13 summarizes the changes in species that occur as pH and  $\Sigma S / \Sigma As$  ratio of the solution change. This diagram is highly schematic in that the positions and slopes of the boundaries among species are not



**Fig. 13** Highly schematic diagram showing approximate predominance fields of various As species as a function of pH and  $\Sigma S / \Sigma As$  ratio for  $\Sigma As + \Sigma S = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ . With the exception of the boundaries between the arsenite species ( $H_3AsO_3^0$ ,  $H_2AsO_3^-$ ,  $HAsO_3^{2-}$ ,  $AsO_3^{3-}$ ), the slopes and the positions of the boundaries are highly uncertain. The letters correspond to species responsible for observed Raman bands as follows: A, 385  $cm^{-1}$ ; B, 400  $cm^{-1}$ ; C, 420  $cm^{-1}$ ; D, 390  $cm^{-1}$ ; E, 330 and 415  $cm^{-1}$ ; and F, 385  $cm^{-1}$ . At  $\Sigma As + \Sigma S = 0.5 \text{ mol kg}^{-1} \text{ H}_2\text{O}$  an additional species with a band at 360–370  $cm^{-1}$  joins species D at pH = 12.6 and intermediate  $\Sigma S / \Sigma As$ .

well constrained. Furthermore, we cannot make any definitive statements regarding the exact stoichiometries of these thioarsenite species owing to a number of factors including: (1) the interference by fluorescence of the glass tubes employed; (2) absence of an internal standard; (3) lack of knowledge of the scattering coefficients of the various species; and (4) the relatively small number of bands that appear to be resolved for each species. However, a number of conclusions can be made regarding the chemical relationships among the various species indicated by the Raman bands.

If we assume that there is only a single species exhibiting a Raman band near  $385\text{ cm}^{-1}$ , then the spectra show that species A occurs at the highest  $\Sigma\text{S}/\Sigma\text{As}$  ratios at all pH values. At pH values of 13.2 and 12.6 and  $\Sigma\text{S} + \Sigma\text{As} = 0.1\text{ mol kg}^{-1}$ , species A appears to be the only or the greatly dominant thioarsenite present at  $\Sigma\text{S}/\Sigma\text{As} = 9$ , and other species begin to take its place as  $\Sigma\text{S}/\Sigma\text{As}$  ratio decreases. At pH values of 10.5 and 8.5 and  $\Sigma\text{S} + \Sigma\text{As} = 0.1\text{ mol kg}^{-1}$ , or at pH = 12.6 and  $\Sigma\text{S} + \Sigma\text{As} = 0.5\text{ mol kg}^{-1}$ , species A is present at  $\Sigma\text{S}/\Sigma\text{As} = 9$ , but other species are present in significant proportion as well. In these cases also, species A is converted to other species as  $\Sigma\text{S}/\Sigma\text{As}$  decreases. If indeed the band near  $385\text{ cm}^{-1}$  arises from a single species, then these results suggest that species A is stable over a wide range of pH as long as  $\Sigma\text{S}/\Sigma\text{As}$  is elevated.

Alternatively, the band near  $385\text{ cm}^{-1}$  may contain contributions from more than one species that happen to have a Raman signal near this frequency. Some evidence for this interpretation comes from Fig. 7. Here it is seen that the band near  $385\text{ cm}^{-1}$  appears to decrease in intensity from pH = 13.2 to pH = 12.6, but then increase again from pH = 12.6 to pH = 10.5. Although it is difficult to be certain whether these apparent changes in intensity are real in the absence of an internal standard, if so they suggest that possibly two different species exist with bands near  $385\text{ cm}^{-1}$ . Moreover, at pH  $\leq 10.5$ , bands at  $385$  and  $415\text{ cm}^{-1}$  coexist, and their intensities seem to be quite insensitive to pH given a range of 3.75 units. One interpretation of the spectra in Fig. 7 is that a species (A) responsible for the band near  $385\text{ cm}^{-1}$  at pH  $> 10.5$  gives way to a second species (F) with a band near  $385\text{ cm}^{-1}$  and one with a band near  $415\text{ cm}^{-1}$  (E), the latter two having a pH-independent relationship to one another. This would account for the relative insensitivity of intensities of the two bands to pH at pH  $\leq 10.5$ , while at the same time the initial appearance of the  $415\text{ cm}^{-1}$  band is pH-dependent. The apparent near constant ratio of intensities of the bands  $385$  and  $415\text{ cm}^{-1}$  above pH = 10.5 could imply that both bands arise from a single species. However, comparison of Fig. 7 and 8 shows that the relative intensities of these two bands, although insensitive to pH, are a strong function of the  $\Sigma\text{S}/\Sigma\text{As}$  ratio, and thus cannot belong to the same species.

Fig. 13 shows that at  $\Sigma\text{S} + \Sigma\text{As} = 0.1\text{ mol kg}^{-1}$  and pH values of 8.5 and 10.5, species F converts to species E as the  $\Sigma\text{S}/\Sigma\text{As}$  ratio decreases. Moreover, as mentioned in the Results section, the relative proportions of species F and E at a given  $\Sigma\text{S}/\Sigma\text{As}$  ratio do not appear to be strongly dependent on pH (cf. Fig. 4, 5 and 7). These observations suggest that species A must possess a higher  $\Sigma\text{S}/\Sigma\text{As}$  ratio than species E, but that there is no loss or gain of protons when species F converts to species E. Thus, the boundary between F and E has been drawn as a vertical, pH-independent boundary. On the other hand, species E is apparently destabilized on increasing pH to 12.6 and higher, whereupon species D, B and C appear in turn.

Species D appears only at pH = 12.6 at intermediate  $\Sigma\text{S}/\Sigma\text{As}$  ratios. It is apparently present at both  $\Sigma\text{S} + \Sigma\text{As}$  values investigated. Because the appearance of species D relative to E depends on the pH, species D may be a less protonated form of species E. As the  $\Sigma\text{S}/\Sigma\text{As}$  ratio continues to decrease, species D is converted to species B.

At pH = 13.2, species A apparently converts directly to species B with decreasing  $\Sigma\text{S}/\Sigma\text{As}$  ratio, without first going

through species D, as was the case at pH = 12.6. With a further decrease in  $\Sigma\text{S}/\Sigma\text{As}$  ratio, species C appears at the expense of species A and B.

### Comparison to previous Raman studies of thioarsenite species

We are aware of only one other Raman study of aqueous thioarsenites—that of Helz *et al.*<sup>24</sup> The latter authors studied a solution containing 1 M NaHS and 0.08 M As ( $\Sigma\text{S}/\Sigma\text{As} = 12.5$ ) at pH 8.2 and 12 at 25 °C. They observed only three bands over the range 150–750  $\text{cm}^{-1}$  at 325, 382 and 412  $\text{cm}^{-1}$ . Upon an increase in pH from 8.2 to 12, the relative intensity of the band at 382  $\text{cm}^{-1}$  increased at the expense of the two bands at 325 and 412  $\text{cm}^{-1}$ . Based on *ab initio* calculations, Helz *et al.*<sup>24</sup> attributed the bands at 382  $\text{cm}^{-1}$  to the species  $\text{AsS}_2(\text{HS})^{2-}$  and the bands at 325 and 412  $\text{cm}^{-1}$  to the species  $\text{AsS}(\text{HS})_2^-$ , which can be related to one another through the simple protonation reaction:



In contrast, Fig. 4, 5 and 7 indicate that the situation may not be as simple. Like Helz *et al.*,<sup>24</sup> we note three bands in the pH range 8.5–10.5, at approximately 325, 382 and 412  $\text{cm}^{-1}$  (in our case, 330, 385 and 415  $\text{cm}^{-1}$ , *i.e.*, our species F and E), and we also observe generally a relative increase in the intensity of the band at 385  $\text{cm}^{-1}$  with increasing pH at pH  $> 10.5$  (the species responsible for the bands at 330 and 415  $\text{cm}^{-1}$  disappears completely by pH = 12.6). However, we further observe that, at constant pH, the intensity of the band at 385  $\text{cm}^{-1}$  decreases relative to that at 415  $\text{cm}^{-1}$  with decreasing  $\Sigma\text{S}/\Sigma\text{As}$  ratio. This observation indicates the existence of two species with different  $\Sigma\text{S}/\Sigma\text{As}$  ratios. Moreover, the relative intensities of the bands at 385 and 415  $\text{cm}^{-1}$  at constant  $\Sigma\text{S}/\Sigma\text{As}$  ratio do not change very much with an increase of pH from 8.4 to 10.5 (Fig. 7). Over such a large pH range, if the species responsible for these bands were related simply by eqn. (1), we would expect much larger changes in relative intensity, as the ratio of concentrations of the species would have to change by one order of magnitude for each unit change in pH. Even in the work of Helz *et al.*,<sup>24</sup> the observed changes in relative intensities of the bands near 382 and 412  $\text{cm}^{-1}$  as a function of pH were relatively small, even though pH was varied by nearly 4 units. If the only reaction occurring was reaction (1), there should have been a much greater change in relative intensities with a change in pH of this magnitude. Based on this reasoning, we are thus forced to conclude that at least three species exist at high  $\Sigma\text{S}/\Sigma\text{As}$  over the pH range investigated. Two species (E and F), which differ only in their  $\Sigma\text{S}/\Sigma\text{As}$  ratio but *not* their degree of protonation, exist at high  $\Sigma\text{S}/\Sigma\text{As}$  and pH  $\leq \sim 10.5$ . As pH increases above 10.5, species E and F together give way to a single species A, which happens to yield a Raman band with a peak very similar to that of species F.

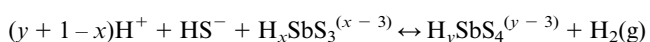
Helz *et al.*<sup>24</sup> provided a list of possible thioarsenite species and their predicted Raman shifts based on *ab initio* calculations. In principle, it should be possible to employ these calculated Raman frequencies to assign stoichiometries to each of the species observed in our study. However, we were unable to match the calculated frequencies of Helz *et al.*<sup>24</sup> to our observed Raman shifts and maintain consistency with the trends of the intensities of the spectral bands as a function of pH and  $\Sigma\text{S}/\Sigma\text{As}$  ratio. We suspect that the main reason is that we have observed at least some species for which Helz *et al.*<sup>24</sup> do not give calculated Raman shifts. Moreover, considering the large number of species we have observed and how close their Raman shifts are, even small uncertainties in the shifts determined from *ab initio* calculations make it difficult to make definite assignments of species stoichiometry.

## As(v) vs. As(III)

In the above discussion, it has been assumed that the thioarsenic species present in our experiments contain arsenic in the As(III) oxidation state. Mikenda *et al.*<sup>37</sup> report Raman bands for the As(v) species  $\text{AsS}_4^{3-}$  in the solid salt  $\text{Na}_3\text{AsS}_4 \cdot 8\text{H}_2\text{O}$  and the band attributed to the symmetrical stretch of this species had a maximum at  $385\text{ cm}^{-1}$ , which is very similar to the peak position for the band attributed in this study to species A. This raises the possibility that the arsenic in species A, and possibly other species, may be present in the As(v) oxidation state rather than the As(III) state as assumed. In a Raman study of thioantimony species, Wood<sup>38</sup> similarly observed that the main thioantimony species in his solutions had bands with a maximum at approximately the same wavenumber as the Sb(v) species  $\text{SbS}_4^{3-}$  reported by Mikenda *et al.*<sup>37</sup> Finally, based on *ab initio* calculations Tossell<sup>39</sup> showed that calculated Raman stretching frequencies for Sb(III)– and Sb(v)–sulfide complexes were very similar and do not permit a distinction among these two oxidation states based on Raman frequencies alone. However, Wood<sup>38</sup> (1989) was able to rule out the presence of a significant concentration of  $\text{SbS}_4^{3-}$  based on the polarization behavior of the Raman bands. On the other hand, others<sup>40,41</sup> have presented EXAFS evidence that aqueous Sb(v)–sulfide species are produced when the Sb(III)–solid  $\text{Sb}_2\text{S}_3$  reacts with aqueous bisulfide.

In the experiments described here, arsenic is clearly in the As(III) form at low  $\Sigma\text{S}/\Sigma\text{As}$  ratios where Raman spectra characteristic of arsenite species were obtained. Sulfide-free solutions containing As(III) were mixed with deoxygenated bisulfide solutions to produce the solutions at high  $\Sigma\text{S}/\Sigma\text{As}$  where thioarsenic species were observed. If these thioarsenic species contain As(v), this implies that oxidation of As(III) occurred upon mixing with the reduced bisulfide solution and formation of the thioarsenic complexes. The question then becomes, what is the oxidant in the reaction? It seems unlikely to be dissolved oxygen, owing to the care taken to exclude this gas during the preparation of the solution. Moreover, even if the solutions were saturated with oxygen, this would result in an  $\text{O}_2$  concentration of no more than  $10\text{ mg kg}^{-1}$ , or  $3.1 \times 10^{-4}\text{ mol kg}^{-1}$ . The lowest As concentration in any of the solutions employed was  $0.01\text{ mol kg}^{-1}$ , so even in a solution saturated in oxygen, there would be too little oxygen available to oxidize all the As(III) initially present. Because all solutions were prepared from degassed water and were handled in an inert atmosphere, the oxygen content should be much lower than  $10\text{ mg kg}^{-1}$ , and any residual oxygen left should be scavenged by the bisulfide in the solutions with high  $\Sigma\text{S}/\Sigma\text{As}$  ratios.

In order to explain the oxidation of Sb(III) to Sb(v) in their study, Mosselmans *et al.*<sup>40</sup> proposed the following reaction:



In this case,  $\text{H}^+$  is the oxidant. Reaction (2) suggests that, except in the special case where  $x = 1 + y$ , substantial shifts in pH should be observed as oxidation occurs, unless the solution is buffered. Thus, if a similar oxidation reaction occurred in our study of As–sulfide species, we should have seen a strong shift in pH as oxidation proceeded. During the preparation of solutions, we did not note any drift in pH, nor did we observe the effervescence of any gases, which could be attributed to production of hydrogen. We cannot rule out the possibility that a pH change occurred in the solution after it was sealed in the capillary tube, but evolution of hydrogen also was not observed after the solution was sealed in the tube. Thus, we feel justified in assuming the presence of As(III)–sulfide species. However, future investigations of this system should take steps to determine definitively the oxidation state of As in these thioarsenic complexes.

Moreover, recently Jayanetti *et al.*<sup>42</sup> have shown that oxidation–reduction reactions can occur during EXAFS measurements owing to the radiolysis of water by intense synchrotron X-ray beams to produce  $\text{H}_2$  and  $\text{O}_2$ . There is therefore the possibility that in the EXAFS studies,<sup>40,41</sup> oxidation of Sb(III) to Sb(v) occurred during measurements as a result of radiolysis. It seems only fair to mention that oxidation–reduction reactions could also be triggered by intense photon beams such as those employed in laser Raman spectroscopy. The resolution of the oxidation state of As and Sb in thio-complexes may require techniques that do not involve intense beams of electromagnetic radiation.

## Implications

Although we can not identify unambiguously the stoichiometries of the thioarsenite species present in our experiments, our results do have some important implications. Our study clearly demonstrates the complexity of the As–S–O–H system in that a relatively large number of species may be present. We have definitive proof of the existence of at least 6 or 7 different thioarsenic species in addition to the various arsenite species, and there may well be more species present that we could not resolve owing to peak overlap. Although detailed band fitting may change the details of our interpretations, our data clearly show the presence of a relatively large number of thioarsenite species. It may be this degree of complexity which explains the discrepancies in interpretations of previous studies. Our study also has implications for EXAFS investigations of such systems. EXAFS is a very powerful technique for the study of species in aqueous solution, but it provides a measure of the average coordination of an element in solution. Where several species exist simultaneously in significant concentrations, the interpretation of EXAFS results may not be straightforward. Thus, it may be necessary that a technique that can “see” individual species, such as Raman spectroscopy, be used in conjunction with EXAFS. Also, the possibility of radiolytic oxidation/reduction EXAFS measurements must be taken into account when making EXAFS measurements on redox-sensitive systems.

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