

RAMAN SPECTRA OF SUBSTITUTED ARSENIC ACIDS

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ABSTRACT. The effect of progressive substitution of oxygen atoms in the arsenate ion $[\text{AsO}_4]^{3-}$ by methyl groups has been studied. The spectrum of methyl arsenate ion $[(\text{CH}_3)_1\text{AsO}_3]^{2-}$ reveals that a tetrahedral skeleton is maintained, the symmetry being C_{3v} . The spectra of normal and secondary arsenates have been re-examined. The spectra of the secondary arsenate ion $[(\text{OH})\text{AsO}_3]^{2-}$ and of the methyl arsenate ion $[(\text{CH}_3)_1\text{AsO}_3]^{2-}$ show similar structural symmetry. Approximate force constants have been calculated according to the central force system. Bond strengths of As—C and As—O appear to be alike in the substituted arsenates.

INTRODUCTION

The present work was undertaken some time ago to study the effect of suitable and progressive substitution of the oxygen atoms in the arsenate ion $[\text{AsO}_4]^{3-}$ by units of masses virtually equal to that of oxygen itself (Guha, 1941), but had to be abandoned for the present before completion owing to unfavourable circumstances. It was, however, realized that some new and interesting data, together with a solution of apparently conflicting reports on arsenates in some older publications have been obtained, which are therefore reported in the present communication notwithstanding their evidently limited scope.

Striking differences are observed in the results reported by several workers on the Raman spectrum of the simple arsenate ion $[\text{AsO}_4]^{3-}$, as can be seen from the following comparison:—

Authors	Raman frequencies of sodium arsenate (solution)
Nisi (1929)—	837
Ghosh and Das (1932)—	349, 462
Fehér-Morgenstern (1937)—	342(<i>w</i>), 398(<i>m</i>), 810(<i>s</i>)
Mitra (1939)—	348(<i>w</i>), 460(<i>w</i>), 837(<i>s</i>), 876(<i>vw</i>)

It was thus thought desirable at the outset to re-examine the spectra of normal arsenate and secondary arsenate (also known commercially as arsenate) with some care. The results, it will be seen, have generally confirmed the work of Fehér and Morgenstern. Substitution of oxygen by methyl group (CH_3) was then introduced, giving methyl arsinic and cacodylic acids respectively, whose relative acid strengths are comparable to that of

arsenic acid itself. The main subject of study was the nature of changes in the skeletal vibrations and their significance, taking the CH_3 group as an approximate mass point nearly equal in weight to that of an oxygen atom. These skeletal vibrations, in view of the large mass of the central atom, are all to be expected below 1000 cm^{-1} , the larger ones being either valence or bending vibrations of hydrogen atoms against heavier nuclei.

EXPERIMENTAL

The solutions of the different substituted arsenic acids and their respective salts were prepared as detailed below. Mercury 4358\AA was utilized as the exciting line and the spectra were recorded on Ilford Golden Isozenith plates with an exposure of about 40 hours in each case.

Methyl arsenic acid, $(\text{CH}_3)\text{AsO}(\text{OH})_2$ —This was prepared by heating a mixture of methyl iodide and an alkaline solution of sodium arsenite according to the method of Quick and Adams (1922). The product so obtained was carefully purified by dissolving in a small bulk of water and reprecipitating by alcohol. A 25% solution in conductivity water was prepared and repeatedly filtered through quantitative filter paper until the solution was optically clear.

A 30% solution of sodium methyl arsenate was obtained by dissolving the acid in two equivalents of sodium hydroxide solution and then repeatedly filtering through a quantitative filter paper.

Dimethyl arsenic acid (cacodylic acid), $(\text{CH}_3)_2\text{AsO}(\text{OH})$ —A 50% solution was prepared by dissolving Merck's pure sample of the acid in conductivity water and then filtering as before.

A 50% solution of potassium dimethyl arsenate was obtained by dissolving the acid in one equivalent of potassium hydroxide.

Secondary and normal arsenates, K_2HAsO_4 and K_3AsO_4 —A saturated solution of secondary potassium arsenate was obtained by dissolving Merck's pure sample in conductivity water. The normal arsenate solution was prepared by carefully neutralizing the solution of the secondary arsenate with the calculated amount of potassium hydroxide.

An experiment was then arranged to qualitatively determine the polarization of the lines. Sodium methyl arsenate and dimethyl arsenic acid solutions were examined. The mercury arc and the condenser were placed at a distance of about 2 ft. from the Wood's tube to reduce error due to obliquity of the incident beam. The plane window of the Wood's tube was coated with black paint leaving a rectangular aperture measuring $5\text{ mm} \times 2\text{ mm}$ in the middle. The image of this window was then focussed on the slit of the spectrograph and a Wollaston double-image prism was interposed to vertically separate the image. The polarization photographs were taken with an exposure of about 40 hours on Ilford Golden Isozenith plates.

The results are shown in the Table I.

TABLE I

Methyl arsenic acid (25% soln.)	Dimethyl arsenic acid (50% soln.)	Sodium methyl arsenate (30% soln.)	Potassium dimethyl arsenate (50% soln.)	K_2HAsO_4 (sat soln.)	K_3AsO_4 (soln.)
167 (1/2)	218 (3)D		220 (4)		
235 (1)	256 (2)	250 (1)D	273 (1)	315 (3) 380 (3)	328 (1) 400 (1)
353 (1/2b)	332 (2b)D	367 (2)D	353 (2b)		
643 (5)	619 (10)P 663 (5) D	613 (5)D	615 (10) 656 (5)	697 (1)	820 (8b)
803 (3b)	754 (2)p 888 (2)p 1290 (1)	810 (5b)p	833 (2) 892 (2) 1288 (2)	830 (10)	
1442 (1b)	1421 (3)D	1460 (10b)	1417 (3)		
2950 (1)	2950 (4)P	2925 (2)P	2950 (4)		
3030 (1/2)	3030 (2)D	3015 (1)	3022 (1)		

P—polarized, *p*—partially polarized, D—depolarized. (Figures within brackets indicate the relative intensities of the Raman lines).

DISCUSSION

It will be seen from the Table that the results obtained for both secondary and tertiary arsenates confirm generally those reported by Fehér and Moigens-tern. Apparently a confusion might have been made between sodium arsenate of commerce, which is in fact the secondary salt Na_2HAsO_4 giving rise in solution to $[(HO)AsO_3]^-$ ions, and the tertiary salt Na_3AsO_4 , which, being deliquescent and highly soluble in water, cannot be easily crystallized and is best prepared in solution by direct neutralization.

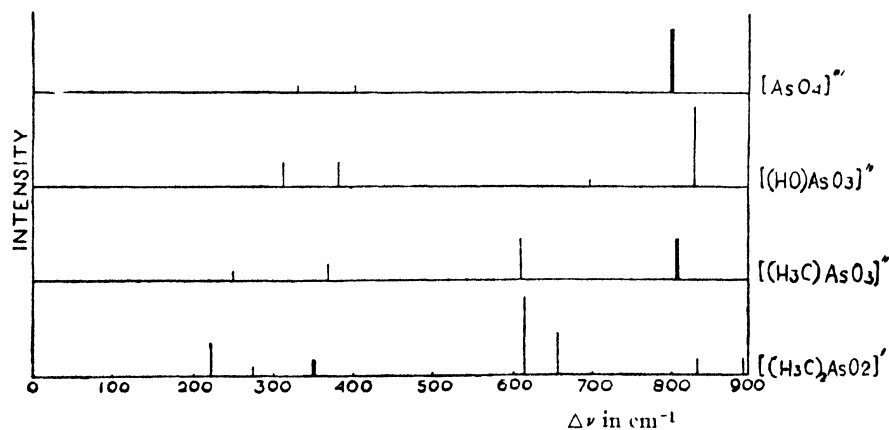


FIG. 1

Graphical representation of Raman frequencies below 1000 cm^{-1}

The presence of only *three* lines instead of *four* in the spectrum of the tetrahedral $[\text{AsO}_4]^{3-}$ ion is believed by the present authors to arise from accidental degeneracy of the ν_1 and ν_3 frequencies. The degeneracy is theoretically derivable for a tetrahedral molecule XY_4 in the case where $m_X \gg m_Y$ (Hibben, 1939).

It will be evident from a comparative study of the skeletal vibrations in the Fig. 1 that a replacement of one of the oxygen atoms by an (OH) group forming the secondary arsenate ion $[(\text{HO})\text{AsO}_3]^{2-}$ disturbs the symmetry with consequent change in the spectrum. The presence of only *four* frequencies with a similar, if not the same, distribution of relative intensities indicates that the tetrahedral structure of the 'skeleton' remains intact and the symmetry is C_{3v} . In the methyl arsenate anion $[(\text{H}_3\text{C})\text{AsO}_3]^{2-}$, the involved reduction of symmetry is similar, though opposite in the sense that the group (CH_3) , unlike (OH), is lighter than oxygen which it replaces. Its spectrum, instead of being that of a symmetrical top having *six* frequencies, shows only four Raman lines of which all but one are depolarized, leading to the conclusion that the tetrahedral skeleton is still maintained, the symmetry again C_{3v} , and that the relative bond strengths of As—C and As—O bonds are essentially the same.

For the purpose of comparison, an approximate calculation of the valency and deformation forces of the anions $[\text{AsO}_4]^{3-}$, $[(\text{HO})\text{AsO}_3]^{2-}$ and $[(\text{H}_3\text{C})\text{AsO}_3]^{2-}$ has been made using the central force system as applied to tetrahedral molecules of the type XY_4 . It has been assumed that for normal arsenate, $\nu_1 = \nu_3 = 800$, $\nu_2 = 328$, $\nu_4 = 400$; for secondary arsenate, $\nu_1 = 830$, $\nu_3 = 607$, $\nu_2 = 315$, $\nu_4 = 380$. The results are given below, along with those for sulphate and similarly substituted anions derived from sulphate for comparison (Gupta and Majumdar, 1941).

Ion	$f \times 10^5$	$f' \times 10^5$	Ion	$f \times 10^5$	$f' \times 10^5$
$[\text{AsO}_4]^{3-}$	3.5	0.6	$[\text{SO}_4]^{2-}$	4.6	1.1
$[(\text{HO})\text{AsO}_3]^{2-}$	3.0	0.9	$[(\text{HO})\text{SO}_3]^-$	4.5	1.5
$[(\text{H}_3\text{C})\text{AsO}_3]^{2-}$	3.7	0.8	$[(\text{H}_2\text{N})\text{SO}_3]^-$	4.9	1.3

The effect of introduction of the second methyl group is much more pronounced, as is shown in the spectrum of the cacodylate ion $[(\text{CH}_3)_2\text{AsO}_2]^-$. A tetrahedral molecule of the type AX_2Y_2 (symm: C_{2v}) has nine frequencies, all supposed to be Raman-active, of which three are polarized. As usual, all the nine frequencies could not be recorded. But the spectrum of the cacodylate ion shows that out of the seven lines recorded, three are polarized, the rest completely depolarized as required by the theory.

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