

THE RAMAN SPECTRA OF ORTHO-PHOSPHORIC ACID AND SOME PHOSPHATES.

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1. Introduction.

IN a recent communication to these *Proceedings*,¹ the author studied the progress of electrolytic dissociation and the effect of polymerisation on the Raman spectrum of iodic acid. This investigation has been extended to other inorganic acids and the present paper deals with the results obtained with ortho-phosphoric acid (H_3PO_4). The Raman spectrum of this acid has been investigated by Nisi² who obtained frequency differences* of 356, 498 and 911 for 84%, 512 and 906 for 50% and 505 and 895 for 25% solutions. These results have been confirmed quite recently by Jeppesen and Bell.³ But in spite of the attempts of several workers to obtain the Raman spectra of the three series of salts of this acid corresponding to the stepwise substitution of the three hydroxyl hydrogen ions, it is surprising that only two of them have so far yielded positive results. Nisi obtained four lines at 358, 518, 889 and 1061 for a 38% solution of dihydrogen-sodium phosphate and Schæfer and his co-workers⁴ observed one line at 924 for the crystals of the tertiary phosphate of ammonium. Thus the Raman spectra studies of this acid and its salts are obviously incomplete.

2. Experimental Arrangements.

One of the chief difficulties experienced by the earlier investigators in obtaining the Raman spectra of phosphoric acid⁵ and the phosphates is the strong continuous spectrum which appears on every plate and masks all faint lines. As mentioned in the previous communications, the pyrex mercury arc designed and used by the author gives much less background than the quartz burners usually employed and have been helpful for giving

¹ Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, 2, 119.

² Nisi, H., *Jap. Jour. Phys.*, 1929, 5, 119.

* The numbers in this and the following pages denote frequency shifts in cm^{-1} .

³ Jeppesen, M. A., and Bell, R. M., *Jour. Chem. Phys.*, 1935, 3, 363.

⁴ Schæfer, Matossi and A derhold, *Zeit. f. Phys.*, 1930, 65, 289.

⁵ Hibben, J. H., *Jour. Amer. Chem. Soc.*, 1931, 53, 2418.

the very long exposures that are necessary in the present work. The constructional details of the arc are given in Fig. 1. Three electrodes A, B and C

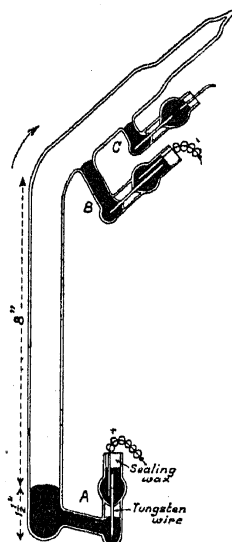


FIG. 1.

are joined to a thick walled pyrex tube of $\frac{3}{4}$ " diameter and 12" long which is bent to the form illustrated. After the introduction of freshly distilled mercury, the tube is evacuated thoroughly for about six hours while the arc is kept running hot and finally sealed off at a vacuum higher than 10^{-5} mm. The electrodes A and C are connected to an induction coil for starting the arc and A and B are connected to 220 volt mains through a rheostat in the usual manner. The arc is run in the vertical position and the mercury distilling from it fills the cathode at the top and overflows, thus keeping a constant level for the cathode. The electrode C may also be dispensed with and the arc started by tilting it in the direction of the arrow. These lamps are found to be very efficient for recording faint lines in crystals and solutions, where the intensity of the unmodified light is enormously great and are quite reliable for continuous use. A slow stream of air directed to the top alone helps to diminish the continuous spectrum further. The general experimental method is the same as for the previous investigations of the author.

3. Results.

The purest sample of ortho-phosphoric acid supplied by E. de Hæn was used as such and its Raman spectrum was obtained for a wide range of concentrations varying from 85% (by weight) to 3%. The product of the time of exposure and the concentration was kept constant throughout. The results are given in Table I. The intense line which appears at all concentrations gradually shifts from 914 to 876 in passing from 85% to 3% solution.

TABLE I.
Ortho-phosphoric Acid H_3PO_4 .

Concentration (% by weight)	Raman lines in cm^{-1}							Remarks
85%					914 st	495 v.w,d	361 v.w,d	Strong continuous spectrum
60%					903 st	495 w,d	361 v.w,d	"
30%	..	1200	—	950	890 v.st	495 m,d	361 w,d	Water bands appear
			(band)					
15%	1427 v.w	1194 w,d	1082 w	959 w	886 v.st	495 w,d	361 w,d	Water bands strong
7.5%	1427 v.w	1194 w,d	1082 w	959 w	886 st	495 w,d	361 v.w,d	
3%	1082 v.w	959 v.w	880 st	"

st=strong; *v.st*=very strong; *m*=medium; *w*=weak; *v.w*=very weak; *d*=diffuse.

It is also qualitatively observed that the intensity of this line increases as the concentration falls off to about 10%. Two other weak and diffuse lines at 495 and 361 appear unshifted at all concentrations. A broad but weak band with a frequency shift of about 950–1200 makes its appearance at about 30% and breaks up into three weak and diffuse lines of frequency differences of 1194, 1082 and 959. Due to the extreme feebleness of these lines their intensity variations on dilution could not be determined. A spectrum of the acid taken with *p*-nitro-toluene as filter to cut off the 4047 radiations, shows a faint line at 1427. The water bands at 3220, 3435 and 3596 brighten up as the dilution increases and the intensities of the bands at 3220 and 3435 are also greater than for the pure water. The increase in the intensity of 3220 is evidently due to the superposition of the weak line at 1427 on this band and the intensity of 3435 is probably enhanced by the vibrations of the OH groups in the acid itself.

Phosphates.—The crystals of the secondary and tertiary phosphates of sodium, potassium and ammonium were prepared from the corresponding primary salts by the addition of the calculated amount of alkali and purified by repeated crystallisations. The results are given in Table II. The crystals yielded only very weak lines even on prolonged exposure and except in the case of tertiary phosphates, their Raman lines are not included in the Table. The exposure time for the aqueous solutions varied from 24 hours to 48 hours.

TABLE II.
Phosphates.

Substance	Raman lines in cm^{-1}					Crystal
Na_3PO_4 17%	1085 v.w	971 m	..			956 w
K_3PO_4 20%	..	984 m	944 m,d			966 w 944 w
$(\text{NH}_4)_3\text{PO}_4$ 31%	1080 v.w	985 m	..	515 v.w	363 v.w	951 w
Na_2HPO_4 17%	1085 w	971 m	886 v.w	
K_2HPO_4 17%	1070 w	965 st	889 w	
$(\text{NH}_4)_2\text{HPO}_4$ 30%	1070 w	975 st	889 w	515 v.w	363 v.w	
$\text{NaNH}_4\text{HPO}_4$ 20%	1085 w	975 m	889 v.w	515 v.w	..	
NaH_2PO_4 27%	1085 m	..	886 st	495 w	356 w	
KH_2PO_4 20%	1080 m	..	869 st	510 w	360 w	
$\text{NH}_4\text{H}_2\text{PO}_4$ 30%	1090 m	..	885 st	515 w	360 w	

4. Discussion of Results.

From the results obtained for the three series of salts of phosphoric acid it is to be inferred that while the three lines at 1085, 495 and 356 appear more or less in the same position in all cases, the intense line shifts from about 885 in the primary salt to about 985 in the secondary and tertiary salts. In the secondary salts the line at 886 is also feebly present. The intensity of the line at 1085 varies from a medium strength in the dihydrogen phosphates to weak in the secondary salts and is very weak in the tertiary salts. These results show that 1085, 980 (*st*), 515 and 363 are the characteristic frequencies of the PO_4 radical 1080, 975(*st*), 889 (*w*), 515 and 363 of the HPO_4 " ion and 1085, 885 (*st*), 515 and 360 of the H_2PO_4 " ion. In the Raman spectrum of the acid, the strongest line which is present even in the lowest concentration, namely 3%, is the one at about 889, which indicates, as shown by Nisi,⁶ that H_2PO_4 " ions predominate at all dilutions. This line is, however, strongly influenced by the concentration of the acid as is shown by a shift of about 34 wave-numbers while passing from 85% to 3%. The appearance of the band between 950–1200 at a concentration of 30% and its further splitting up into three lines in lower concentrations, two of which, namely, 959 and 1082, correspond to those of HPO_4 " ion, suggests that the further ionisation

⁶ Nisi, H., *loc. cit.*

of $\text{H}_2\text{PO}_4' \rightarrow \text{H}' + \text{HPO}_4''$ begins at this stage. This band may be present also at higher concentrations and is probably masked by the continuous spectrum. The percentage of ionisation from $\text{H}_2\text{PO}_4' \rightarrow \text{HPO}_4''$ remains, however, low even in very dilute solutions as is shown by the weakness of the line at 975. These facts are also in agreement with other physico-chemical measurements.⁷ The weak line at 1427 and the increased intensity of the water band at 3435 are, as indicated earlier, due to the OH in the structure of the incompletely ionised acid.

5. *The Structure of Phosphates.*

In Table III, the Raman frequencies ascribed to the PO_4 radical are compared with those of sulphates and selenates.⁸ The force constants calculated on the basis of Dennison's dynamical theory are also given. It can be seen from these results, that a close correspondence exists between the frequencies and the force constants of these three radicals indicative of a

TABLE III.

Ion	Raman lines in cm^{-1}				$f \times 10^{-5}$	$f' \times 10^{-5}$	$P \times 10^{-5}$
	ν_1	ν_2	ν_3	ν_4			
PO_4'''	985	361	1085	515	5.23	0.967	0.185
SO_4''	983	342	1115	623	4.57	1.14	0.74
SeO_4''	835	447	875	415	4.22	0.59	0.51

tetrahedral structure for the PO_4''' ion as in the case for the SO_4'' . The infra-red measurements⁹ of lithium phosphate give reflection maxima at about 9.25μ and $16\mu - 19.1\mu$ which correspond fairly closely to the active frequencies 1085 and 515 in the Raman effect. But the slight variations in the frequency shift, 980, of the symmetrical oscillation in the presence of different cations, namely, potassium, sodium and ammonium, are probably due to a small deviation from the tetrahedral symmetry.

In conclusion, the author wishes to thank Prof. Sir C. V. Raman for his interest in the work.

⁷ Mellor, *Treatise of Inorganic Chemistry*, Vol. VIII.

⁸ Ganesan, A. S., *Proc. Ind. Acad. Sci.*, A, 1934, 1, 156.

⁹ Langford, G., *Phys. Rev.*, 1911, 33, 137.

Summary.

The Raman spectra of ortho-phosphoric acid for a wide range of concentrations and of the primary, secondary and tertiary phosphates of sodium, potassium and ammonium have been obtained. The acid has yielded new lines which indicate the ionisation of $\text{H}_3\text{PO}_4 \rightarrow \text{H}^\circ + \text{H}_2\text{PO}_4'$ and the further ionisation of $\text{H}_2\text{PO}_4' \rightarrow \text{H}^\circ + \text{HPO}_4''$. Weak lines characteristic of the OH oscillations have also been observed for the acid. The three series of phosphates give characteristic spectra which are identified as due to $\text{H}_2\text{PO}_4'$, HPO_4'' and PO_4''' ions. The frequency shifts of the PO_4 radical are compared with those of SO_4 and SeO_4 and the force constants are evaluated.