

Hoekstra and Siegel.<sup>15</sup> The upper limit of this range, 0.355, should be viewed with caution since it is based on one value which was not well determined. In any event, on the basis of currently available structural data, one limit for  $x$  in the pyrochlore structure is

(18) Hoekstra and Siegel (ref 8, Fig. 3) gave the limits of the oxygen positional parameter in the pyrochlore structure to be about 0.27–0.30, and these limits are presumably based on the authors' choice of origin,  $O_6$ . These limits correspond to a range of 0.355–0.325 on the basis of the origin at the B cation ( $B_6$ ). It would appear that this incorrect range resulted from the indiscriminate use of  $x$  parameters from various pyrochlores where different origins were used and from the failure to transform such data to a common origin. Furthermore, the authors' conclusion that the pyrochlore structure has not been observed in the region of regular octahedra around the B cations is also incorrect.

about midway between the values for an ideal cube around A and a regular octahedron around B. The other limit is just the other side of a regular octahedron around B.

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## Raman Spectra and Structures of Arsenious Acid and Arsenites in Aqueous Solution<sup>1</sup>

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The molecular species of As(III) in aqueous solution have been studied by the Raman effect. Utilizing the Job method of continuous variation, solutions with  $[\text{OH}^-]/[\text{As(III)}]$  between 3.5 and 15 have been shown to contain the four species  $\text{As(OH)}_3$ ,  $\text{AsO(OH)}_2^-$ ,  $\text{AsO}_2(\text{OH})^{2-}$ , and  $\text{AsO}_3^{3-}$ . The Raman spectra are consistent with a  $C_{3v}$  point group assignment for both  $\text{As(OH)}_3$  and  $\text{AsO}_3^{3-}$ .  $C_s$  symmetry has been shown for  $\text{AsO(OH)}_2^-$  and probably for  $\text{AsO}_2(\text{OH})^{2-}$ , although experimental data on the latter species were most difficult to obtain, since the spectra of all species are overlapped to a large extent. The As–O stretching vibrations, insensitive to  $\text{D}_2\text{O}$ , are between 790 and 750  $\text{cm}^{-1}$ , whereas the symmetric As–OH stretching modes, all exhibiting an isotope effect, are at 710  $\text{cm}^{-1}$  for  $\text{As(OH)}_3$  and 570  $\text{cm}^{-1}$  for  $\text{AsO(OH)}_2^-$ . The species  $\text{As(OH)}_3$  is also identified from its Raman spectrum as the only major component in acidic aqueous solutions of  $\text{As}_4\text{O}_6(\text{s})$ . The existence of  $\text{HAsO}_2$  is ruled out. Furthermore, there is no evidence for polymerization in basic solutions within an  $[\text{As(III)}]$  range of 0.6–5.0  $M$ .

### Introduction

Little is known of the structure of arsenious acid or its ionized forms in aqueous solutions. For the weak acid a single dissociation constant has generally been reported ( $\text{p}K_a \approx 10$ ); this fact has given rise to the formulation  $\text{HAsO}_2$ , although no unambiguous structural evidence exists for this. In a recent summary of various properties of aqueous solutions of As(III), Jander and Hofmann<sup>2</sup> supported the existence of an equilibrium between  $\text{HAsO}_2$  and  $\text{H}_3\text{AsO}_3$  in solution. Their findings rule out the existence of any polymeric aqueous solution species for  $[\text{As(III)}]$  up to approximately 0.3  $M$ . The structural aspects of arsenious acid are intriguing with respect to its congeners, nitrous and phosphorous acids. Nitrous acid, although not known in the liquid state, has a bent structure  $\text{HO–N–O}$ , whereas phosphorous acid corresponds to the formula  $\text{H}_2(\text{HPO}_3)$  with a four-coordinate P atom. The existence of the H–P bond has been firmly established by the Raman spectrum of a phosphorous acid solution in which the H–P vibration is observed as well as by the proton resonance spectrum

in which the P-bound hydrogen shows a considerable chemical shift away from bulk solvent protons.

The adaptability of the Raman technique to the study of arsenious acids was recognized by Fehér and Morgenstern.<sup>3</sup> These authors found no Raman line attributable to an As–H vibration but their photographically recorded spectra were insensitive to any spectral changes taking place upon addition of base to the weak acid. Furthermore, since the Raman spectrum of the ortho form ( $\text{K}_3\text{AsO}_3$  in solution) was essentially the same as that of aqueous solutions of  $\text{As}_4\text{O}_6 + 4, 8,$  and  $12 \text{ NaOH}$ , they concluded that an equilibrium existed between the ortho and meta forms in which the latter predominates.

The pH and conductometric titrations of Bhatnagar and Govind,<sup>4</sup> however, again lend support to the existence of several arsenites in solution formed when the ratios of  $\text{As}_4\text{O}_6$  to  $\text{NaOH}$  are 1:4, 1:8, and 1:12, respectively. The highest concentration studied, however, was 0.2  $M$ . Thus, it appears still uncertain what stoichiometric species and what structural species actually exist in solutions of arsenites. The data of Bhatnagar and Govind support the pyro form (*i.e.*,

(1) Supported by a research grant from the Office of Saline Water, U. S. Department of the Interior.

(2) G. Jander and H. Hofmann, *Z. Anorg. Allgem. Chem.*, **296**, 134 (1958).

(3) F. Fehér and G. Morgenstern, *ibid.*, **232**, 177 (1937).

(4) C. S. Bhatnagar and K. Govind, *Z. Naturforsch.*, **21b**, 190 (1966).

$\text{As}_2\text{O}_5^{4-}$ ) as an intermediate species, whereas Jander and Hofmann had ruled out *any* associated species. The absence of polymeric species in dilute solutions does not preclude their existence in more concentrated solutions in which Raman spectra are observed. The present Raman spectroscopic investigation of this system is an attempt to answer these basic questions which have been raised. This method is applicable to a higher concentration range than has previously been attempted. Furthermore, photoelectric recording of the spectral data gives quantitative intensity information which could not be readily obtained in earlier photographic work.

### Experimental Section

**Apparatus.**—All Raman spectra were obtained on a Cary 81 recording spectrophotometer using the 4358-Å exciting line of a low-pressure mercury vapor arc. The solutions were contained in 7-ml sample tubes surrounded by a Wratten 2A gelatin filter (Kodak) inside cylinders made from polaroid sheets (Bausch and Lomb). The Wratten filter helps to isolate the exciting frequency from the mercury continuum, whereas the polaroids were used for qualitative polarization measurements according to the method of Edsall and Wilson.<sup>5</sup> All solutions were filtered, prior to recording their spectra, through cellulose membranes with a 100- $\mu$  pore size (Millipore Filter Corp.) or through *fine* glass frits. A Varian A-60 pmr spectrometer was used for qualitative investigations of various solutions. The resolution of complex spectral envelopes was aided by the use of an analog computer (Du Pont Instrument Products Division).

**Preparation of Samples.**—The reagents were all of AR grade quality and used without further purification.  $\text{As}_4\text{O}_6$  (Mallinckrodt or J. T. Baker) was dissolved in distilled water by continuous stirring for several days at room temperature in order to obtain sufficient concentration to give a spectrum.  $\text{As}_4\text{O}_6$  solutions were also obtained by boiling a small excess of the oxide in water under reflux; on cooling,  $\text{As}_4\text{O}_6$  settled out leaving behind a saturated solution which was used for further work. The solubility of  $\text{As}_4\text{O}_6$  is greatly enhanced by the addition of base (NaOH, Mallinckrodt pellets). Solutions of known composition were prepared according to the Job method of continuous variation<sup>6</sup> for which  $[\text{As(III)}] + [\text{OH}^-] = 8.0 M$  and the ratio  $R = [\text{OH}^-]/[\text{As(III)}]$  ranged from 3.5 to 15. Also, solutions with a concentration sum of 12.0  $M$  and  $R$  values between 3.5 and 7.0 were studied. All solutions for the Job method were made by combining weighed amounts of both  $\text{As}_4\text{O}_6$  and NaOH, followed by the addition of 5.0 ml of a 2.0  $M$   $\text{NaNO}_3$  (Mallinckrodt) solution and distilled water to a final volume of 50 ml. The solutions were then filtered and stored in screw-capped polyethylene bottles. The final value of  $[\text{NO}_3^-] = 0.20 M$  is adequate to show only the strong  $\nu_1(A_1')$  Raman line and was used as an internal standard for both frequency (1048  $\text{cm}^{-1}$ ) and intensity.  $\text{NaAsO}_2$  (Baker and Adamson) was used as a source of readily soluble As(III) in conjunction with experiments in  $\text{D}_2\text{O}$  (assayed at 99.7%). Another set of solutions, maintaining constant  $[\text{As(III)}]$  but varying  $[\text{OH}^-]$ , was obtained by the successive addition of NaOH pellets in weighed amounts to a constant volume of solution. The starting material, *i.e.*, no added NaOH, was a solution with  $R = 4.0$ , corresponding to a concentration sum of 12.0  $M$ . These solutions were treated in the same manner as the Job solutions with respect to handling and storage. Raman spectra of solids were obtained by the use of conical sample holders previously described.<sup>7</sup>

**Analyses.**— $\text{As}_4\text{O}_6(s)$  was identified by its characteristic Raman spectrum if its presence as a reaction product was suspected. Solutions were quantitatively analyzed for As(III) by iodate

titration as outlined by Vogel.<sup>8</sup> Based on analytical results, it was seen that no precautionary measures would have to be taken to exclude air (*i.e.*, to prevent oxidation of As(III) in sample preparations) even at high alkalinity, as long as spectra were recorded within a few days' time. A considerable loss (up to 25%) of As(III) was noted for highly alkaline solutions ( $R > 10$ ) on standing, even in capped polyethylene bottles, for periods of 1 year or longer.

### Results

**Solids.**—The Raman spectra of the solids  $\text{As}_4\text{O}_6$  and  $\text{NaAsO}_2$  have been obtained. The frequencies determined are given in Table I, along with the stronger lines observed by Cheremisinov<sup>9</sup> for  $\text{As}_4\text{O}_6$ . Cher-

TABLE I

RAMAN SPECTRA OF $\text{As}_4\text{O}_6$ AND $\text{NaAsO}_2$	
Compound	—Observed frequencies, $\text{cm}^{-1}$ , and intensities <sup>a</sup> —
$\text{As}_4\text{O}_6$ (Cheremisinov <sup>9</sup> )	270 s, 365 vs, 473 s, 550 s, 780 av
$\text{As}_4\text{O}_6$ (this work, $\pm 1$ $\text{cm}^{-1}$ )	86 vs, 269 s, 371 vs, 473 m, 561 m, 782 m
$\text{NaAsO}_2$	240 w, 270 w, 325 w, 510 m, 555 s, 700 w, 835 s, 1230 m, b, 1380 m, b

<sup>a</sup> s, strong; m, medium; w, weak; b, broad; v, very.

emisinov's weak spectral lines for  $\text{As}_4\text{O}_6$  could not be found with our photoelectric recording apparatus. However, the line at 86  $\text{cm}^{-1}$  has not been previously reported; it is presumably a cage deformation mode.

**Solutions.**—The spectral character of the solutions studied is very different from those of the solids mentioned above. Whereas the solids show well-separated Raman lines, the solution spectra are generally broad and overlapped in the region from 250 to 900  $\text{cm}^{-1}$ . (Scans were made beyond 1100  $\text{cm}^{-1}$  to include the  $\nu_1$  line of  $\text{NO}_3^-$  at 1048  $\text{cm}^{-1}$ , used as an internal standard.) The Raman spectra of the solids differ significantly from those of the solutions, both in frequencies and in relative intensities, indicating the existence of different structural species in the two phases.

**Job Solutions.**—The NaOH-containing solutions showed marked changes in their spectra as the ratio  $R = [\text{OH}^-]/[\text{As(III)}]$  was changed. Some of these spectra are reproduced in Figure 1. It is convenient to divide the spectra into three regions: (1) 250–425  $\text{cm}^{-1}$ ; (2) 425–675  $\text{cm}^{-1}$ ; and (3) 675–900  $\text{cm}^{-1}$ .

The first region between 250 and 425  $\text{cm}^{-1}$  stretches along the Stokes side of the exciting line, such that any Raman bands here are properly described as shoulders to the 4358-Å exciting line. Small, weak, and broad bands are seen in this region for all ratios studied. It is quite apparent that at low  $R$  values (3.6–4.4) the prominent bands are at  $\sim 320$  and 370  $\text{cm}^{-1}$ . At intermediate ratios (4.5–5.7) there are also two bands at  $\sim 335$  and 390  $\text{cm}^{-1}$ , although the latter is very weak. Finally, at ratios above 6.0 only a single band is observed at  $\sim 340$   $\text{cm}^{-1}$ . However, here the As(III) concentration is, of necessity, so low that the weaker of the two bands may be expected to be obscured. The

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(7) R. H. Busey and O. L. Keller, *J. Chem. Phys.*, **41**, 215 (1964).

(8) A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1961, p 376.

(9) V. P. Cheremisinov, *Opt. Spectry.*, **7**, 293 (1959); *Opt. Spektrosk.*, **7**, 454 (1959).

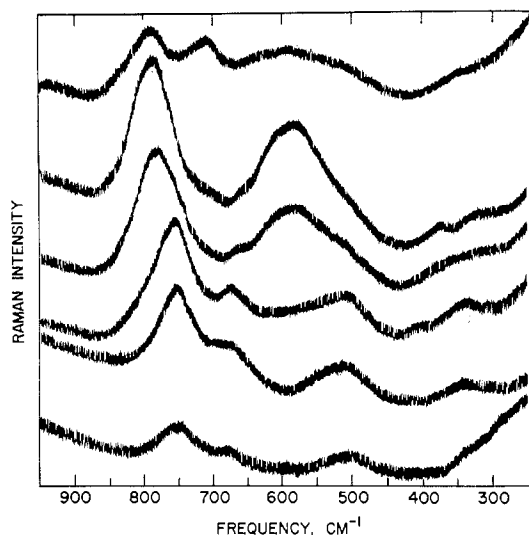


Figure 1.—Raman spectra of aqueous arsenite solutions composed of dissolved  $\text{As}_2\text{O}_3$  and  $\text{NaOH}$ . From top to bottom,  $R = [\text{OH}^-]/[\text{As(III)}] = 3.6, 4.0, 4.4, 5.3, 6.1,$  and  $15$ .

degree of polarization could not be unambiguously determined for any of these weak Raman lines, although they appear depolarized.

The second region shows shifting maxima dependent on  $R$  and is at its narrowest at  $R = 4.0$ , with an apparent band maximum at *ca.*  $600\text{ cm}^{-1}$ . Comparing several spectra, the  $425\text{--}675\text{-cm}^{-1}$  region shows well-defined changes in slope (or asymmetry) and shoulders suggestive of the presence of several contributing Raman lines. Polarization measurements show at least one component to be polarized, although weakly. A spectrum containing  $\text{NaOH}$ , corresponding to a high  $R$  value ( $\sim 10$ ), but no  $\text{As(III)}$  shows a medium-intensity Raman band at  $\sim 475\text{ cm}^{-1}$ . This  $475\text{-cm}^{-1}$  band is generally attributed to the restricted rotation of  $\text{H}_2\text{O}$ —its position and intensity being sensitive to temperature, solute, etc.<sup>10,11</sup> In the  $\text{As(III)}$  spectra, a similar contour is observed with approximately the same intensity, but it appears at  $510\text{ cm}^{-1}$ . It is constant in position (though not intensity) throughout all  $R$  values studied. Furthermore, it is uncertain whether this line is depolarized. The  $425\text{--}675\text{-cm}^{-1}$  region becomes less complicated by overlapping bands as the ratio  $[\text{OH}^-]/[\text{As(III)}]$  increases, containing only two bands at  $R = 15$  ( $670$  and  $510\text{ cm}^{-1}$ ).

The third spectral region is that between  $675$  and  $900\text{ cm}^{-1}$ . Here lie the most intense lines, clearly polarized and quite well defined in position. At lowest  $R$  values, a strong, sharply peaked line at  $710\text{ cm}^{-1}$  is observed; it diminishes sharply in intensity as  $R$  increases and is no longer apparent at  $R = 4.2$ . Paralleling this intensity change is a decrease in intensity at  $\sim 650\text{ cm}^{-1}$ . With further increase in the  $R$  value beyond  $4.0$ , a second very intense and broad line apparently shifts from  $790\text{ cm}^{-1}$  to an observed minimum frequency at  $750\text{ cm}^{-1}$  in the highest  $R$  values studied (*i.e.*,  $[\text{OH}^-]/[\text{As(III)}] = 15$ ). Accompanying this shift, intensities

in the middle region change (decrease) considerably, most notably in the range  $R = 4.2\text{--}5.0$ , where the intensities of bands decrease by a factor of 2 or more.

**$\text{As}_2\text{O}_3$  Solutions.**—The spectra of solutions saturated with  $\text{As}_2\text{O}_3$  clearly show two lines due to  $\text{As(III)}$  species: a strong, sharp, polarized line at  $710\text{ cm}^{-1}$  and a depolarized shoulder at  $655\text{ cm}^{-1}$  (Figure 2). These spectra, however, have some additional features: (1) a very broad, medium-intensity band stretching from  $300$  to  $550\text{ cm}^{-1}$  with an intensity maximum near  $460\text{ cm}^{-1}$  and (2) a weak, broad band centered around  $790\text{ cm}^{-1}$ . The latter is most likely a single line and is depolarized. The former broad and asymmetric band appears to have at least one polarized line as an envelope component.

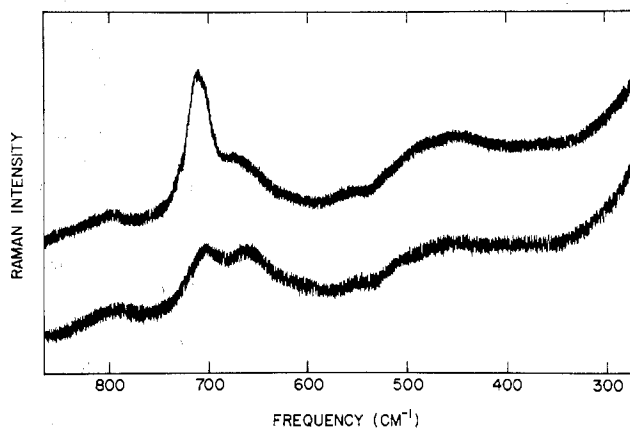


Figure 2.—Raman spectrum of an aqueous solution of  $\text{As}_2\text{O}_3$ ;  $[\text{As(III)}] \approx 0.2\text{ M}$ : upper trace, incident polarization perpendicular to sample tube; lower trace, parallel to sample tube.

A sample of  $\text{H}_2\text{O}$  run in the same tube under identical conditions also shows these features mentioned above, *i.e.*, the depolarized, weak line at  $790\text{ cm}^{-1}$  and the very broad band with some polarized component(s) between  $300$  and  $550\text{ cm}^{-1}$ . The exact nature of these bands is uncertain. They are seen in spectra obtained by  $\text{Hg}$  excitation (Weston<sup>12</sup>) but are much less clear upon laser excitation<sup>13</sup>. Some Raman intensity originates from the use of Pyrex-glass sample tubes which undoubtedly contributes to the observed spectral features. We have not been further concerned with these Raman bands, since they can be subtracted from the  $\text{As(III)}$  spectrum of interest.

The pH of  $\text{As}_2\text{O}_3$  solutions in water is  $\sim 4$ . Acidification with various strong acids to a pH as low as  $\sim 0$  has revealed no significant spectral changes; *i.e.*, the strong  $710\text{-cm}^{-1}$  line and the  $655\text{-cm}^{-1}$  shoulder remain unchanged in position and relative intensities.

We have also observed the proton magnetic resonance spectrum of a Job solution with  $R = 4.0$  as well as that of a saturated solution of  $\text{As}_2\text{O}_3$ . In both, only a single resonance line characteristic of bulk solvent water was observed, indicating rapid exchange between species hydrogens (if any) and solvent protons.

(10) G. E. Walrafen, *J. Chem. Phys.*, **44**, 1546 (1966).

(11) D. A. Draeger and D. Williams, *ibid.*, **48**, 401 (1968).

(12) R. E. Weston, *Spectrochim. Acta*, **18**, 1257 (1962).

(13) G. E. Walrafen, Bell Telephone Laboratories, Inc., private communication, 1967.

**Treatment of Job Data. Normalized Intensities.**—

For all solution spectra, base lines were constructed visually to be smooth and continuous curves without breaks or sharp slope changes. From these base lines, the heights of the noise-averaged spectral envelopes were measured at 25-cm<sup>-1</sup> intervals, as well as the height of the NO<sub>3</sub><sup>-</sup> line, all in arbitrary intensity units. For the multiple runs of a single solution (on the average, five traces per solution), the height at any frequency divided by the height of the NO<sub>3</sub><sup>-</sup> line was averaged to give a net, normalized intensity for each solution computed at 25-cm<sup>-1</sup> intervals. These normalized intensities are tabulated *vs.*  $R$ , the ratio of  $[\text{OH}^-]/[\text{As(III)}]$ , in Tables II and III. The tabulated values clearly reveal three pieces of information: (1) there are some marked intensity decreases between  $R = 3.5$  and 4.0 shown especially by the frequencies around 700 cm<sup>-1</sup> (solutions with  $R < 3.5$  could not be studied owing to the limited solubility at a fixed ion concentration sum); (2) there is a definite maximum at  $R = 4.0$ , quite sensitive to a change in ratio of  $\pm 0.2$  (e.g., the frequencies at 575 and 775 cm<sup>-1</sup>); (3) there appears a constant or even slowly rising intensity at higher  $R$  values in the range 5.0–7.0, decreasing, finally, as the  $[\text{As(III)}]$  diminishes at very high ratios (e.g., 750 and 675 cm<sup>-1</sup>).

TABLE II

NORMALIZED HEIGHTS OF SPECTRA AT 25-CM<sup>-1</sup> INTERVALS FOR SOLUTIONS OF VARYING RATIOS,  $R = [\text{OH}^-]/[\text{As(III)}]$ ;  $[\text{OH}^-] + [\text{As(III)}] = 8.0 M$

Freq. cm <sup>-1</sup>	$R$									
	3.7	3.9	4.1	4.3	5.0	5.5	6.2	7.0	10.0	15.0
875	4	4	6	4	4	3	1	2	0	0
850	12	15	15	13	11	7	5	6	2	3
825	35	41	44	34	23	20	15	13	7	6
800	70	89	108	87	59	43	31	26	17	11
775	66	93	108	91	74	60	54	49	33	22
750	54	60	54	56	70	62	62	60	47	33
725	60	47	33	37	42	38	40	41	33	28
700	68	42	26	24	32	29	28	31	24	20
675	51	35	23	24	30	30	28	30	22	18
650	49	39	29	30	31	27	26	26	19	13
625	55	54	50	41	37	27	25	22	12	9
600	65	73	79	63	46	31	24	21	10	7
575	63	75	75	65	45	30	24	18	11	7
550	55	64	62	51	28	28	25	20	14	8
525	45	47	47	42	29	28	28	23	16	12
500	39	36	36	33	35	27	29	26	19	15
475	29	26	28	25	28	22	25	22	17	13
450	16	16	20	20	20	16	17	16	11	8
425	10	10	14	15	15	10	9	10	5	4
400	6	8	12	10	12	8	5	8	3	2
375	8	11	14	12	13	10	5	7	0	0
350	11	12	17	12	12	9	6	8	0	0
325	9	11	15	10	8	7	5	5	0	0
300	7	10	11	8	0	2	4	2	0	0
275	4	4	4	2	0	0	0	0	0	0

All the foregoing experimental results for the Job solutions were obtained from Raman spectral traces run on a compressed frequency scale of 100 cm<sup>-1</sup>/in. of chart paper. In order to obtain greater accuracy in peak positions and, in addition, to be able to resolve

TABLE III

NORMALIZED HEIGHTS OF SPECTRA AT 25-CM<sup>-1</sup> INTERVALS FOR SOLUTIONS OF VARYING RATIOS,  $R = [\text{OH}^-]/[\text{As(III)}]$ ;  $[\text{OH}^-] + [\text{As(III)}] = 12.0 M$

Freq. cm <sup>-1</sup>	$R$									
	3.5	3.65	3.8	4.0	4.2	4.5	5.0	5.5	6.0	7.0
875	1	5	4	3	4	4	4	1	1	2
850	14	16	14	11	13	6	11	7	6	4
825	42	47	44	40	39	27	28	21	18	12
800	69	88	96	106	102	71	62	47	40	28
775	65	88	103	137	130	104	92	83	75	61
750	61	77	75	91	87	96	94	100	105	98
725	84	79	65	49	46	55	60	64	67	68
700	130	95	64	31	26	33	34	41	40	45
675	92	65	44	20	26	31	38	41	40	43
650	83	63	43	29	33	35	36	38	33	38
625	68	67	53	49	50	43	36	32	23	26
600	63	72	74	83	76	57	43	30	21	22
575	57	70	74	86	78	57	38	30	21	22
550	53	65	67	77	70	55	36	29	30	25
525	58	58	51	51	48	41	34	34	34	33
500	50	47	43	37	35	33	34	35	33	36
475	39	33	26	23	22	25	19	24	23	28
450	24	16	16	11	11	10	6	11	10	15
425	11	7	6	3	4	0	2	4	4	7
400	2	2	0	0	2	0	0	5	3	7
375	7	9	5	6	11	4	2	4	4	4
350	10	12	13	9	13	8	8	7	12	6
325	9	12	12	11	15	10	6	10	14	9
300	6	9	6	9	11	4	0	3	2	2
275	0	5	0	0	7	0	0	0	0	0

the entire spectral envelope into its component bands, the following sets of additional spectra were obtained.

(1) NaAsO<sub>2</sub> was dissolved in both H<sub>2</sub>O and in D<sub>2</sub>O. Spectra of their solutions were taken at an expanded frequency scale of 40 cm<sup>-1</sup>/in. The spectrum of NaAsO<sub>2</sub> in H<sub>2</sub>O is identical with that of the Job solution in which  $R = 4.0$  (i.e., they are superimposable when both the frequency scales of the recorder and the  $[\text{As(III)}]$  match). However, the spectrum of NaAsO<sub>2</sub> in D<sub>2</sub>O shows an apparent frequency shift of the band maximum at  $\sim 600$  cm<sup>-1</sup> down a reproducible 5 cm<sup>-1</sup> to lower frequency. The strong 790-cm<sup>-1</sup> band maximum is unaffected by this solvent change.

(2) As<sub>2</sub>O<sub>3</sub> was dissolved in D<sub>2</sub>O; the strong, polarized line previously seen at 710 cm<sup>-1</sup> in H<sub>2</sub>O is shifted to  $\sim 690$  cm<sup>-1</sup>.

**Investigation of Polymerization.**—Since there is some uncertainty concerning the existence of polymeric or associated species of As(III),<sup>2,4</sup> the following experiments have been carried out to determine whether or not polymerization occurs.

(1) The Job solution,  $R = 4.5$ , sum = 12.0  $M$ , was studied as a function of temperature between 20 and 80° by surrounding the sample tube with circulating, thermostated water. No spectral changes were observed, indicating the absence of temperature-sensitive monomer-polymer equilibria.

(2) There appears to be no detectable spectral difference between the Job solutions studied at 8.0 or 12.0  $M$  sums (except for total intensity which is dependent on the  $[\text{As(III)}]$ ).

(3) The spectrum of the saturated solution of

$\text{As}_4\text{O}_6$  with  $[\text{As(III)}] \simeq 0.2 M$  has its most prominent spectral lines at 710 and  $655 \text{ cm}^{-1}$ . The same line positions and intensity ratios are observed in the Job solutions of lowest  $R$  values in which the  $[\text{As(III)}]$  is as high as  $2.67 M$ .

(4) Finally, a dilution study was made on the  $\text{As}_4\text{O}_6\text{-NaOH-H}_2\text{O}$  system. A solution of  $R = 4$  with  $[\text{As(III)}] = 5.0 M$  was prepared, and its spectrum was recorded. This concentrated solution was then diluted by a factor of 2, and the spectrum was rerecorded; a second and third dilution followed, after which the  $\text{NO}_3^-$  internal standard peak at  $1050 \text{ cm}^{-1}$  became too small to be reliable for intensity measurements. The entire spectrum, at each concentration, was resolved into its component bands and the height of each band was divided by the height of the corresponding  $\text{NO}_3^-$  band. The normalized intensities thus produced were constant (within experimental error limits) for each component Raman band. It appears that over these concentration ranges there is no concentration-dependent polymerization, as judged by the constancy of resolved band frequencies and intensities. It is concluded that the aqueous  $\text{As(III)}$  solutions can be interpreted solely in terms of monomeric chemical species.

### Discussion

**Interpretation of Spectra.**—From Figure 1 and the Job data in Tables II and III, showing the normalized spectral intensity changes with  $R$ , it is inferred that there is a *minimum* of three distinct chemical species, each giving rise to its own Raman spectrum. The observed spectral changes are due to the gradual appearance and/or disappearance of these species.

**$\text{As(OH)}_3$ .**—The frequencies  $650\text{--}700 \text{ cm}^{-1}$  show increasing intensities as  $R$  decreases from approximately 4.0 to 3.5; in particular, the intensity at  $700 \text{ cm}^{-1}$  (from Table III) increases by a factor greater than 4. The spectra of  $\text{As}_4\text{O}_6$  solutions (Figure 2) show these spectral lines at 710 and  $655 \text{ cm}^{-1}$ ; it seems that the same chemical species is giving rise to these spectral lines in the Job solutions of low  $R$  values as well as in the  $\text{As}_4\text{O}_6$  solutions. The assignment of this species as  $\text{As(OH)}_3$  is consistent with the Job data for low  $R$  values in that an approach of the spectral intensity to a maximum at  $R = 3.0$  is indicated, but rests heavily on the following evidence. (1) The coordination number 3 is well established for many  $\text{As(III)}$  species, as in all  $\text{AsX}_3$  where  $\text{X} = \text{H, F, Cl, Br, I, C}_6\text{H}_5$ , etc. (2) The structures  $\text{HAsO}_2$  (three-coordinate) and the phosphorous acid-like  $\text{H}_2(\text{HAsO}_3)$  are both unlikely because no Raman lines assignable to  $\text{As-H}$  vibrations (which should occur at *ca.*  $2000 \text{ cm}^{-1}$ ) have been observed in either Fehér's work<sup>9</sup> or this study. Furthermore, the pmr spectrum consists of a single resonance line, indicating rapid exchange between protons of the  $\text{As(III)}$  species and the solvent  $\text{H}_2\text{O}$ ; it was studied for  $\text{As}_4\text{O}_6$  solutions as well as for more acidic and basic solutions. (3) Evidence against the existence of  $\text{HO-As-O}$  (two-coordinate) is that no Raman lines

such as are found between  $750$  and  $790 \text{ cm}^{-1}$  in basic arsenite solutions have been observed in solutions of the acid which could be assigned to  $\text{As-O}$  (as opposed to  $\text{As-OH}$ ) vibrations. These should occur at higher frequencies than the polarized  $710\text{-cm}^{-1}$  line, attributed to the symmetric stretching mode of  $\text{As(OH)}_3$ . (4) The  $710\text{-cm}^{-1}$  line is shifted to  $\sim 690 \text{ cm}^{-1}$  in  $\text{D}_2\text{O}$  solution, attributed to the symmetric stretch of  $\text{As(OD)}_3$ . From all of the foregoing evidence it seems that the predominant species in neutral and acidic aqueous solutions of  $\text{As}_4\text{O}_6$  is  $\text{As(OH)}_3$ .

Based on the number of *observed* Raman lines, the structure of  $\text{As(OH)}_3$  could be interpreted in terms of planar ( $\text{D}_{3h}$ ) or pyramidal ( $\text{C}_{3v}$ ) symmetry. The planar  $\text{AsX}_3$  should give rise to three Raman-allowed vibrations whereas a four-atom  $\text{C}_{3v}$  structure is expected to give rise to four normal modes all of which are Raman active. (In this discussion of  $\text{As(OH)}_3$ , the  $-\text{OH}$  group is treated as a single moiety with regard to skeletal vibrations. The vibrations within the  $-\text{OH}$  group itself are at higher frequencies and are masked by  $\text{H}_2\text{O}$  vibrational modes. Other authors have demonstrated the validity of this simplification, *e.g.*, Lippincott, *et al.*,<sup>14</sup> for aluminate and zincate ions, Fordyce and Baum<sup>15</sup> for  $\text{Zn(OH)}_4^{2-}$ , and Carreira, *et al.*,<sup>16</sup> for aluminate.) From a consideration of the relative line positions in the Raman spectrum the pyramidal structure ( $\text{C}_{3v}$ ) is to be preferred over the planar structure. In general, in  $\text{XY}_3$  molecules having  $\text{C}_{3v}$  symmetry, the symmetric stretching mode is at higher frequency than the asymmetric stretching mode, although the reverse is sometimes observed. For structures having  $\text{D}_{3h}$  symmetry, however, the asymmetric stretching mode is at higher frequency. This  $\text{D}_{3h}$  pattern is preserved for light as well as heavy central atoms as, for example, in the boron trihalides<sup>17</sup> or the antimony pentahalides.<sup>18</sup> In the case of  $\text{As(OH)}_3$ , only two lines are clearly observed ( $710$  and  $655 \text{ cm}^{-1}$ ) in which the higher frequency line is polarized and assigned as the symmetric stretching motion. The two lower frequency modes may be of low intensity and obscured by a solvent band, as previously mentioned. Thus, the assignment of the  $\text{As(OH)}_3$  species as pyramidal ( $\text{C}_{3v}$ ) is consistent with the Raman spectrum and the relative positions of the two stretching vibrations. Furthermore, many  $\text{AsX}_3$  structures have been shown to be pyramidal as, for example, all of the arsenic trihalides. None of the experiments excludes the possibility of the polymerization of  $\text{As(OH)}_3$ . Because of limited solubility of  $\text{As}_4\text{O}_6$  in  $\text{H}_2\text{O}$ , concentrations could not be varied sufficiently to show spectral changes on dilution.

**$\text{AsO(OH)}_2^-$ .**—Addition of base to the weak acid, arsenious acid, may be written as  $\text{As(OH)}_3 + \text{OH}^- \rightarrow \text{AsO(OH)}_2^- + \text{H}_2\text{O}$ . In such a formulation, the

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(15) J. S. Fordyce and R. L. Baum, *ibid.*, **43**, 843 (1965).

(16) L. A. Carreira, V. A. Maroni, J. W. Swaine, Jr., and R. C. Plumb, *ibid.*, **45**, 2216 (1966).

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arsenic three-coordination remains intact while a species with a formal ratio  $[\text{OH}^-]/[\text{As(III)}] = 4.0$  is produced. The addition of hydroxide rather than the abstraction of an acidic proton would necessarily give rise to a four-coordinate  $\text{As}(\text{OH})_4^-$ . Its symmetry would probably be a *distorted* tetrahedron, owing to the accommodation of the lone-pair electrons in its structural framework, whereas that of  $\text{AsO}(\text{OH})_2^-$ , with only a mirror plane, would belong to the  $C_s$  point group. Hence, the vibrational representation,  $\Gamma_{\text{vib}} = 4A' + 2A''$ , for the  $C_s$  point group predicts six active Raman lines, of which four are totally symmetric vibrations and, thus, polarized. Furthermore, the molecule ion now possesses two kinds of As-O vibrations: (1) the As-O stretch and (2) the As-OH stretches; there must be both a symmetric and an asymmetric  $-\text{As}(\text{OH})_2$  stretching mode with respect to the symmetry plane. The first is expected at a higher frequency (*i.e.*, As-O is considered a "tighter" bond and has a larger bond stretching force constant than As-OH). All bending modes would, of course, be expected at lower frequencies. The Job and Raman data presented here appear consistent with a species having the  $C_s$  symmetry for  $\text{AsO}(\text{OH})_2^-$ . The strong, polarized line at  $790\text{ cm}^{-1}$ , considerably higher in frequency than the highest frequency observed for  $\text{As}(\text{OH})_3$ , is assigned to As-O. The band observed in Job solutions with  $R \sim 4$  with its maximum at  $\sim 600\text{ cm}^{-1}$  shows sufficient detail such that it may be resolved into its components of three lines: one due to the solvent at  $510\text{ cm}^{-1}$  (as previously mentioned) and two other lines of about equal intensity at  $610$  and  $570\text{ cm}^{-1}$ . The polarization data for this band suggest that both the  $510$ - and  $570\text{ cm}^{-1}$  lines are slightly polarized and that the  $610\text{ cm}^{-1}$  line is depolarized. Both the  $600$ - and  $575\text{ cm}^{-1}$  frequencies parallel the intensity changes of the  $790\text{ cm}^{-1}$  line, maximizing at  $R = 4$ . It is thus quite reasonable to assume that the  $610\text{ cm}^{-1}$  line is due to the asymmetric  $-\text{As}(\text{OH})_2$  motion, and the  $570\text{ cm}^{-1}$  line is due principally to its symmetric vibration. The weak lines observed around  $320$  and  $370\text{ cm}^{-1}$  represent two of the three possible bending modes. For the  $C_s$  model, two of these should be polarized bending modes, since they are symmetric with respect to the symmetry plane. It was mentioned earlier that no statement may be made quantitatively about their degree of polarization. Even in a well-characterized system such as  $\text{AsCl}_3$ , the symmetric bending mode at  $195\text{ cm}^{-1}$  is only slightly polarized and also the weakest line in the spectrum.<sup>19,20</sup> Additional support for the  $\text{AsO}(\text{OH})_2^-$  structure comes from the experiments in  $\text{D}_2\text{O}$ . The As-O vibration, which we have assigned to the  $790\text{ cm}^{-1}$  line, should not exhibit an isotope effect, whereas the As-OH stretching region  $\sim 600\text{ cm}^{-1}$  should be lowered in frequency. Comparing the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions of  $\text{NaAsO}_2$ , we find exactly this expected phenomenon. If the  $790\text{ cm}^{-1}$  line had involved stretching of As-OH, it would have shown the pre-

TABLE IV  
FREQUENCY ASSIGNMENTS OF THE HYDROLYZED As(III) SPECIES

Freq, $\text{cm}^{-1}$	Mode	Assignment
	$\text{As}(\text{OH})_3$ , $C_{3v}$ , $2A_1 + 2E$	
710 p	$\nu_1 (A_1)$	Sym str
655 dp	$\nu_3 (E)$	Asym str
	$\nu_2, \nu_4$	Not obsd
	$\text{AsO}(\text{OH})_2^-$ , $C_s$ , $4A' + 2A''$	
790 p	$\nu_1 (A')$	As-O str
610 dp	$\nu_3 (A'')$	$\text{As}(\text{OH})_2$ asym str
570 p	$\nu_2 (A')$	$\text{As}(\text{OH})_2$ sym str
370 } 320 }	$\nu_3, \nu_4, \nu_6$	Bending modes
	$\text{AsO}_2(\text{OH})^{2-}$ , $C_s$ , $4A' + 2A''$	
$\sim 810$ dp?		$\text{AsO}_2$ asym str
$\sim 770$ p?		$\text{AsO}_2$ sym str
670-520?		AsOH str; bending modes
	$\text{AsO}_3^{3-}$ , $C_{3v}$ , $2A_1 + 2E$	
752 p	$\nu_1 (A_1)$	Sym str
680 dp	$\nu_3 (E)$	Asym str
340	$\nu_2, \nu_4$	Bending modes

dicted shift of  $\sim 20\text{ cm}^{-1}$ . It seems clear that the  $790\text{ cm}^{-1}$  line is not due to an As-OH stretch (but, rather, an As-O), while the  $600\text{ cm}^{-1}$  region does involve As-OH stretching. The species  $\text{AsO}(\text{OH})_2^-$  is thus similar in structure and in spectrum to the isoelectronic  $\text{SeO}(\text{OH})_2^{2-}$ .<sup>21</sup>

**$\text{AsO}_3^{3-}$ .**—As the ratio  $R$  is increased, additional spectral changes take place but they appear to coalesce and become unobservable at  $R \approx 10$ , except for over-all intensity changes due to dilution. In solutions with high ratios ( $R = 15$ ) a four-line Raman spectrum is observed ( $\text{cm}^{-1}$ ):  $752$  s, polarized;  $680$  m, depolarized;  $510$  m, slightly polarized;  $340$  vw. Since the  $510\text{ cm}^{-1}$  line is attributed to the solvent, only three Raman lines are assignable to arsenic species. This observed decrease in the number of active fundamentals is, however, well in accord with an increasing symmetry of the species present. Thus, a  $C_{3v}$  point group molecule ion such as  $\text{AsO}_3^{3-}$  should show only four lines:  $2A_1 + 2E$ . It is expected that the symmetric As-O stretching mode lies at a higher frequency than the asymmetric mode, as in other pyramidal  $\text{AsX}_3$  types ( $\text{AsCl}_3$ ,  $\text{As}(\text{OH})_3$ ). The bending modes are known to be weaker, as in  $\text{AsCl}_3$ , and may well be of such low intensity to allow only one to be seen.

**$\text{AsO}_2(\text{OH})^{2-}$ .**—The stepwise dissociation of  $\text{As}(\text{OH})_3$  demands the presence of  $\text{AsO}_2(\text{OH})^{2-}$ , although possibly at lower concentration, between the assigned species  $\text{AsO}(\text{OH})_2^-$  and  $\text{AsO}_3^{3-}$ . Raman evidence for the formation of this intermediate species rests on an attempted synthesis of observed spectra in the region of  $R \approx 6.0$  by using the known spectra for  $\text{AsO}(\text{OH})_2^-$  and  $\text{AsO}_3^{3-}$ . A considerable spectral region between  $520$  and  $670\text{ cm}^{-1}$  cannot be accounted for by these two species alone. Furthermore, the highest frequency band cannot be synthesized as a combination of the  $790$ - and  $752\text{ cm}^{-1}$  lines of  $\text{AsO}(\text{OH})_2^-$  and  $\text{AsO}_3^{3-}$ , respec-

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tively, in that there is observed too much spectral intensity near  $810\text{ cm}^{-1}$ . It is noteworthy that in both  $\text{As}(\text{OH})_3$  and  $\text{AsO}_3^{3-}$  the asymmetric stretching modes come at lower frequency than the symmetric modes; in  $\text{AsO}(\text{OH})_2^-$  the asymmetric stretching mode ( $610\text{ cm}^{-1}$ ) is at higher frequency than the symmetric  $-\text{As}(\text{OH})_2$  stretch ( $570\text{ cm}^{-1}$ ) as with  $\text{C}_{2v}$  structures in general. It is, thus, reasonable to expect that the asymmetric  $-\text{AsO}_2$  mode of the  $\text{AsO}_2(\text{OH})^{2-}$  comes at a higher frequency than its symmetric  $-\text{AsO}_2$  stretching mode. Carrying this reasoning one step further, we

might expect the symmetric  $-\text{AsO}_2$  motion to be approximately midway between the observed frequencies of  $\text{AsO}(\text{OH})_2^-$  and  $\text{AsO}_3^{3-}$  ( $790$  and  $752\text{ cm}^{-1}$ , respectively) or at  $\sim 770\text{ cm}^{-1}$ ; the asymmetric mode may well fall  $\sim 40\text{ cm}^{-1}$  higher or near  $810\text{ cm}^{-1}$ . Indeed, the observed spectra in this region show greater intensity than is expected if only  $\text{AsO}(\text{OH})_2^-$  and  $\text{AsO}_3^{3-}$  are present. Thus, the expected species  $\text{AsO}_2(\text{OH})^{2-}$  apparently does have a Raman spectrum at anticipated frequencies. Table IV summarizes the frequency assignments.

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## Reactions of Dimethylgallium(III) Hydroxide. Raman, Infrared, and Proton Magnetic Resonance Spectra of the Dimethylgallium(III) Aquo Ion and Several of Its Compounds<sup>1</sup>

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Dimethylgallium(III) hydroxide reacts readily with both acids and bases without rupture of the gallium-carbon bonds. The Raman, infrared, and pmr spectra of aqueous solutions of dimethylgallium(III) nitrate and perchlorate and of sodium dihydroxodimethylgallate(III) have been measured, and they are consistent only with an angular structure for the dimethylgallium(III) moiety. The skeletal vibrational frequencies of the aquo ion are very similar to those of dimethylgallium(III) hydroxide and acetylacetonate suggesting that the labile aquo complex is  $(\text{CH}_3)_2\text{Ga}(\text{OH}_2)_2^+$  analogous to the known and isoelectronic  $(\text{CH}_3)_2\text{Ga}(\text{NH}_3)_2^+$ . Thus in aqueous solution  $(\text{CH}_3)_2\text{Ga}^{\text{III}}$  adopts a structure analogous to that of the isoelectronic  $(\text{CH}_3)_2\text{Ge}^{\text{IV}}$  rather than the isoelectronic  $(\text{CH}_3)_2\text{Zn}$ . Pmr and Raman spectra indicate that only one molecular species of dimethylgallium(III) hydroxide exists in solutions with organic solvents. The similarity of the Raman and infrared spectra of the solid hydroxide which contains  $[(\text{CH}_3)_2\text{GaOH}]_4$  molecules and the corresponding solution spectra suggests that the tetramer persists in solution. The pmr data show that the dimethylgallium hydroxide polymer is very flexible in contrast to  $[(\text{CH}_3)_2\text{AuOH}]_4$  which has a somewhat similar structure and which behaves in solution as a stereochemically rigid molecule. The vibrational frequencies and intensity data indicate an increase in the C-Ga-C bond angle in the sequence  $(\text{CH}_3)_2\text{Ga}(\text{OH})_2^-$ ,  $[(\text{CH}_3)_2\text{GaOH}]_4$ , and  $(\text{CH}_3)_2\text{Ga}(\text{OH}_2)_2^+$ .

### Introduction

By comparing a series of analogous organometallic moieties under comparable conditions as, for example, the aquo complexes in moderately dilute solutions, it is possible to study trends in the nature of the metal-carbon bonds. The use of solutions eliminates problems with low site symmetry often encountered with crystals. Metal ions with two  $\text{CH}_3$  groups in the first coordination sphere are particularly simple systems for study. With a ligand like water, which has a rather electronegative donor atom, the heavy-metal dimethyls  $(\text{CH}_3)_2\text{Tl}^+$ ,  $(\text{CH}_3)_2\text{Pb}^{2+}$ , and  $(\text{CH}_3)_2\text{Sn}^{2+}$  have a linear structure similar to the isoelectronic molecules  $(\text{CH}_3)_2\text{Hg}$  and  $(\text{CH}_3)_2\text{Cd}$ .<sup>4</sup> The dimethyltin(IV) moiety also exhibits an angular structure in many compounds with less electronegative ligands, and the angular  $\rightarrow$  linear transition appears to be accompanied

by a rather large increase in the s character of the metal orbitals used in bonding the carbon atoms.

Trends among the lighter metal alkyls have been much less thoroughly investigated. The dimethylgermanium(IV) entity which is isoelectronic with the linear molecule  $(\text{CH}_3)_2\text{Zn}$  has a bent structure in aqueous solutions; however, it is completely hydrolyzed to the uncharged dihydroxide.<sup>5</sup>

The first aim of this investigation was to determine whether the dimethylgallium(III) moiety can exist in solution as an aquo cation and, if so, to ascertain the structure of the solute, that is, whether it is linear as the isoelectronic dimethylzinc(II) or angular as the isoelectronic dimethylgermanium(IV) moiety. Raman spectroscopy is a particularly suitable technique for this purpose. In the presence of ammonia, dimethylgallium(III) chloride forms  $(\text{CH}_3)_2\text{GaCl}\cdot 2\text{NH}_3$  which has been shown to have an ionic lattice and to contain the cation  $(\text{CH}_3)_2\text{Ga}(\text{NH}_3)_2^+$ .<sup>6</sup>

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