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## RAMAN EFFECT OF SOME COMPLEX PHOSPHATES

GEO. GLOCKER AND J. A. CAMPBELL\*

The most common acid of pentavalent phosphorus is orthophosphoric acid,  $H_3PO_4$ , and all the other acids may be looked upon as being derived from it by the process of dehydration. Thus two molecules of the ortho acid between them can lose one molecule of water forming pyrophosphoric acid,  $H_4P_2O_7$ . Upon still stronger dehydration one molecule of water can be eliminated from each molecule of the ortho acid and the resulting product  $HPO_3$  is known as metaphosphoric acid which was extensively investigated by Graham (1). Metaphosphoric acid and its salts show a great tendency to polymerize to  $(NaPO_3)_n$  and will form crystalline or glass-like materials, the polymetaphosphates. They show a similarity to the corresponding silicon can have only a positive charge of four units. The polymetaphosphates are enclosed within oxygen-ion tetrahedra and that some of the divalent oxygen ions are common to two tetrahedra. These ideas have been developed by Bragg (2) and Pauling (3) in the case of silicates. The difference between phosphate-glasses and silicon glasses lies in the number of metal ions that can associate with a given oxygen tetrahedron, due to the fact that phosphorus is pentavalent whereas silicon can have only a positive charge of four units. The polymetaphosphates can assume ring-structures, where the highest symmetry is obtained. Straight chain polymers of sodium metaphosphate have always one pentavalent phosphorus ion surrounded by three divalent oxygen ions, whereas in the ring structures, all phosphorus ions are located within oxygen tetrahedra. Oxygen ions from neighboring tetrahedra can be arranged in eclipsed or staggered fashion. In the first case the geometry of regular tetrahedra gives the distance ( $d$ ) between phosphorus ions in the  $n$ -numbered ring as

$$d(P-P) = 3.43 \sin \{[(n-2)/2n] \pi + \beta\}$$

where the constant 3.43 arises from the ionic diameter of oxygen ( $1.4A^\circ$ ) (Ref. 3) and  $\beta$  is half the difference between  $180^\circ$  and the central tetrahedral angle ( $109^\circ 28'$ ) ( $\beta=35^\circ 16'$ ). In this case the pentamer should be the stable configuration since the distance between phosphorus ions would be largest ( $3.43 A^\circ$ ). However, the staggered position for oxygen ions should be preferable since here the neighboring oxygen ions are farther apart. Now the hexamer is the structure showing the largest P-P distance, as can be seen from geometry:

$$d(P-P) = (2/\sqrt{3}) [\cos^2 \{(6-n)/6n\} \pi + 1/8]^{1/2} \times s$$

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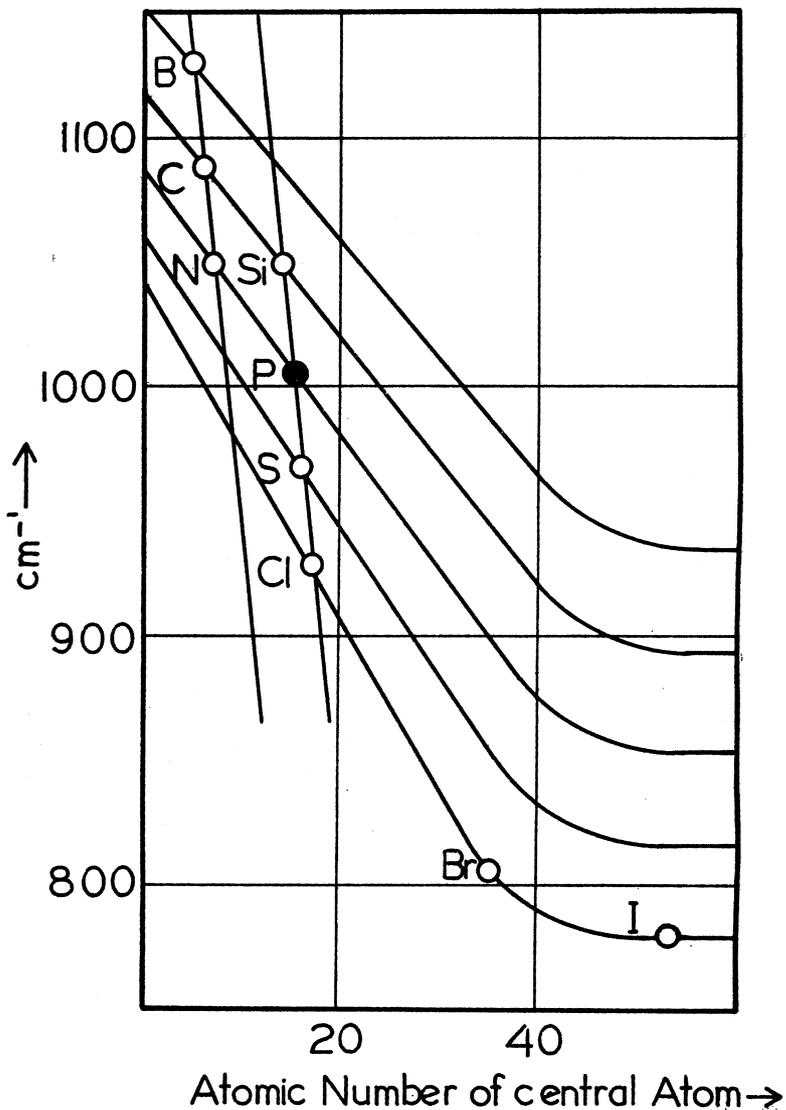


Fig. 1. Symmetric vibration of  $\text{XO}_3$  and atomic number of central atom.

where  $s$  is the oxygen diameter ( $2.8 \text{ \AA}$ ). For the hexagon ( $n=6$ ) this distance is  $3.43 \text{ \AA}$ . Lower polymers (than  $n=6$ ) would hardly be expected since the phosphorus ions would have to approach one another too closely ( $n=2$ ,  $1.98 \text{ \AA}$ ;  $n=3$ ,  $3.12 \text{ \AA}$ ;  $n=4$ ,  $3.38 \text{ \AA}$  for the eclipsed case and  $n=4$ ,  $3.32 \text{ \AA}$ ;  $n=5$ ,  $3.41 \text{ \AA}$  for the staggered case). Higher membered rings again show smaller P-P distances indicating their lesser stability. However even a ten-membered ring ( $d=3.28 \text{ \AA}$ ) is not very far from the maximum  $3.43 \text{ \AA}$  attained in the six-membered staggered ring. The great complexity of silicates (chains, sheets and solids) of similar structure can be repeated with the metaphosphates at least in thought since actual knowledge of these compounds is very meagre. However, as a working hypothesis it may be supposed that sodium metaphosphate, especially after heat treatment will most likely exist as hexameta-phosphate rings. At high enough temperature these rings may break up into smaller molecular fragments.

Another group of phosphates is the class of polyphosphates based on pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) and formed by the addition of  $n$  molecules of sodium metaphosphate; as for example, sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) and sodium tetrapolyphosphate ( $\text{Na}_6\text{P}_4\text{O}_{13}$ ). If it is supposed that in these structures the pentavalent phosphorus ions are surrounded by a regular tetrahedron of divalent oxygen ions, then the polyphosphates are straight chain compounds. In any melt con-

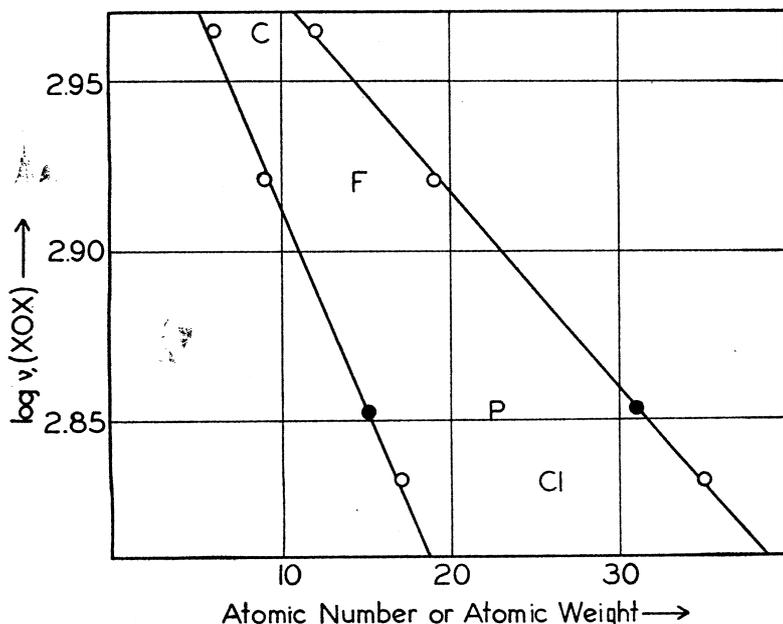
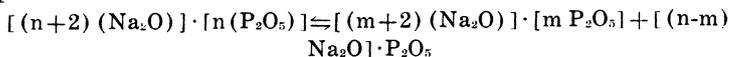


Fig. 2. Logarithm of symmetric frequency of X-O-X and atomic number or atomic weight of X.

taining sodium pyrophosphate and sodium metaphosphate, one may after sufficient time expect the equilibrium



or



The value of  $m$  will depend on the relative stability of  $\text{Na}_{m+2} \text{P}_m \text{O}_{3m+1}$  and the most stable polymer of sodium metaphosphate which can be formed from  $(n-m)$  metaphosphate molecules at the temperature of the experiment. Hence the melt of mixtures of pyro and metaphosphates will contain the stablest polyphosphate and the most stable polymetaphosphate.

It was hoped that the Raman Spectra of polymeta phosphates and polyphosphates might show a difference supporting the above mentioned views regarding their structure. To this end so-called trimetaphosphate, sodium hexametaphosphate, sodium tripolyphosphate and so-called sodium tetrapolyphosphate were prepared (4) and the Raman lines of their respective solutions were determined. So-called sodium trimetaphosphate prepared by Beans and Kiehl (5) was thought by them to be the monomer but Boule (6) came to the conclusion that the monomer, dimer, trimer and tetramer were really the same compound. Later work by Partridge, Hicks and Smith (7) supports this view. The Raman spectrum of the substance prepared by the method of Beans and Kiehl (5) was too weak for use and further work will be necessary to obtain it. Perhaps the most important modification of sodium metaphosphate is the glass obtained by quenching its melt. Its water solution has the property of sequestering alkaline earth ions in order to render them inactive towards their usual precipitating agents (8). Complex formation alone cannot explain this remarkable behavior and some sort of surface action seems more likely to be responsible. From the work of Partridge et al (7) it appears that the only polyphosphate obtained from melts of sodium pyrophosphate and sodium metaphosphate is the tripolyphosphate. This material was prepared as also the so-called tetrapolyphosphate, even though its existence is not confirmed. The latter substance is supposedly contained in some commercial materials of appropriate composition.

#### RAMAN STUDIES

The solutions of the above mentioned phosphates are usually colloidal when first prepared and they have to be carefully filtered until they show no Tyndall effect before it is possible to investigate their Raman spectra. The scattering power of these substances was found to be very low as was to be expected from the strong electrostatic bonds contained in their structure. Hence, after a twelve hour exposure, only the strongest vibrations were observed as very weak lines on the photographic plates.

Table I  
Raman Lines of Phosphate Solutions

Substance	cm <sup>-1</sup>					
Sodium hexametaphosphate .....	513	693	876	976	1082	1145
Sodium tripolyphosphate .....	500	660	.....	950	.....	?
Sodium tetrapolyphosphate .....	509	698	.....	975	.....	1112

These solutions show lines at 510, 680, 970 and 1082 cm<sup>-1</sup>. The line at about 510 cm<sup>-1</sup> appears to be the frequency  $\nu_{156}$  while the line at 970 cm<sup>-1</sup> is  $\nu_1$  or the symmetrical breathing vibration of PO<sub>4</sub><sup>---</sup>. The 1082 cm<sup>-1</sup> frequency may well be the asymmetric vibration  $\nu_{789}$  of the orthophosphate ion (Ref. 10, page 146).

### THE SYMMETRICAL PO<sub>3</sub> FREQUENCY

The breathing vibration of the metaphosphate ion lies at about 1000 cm<sup>-1</sup> as can be seen in Fig. 1 where the lines of the XO<sub>3</sub>-group are related to the atomic number of the central ion. Since this frequency is not found in these solutions it appears that metaphosphate ions exist in their polymeric forms only. It should be noted that the SiO<sub>3</sub><sup>---</sup>-frequency at 1050 cm<sup>-1</sup> (11) was arbitrarily identified with this ion because of the good fit obtained in Figure 1. This agreement may therefore be taken as indicating the validity of this assignment until contrary proof is furnished. Similarly the SO<sub>3</sub><sup>---</sup>-frequency at 968 (11) was taken instead of a later value (988) because it fits so well into the empirical scheme. Again this circumstance may be taken to a point in favor of the lower frequency. The fundamentals of XO<sub>3</sub> used in the construction of Fig. 1 are shown in Table 2.

Table 2.  
Totally Symmetric Vibrations

Structure	cm <sup>-1</sup>	Ref.	Structure	cm <sup>-1</sup>	Ref.
BO <sub>3</sub> <sup>---</sup>	1130	11	BrO <sub>3</sub> <sup>-</sup>	806	9,12
CO <sub>3</sub> <sup>---</sup>	1088	9,12	IO <sub>3</sub> <sup>-</sup>	779	"
NO <sub>3</sub> <sup>-</sup>	1050	"	H <sub>3</sub> C-O-CH <sub>3</sub>	922	10
SiO <sub>3</sub> <sup>---</sup>	1050	11	F-O-F	833	12
SO <sub>3</sub> <sup>---</sup>	968	"	Cl-O-Cl	680	"
ClO <sub>3</sub> <sup>-</sup>	930	9,12	(P-O-P)	(700)	....

### THE SYMMETRICAL X-O-X FREQUENCY

The group X-O-X is a prominent feature of these polyphosphates and the frequencies of radicals of this type were compared with the atomic weights or atomic number of the X-atom. By interpolation it was found that the breathing vibration of P-O-P is about 700 cm<sup>-1</sup>. This value checks the frequency found at 660 cm<sup>-1</sup> sufficiently well so that it may be supposed to be due to the symmetrical motion of the phosphorus nuclei about their common oxygen ion. The frequencies used are shown in Table 2, and plotted as their logarithms in

relation to the atomic number and atomic weight of the X-atoms (Fig. 2).

The lines 876 and 1145, 1112  $\text{cm}^{-1}$  appear in many silicate glasses (11) and they may be components of the triplets  $\nu_{456}$  and  $\nu_{780}$ . Only a complete analysis of the vibration problem can settle this question. It is interesting to note that these two lines appear in hexametaphosphate and not in the polyphosphates. Before this finding can be accepted, these experiments will have to be repeated with a faster spectrograph in order to obtain more of the weak lines of these solutions. The experimental results are still too meagre to permit correlation to the ring structure or chain configuration mentioned earlier.

#### SUMMARY

The Raman spectra of sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub> (I); sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) (II); and sodium tetrapolyphosphate ( $\text{Na}_4\text{P}_4\text{O}_{13}$ ) (III) have been studied in solution and the following lines have been found: 510  $\text{cm}^{-1}$  ( $\nu_{456,56}$  of  $\text{PO}_4^{3-}$ ) and 970  $\text{cm}^{-1}$  ( $\nu_1$  of  $\text{PO}_4^{3-}$ ) in all cases; 1082  $\text{cm}^{-1}$  ( $\nu_{780}$  of  $\text{PO}_4^{3-}$ ) in I; 690  $\text{cm}^{-1}$  ( $\nu_1$  of P-O-P) in all cases. The lines 876 (I), 1145 (I) and 1112 (III) may be components of  $\nu_{156}$  and  $\nu_{780}$  respectively in case the selection rules are different for the polymers than for the orthophosphate ion. These last mentioned lines may serve to distinguish polymetaphosphates from polyphosphates in case the present findings can be substantiated.

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