The Infra-red Spectra of Some Inorganic Phosphorus Compounds.

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[Reprint Order No. 4340.]

The infra-red spectra of 92 salts of phosphorus oxy-acids have been examined in the rock-salt region. Characteristic frequencies are suggested for P–N and P–O–P linkages. Confirmation of a number of frequency assignments made by other workers has been obtained. The absorption frequencies are found to be largely independent of the positive ion, but show considerable variation with the nature of the anion. General absorption bands characteristic of each class of negative ion are listed and their possible use in analysis is indicated. Effects of crystal and molecular structure on the absorption spectra are discussed, and some useful structural information is derived.

Although several papers have recently dealt with the infra-red absorption spectra of organophosphorus compounds, comparatively little attention has been paid to the inorganic derivatives. Miller and Wilkins (*Analyt. Chem.*, 1952, **24**, 1253) record the spectra of a few orthophosphates, but no systematic study of the salts of the other phosphorus oxy-acids appears to have been made. In this work, the spectra of 92 salts have been examined as fine powders in the 5000—650-cm.$^{-1}$ region. These have been investigated with a view to assigning characteristic frequencies to molecular groupings and generally correlating absorption with molecular structure. The use of such spectra in qualitative and quantitative analysis is also discussed.

Experimental.—The compounds examined were mainly products made in these laboratories, though in some instances commercially available materials of "AnalaR" grade were used. Most of the materials had previously been obtained in a high state of purity for other purposes. All spectra were recorded from 5000 to 650 cm.$^{-1}$, a Perkin–Elmer 21C Double Beam Spectrometer being used. The materials were examined as fine powders spread on rock-salt plates. This was accomplished by using a grinding and sedimenting technique similar to that described by Hunt, Bonherd, and Wisham (*ibid.*, 1950, **22**, 1478) although simple grinding sufficed in some cases. Several recent papers (Lecomte, *Analyt. Chim. Acta*, 1948, **2**, 727; Hunt, Bonherd, and Wisham, *loc. cit.*; Keller, Spotts, and Biggs, *Amer. J. Sci.*, 1952, **250**, 453) deal with infra-red absorption of dry powders. The most satisfactory spectra in this case were obtained from powders with particle sizes not greater than about 2·5 μ. A decrease in transmittance above 2000 cm.$^{-1}$ due to scattered radiation was observed in many spectra, but the scattering was not removed on decreasing the maximum particle size to less than 0·5 μ. By taking spectra with Nujol mulls in the high-frequency region, sharper absorptions were obtained in some instances. Specimens were usually about 0·01 mm. thick, thicker samples being used when searching for weak absorptions. Slit widths were 0·038 mm. at 2000 cm.$^{-1}$ and 0·028 mm. at 700 cm.$^{-1}$. Errors in frequency measurement are probably not greater than ±3 wave-numbers in most parts of the spectrum, although with broad peaks and shoulder bands they may be greater.

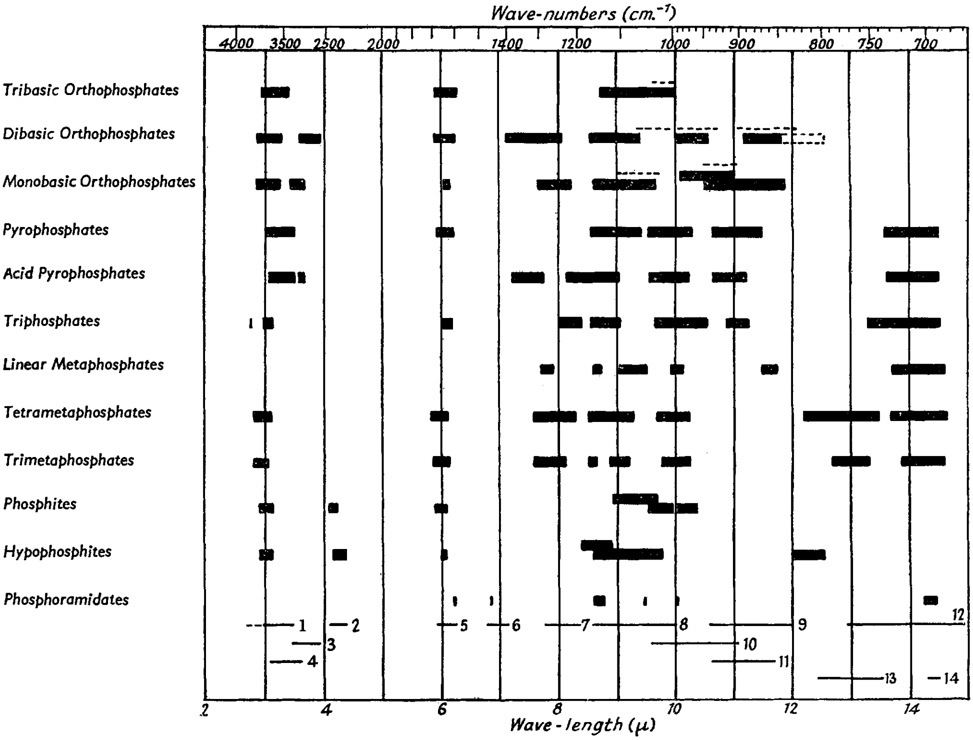
Results and Discussion

A considerable variation in the quality of the spectra was observed. Some salts, *e.g.*, hypophosphites and cyclic metaphosphates, gave very well-defined spectra, whereas others, particularly some acid orthophosphates, gave broad and poorly resolved peaks. Typical examples are shown in the Figure. The principal absorption bands produced by the various types of anion are summarised in Table 1. These general absorption regions are suggested only inasmuch as the present range of compounds is concerned. Some characteristics of the spectra below 1500 cm.$^{-1}$ are as follows :

Orthophosphates.—The tribasic derivatives give broad absorptions between 1150 and 1000 cm.$^{-1}$, containing only partly resolved peaks in many cases. The absorption generally consists of one very strong broad band between about 1060 and 1000 cm.$^{-1}$, with two or more weaker bands. The spectra of the acid orthophosphates are more complex. Whilst the strongest peaks usually lie near 1100 cm.$^{-1}$, several additional medium or weak peaks occur in the regions shown in the Table. These bands can be compared with those given by Miller and Wilkins (*loc. cit.*), shown as broken lines.

Pyrophosphates.—The spectra of these compounds are generally better resolved and more consistent than those of the orthophosphates. The strongest absorption, usually consisting of an imperfectly resolved doublet, lies in the region 1170—1060 cm.$^{-1}$. At lower frequencies, bands at 1045—970 cm.$^{-1}$ (two peaks of variable intensity), 940—870 cm.$^{-1}$ (one strong broad absorption and some weaker peaks), and 735—690 cm.$^{-1}$ (one peak of medium intensity) are usually found. The acid pyrophosphates produce similar absorptions in roughly the same regions with the additional bands shown in the Table.

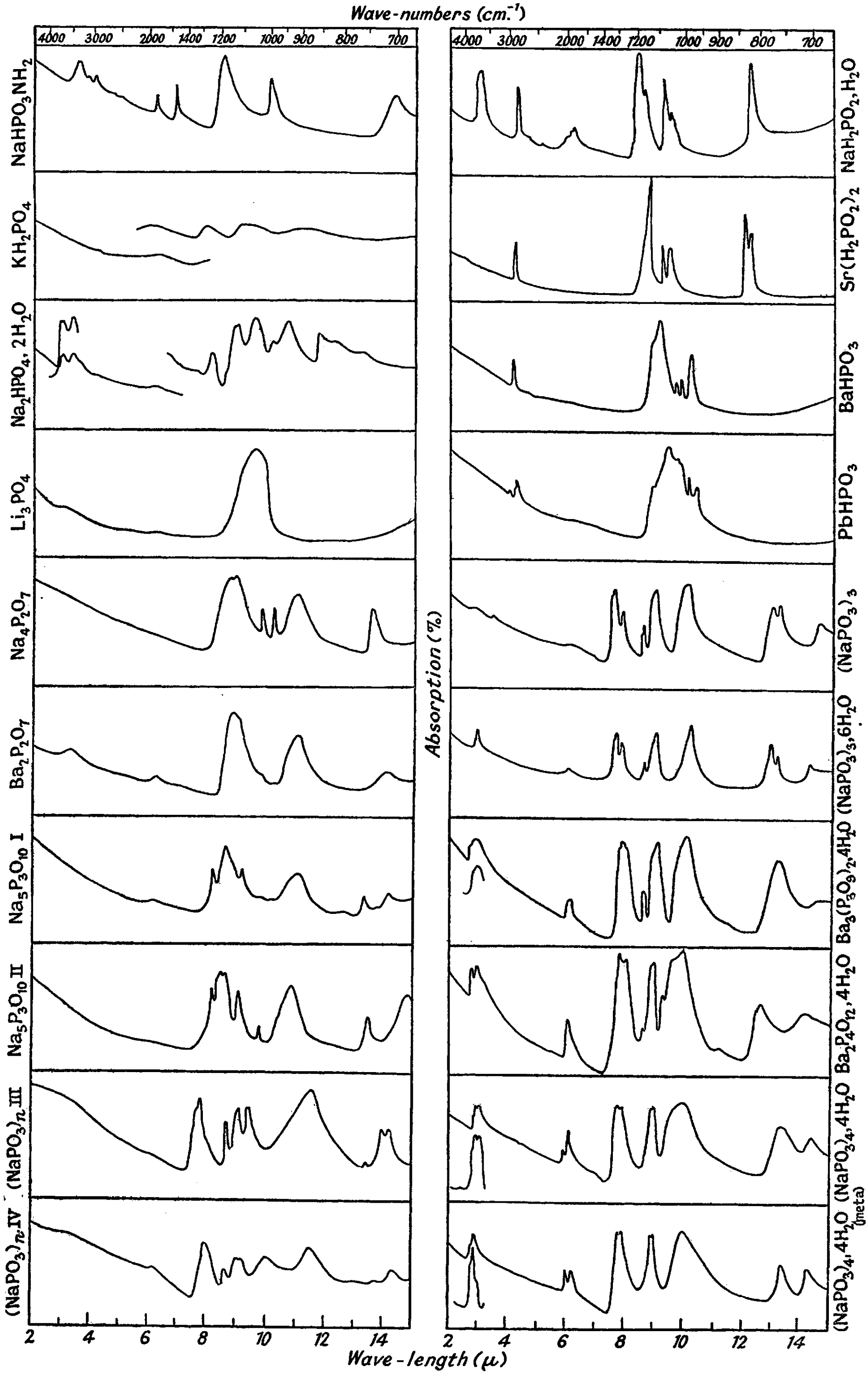
TABLE 1. *Principal regions of absorption for salts of phosphorus oxy-acids.*



1, O–H stretching in hydrates.
2, P–H stretching.
3, P–O–H stretching.
4, Banded N–H stretching.
5, O–H bending in hydrates.
6, NH_4^+ ion.
7, P=O stretching in triphosphates and metaphosphates.
8, Ionic P–O stretching.
9, P–O–H bending.
10, Other modes of P–O stretching.
11, P–O–P stretching.
12, Harmonics of P–O–P bending.
13, P–O–P in ring systems.
14, P–N stretching.

Triphosphates.—The strongest absorptions in each spectrum are found in the region 1170—1100 cm.$^{-1}$. In addition, a single strong absorption appears in the region 1250—1085 cm.$^{-1}$, and a strong absorption at 920—885 cm.$^{-1}$ in all salts. Two absorptions appear at 1040—955 cm.$^{-1}$ in most cases, and usually two at 755—690 cm.$^{-1}$.

Cyclic Metaphosphates.—The spectra of the metaphosphates are very characteristic, one of the most noteworthy features being the appearance of very strong absorption, usually a triplet, in the 1315—1205-cm.$^{-1}$ region. The very strong broad absorption near 1000 cm.$^{-1}$ is also a distinguishing feature of these compounds. Yet another characteristic is the occurrence of two strong absorptions near 770 cm.$^{-1}$ in addition to medium or weak bands near 700 cm.$^{-1}$. The spectra of a trimetaphosphate and a tetrametaphosphate of a


Wave-numbers (cm.$^{-1}$)
4000 3000 2000 1400 1200 1000 900 800 700
$NaHPO_3NH_2$
KH_2PO_4
$Na_2HPO_4,2H_2O$
Li_3PO_4
$Na_4P_2O_7$
$Ba_2P_2O_7$
$Na_5P_3O_{10}$ I
$Na_5P_3O_{10}$ II
$(NaPO_3)_n$ III
$(NaPO_3)_n$ IV
NaH_2PO_2,H_2O
$Sr(H_2PO_2)_2$
$BaHPO_3$
$PbHPO_3$
$(NaPO_3)_3$
$(NaPO_3)_3,6H_2O$
$Ba_3(P_3O_9)_2,4H_2O$
$Ba_2P_4O_{12},4H_2O$
$(NaPO_3)_4,4H_2O$
$(NaPO_3)_4,4H_2O$ (meta)
Absorption (%)
2 4 6 8 10 12 14
Wave-length (μ)

particular metal are always recognisably different, although the general regions of absorption for these two classes of anion are not greatly different (see Table).

"Linear" Metaphosphates.—The spectra of these compounds exhibit a number of differences from those of the cyclic derivatives. The absorption at 1300—1265 cm.$^{-1}$ usually consists of a single very strong peak, and the very strong broad absorption at 870—850 cm.$^{-1}$ appears to replace the band near 770 cm.$^{-1}$ in the cyclic compounds.

Phosphites and Hypophosphites.—These materials usually give very well-defined spectra, a typical example being strontium hypophosphite (see Figure). The phosphites exhibit several strong absorptions between 1130 and 1035 cm.$^{-1}$ and medium or strong bands at 995—960 cm.$^{-1}$. The hypophosphites on the other hand give absorptions between 1190 and 1025 cm.$^{-1}$ and very strong characteristic absorptions near 820 cm.$^{-1}$.

Phosphoramidates.—Absorptions are found at 1618—1615 and 1470—1468 cm.$^{-1}$, and strong bands at 1162—1143, 994—993, and 697—691 cm.$^{-1}$.

The use of Table 1 for qualitative analysis of phosphate anions, in the form of dry powders, is obvious. Complete identification of a particular metal salt is possible by using the data in Table 2, although failure to match observed bands exactly could result from the same salt's being present in a different crystalline form. No completely satisfactory infra-red technique for quantitative analysis of powders has yet been evolved (Hunt, Bonherd, and Wisham, *loc. cit.*), but the use of the foregoing data in a semi-quantitative manner should be practicable.

Care is needed if spectra are obtained from Nujol mulls. Among the few salts which were also examined in Nujol, some important discrepancies were observed. An absorption found in silver orthophosphate, for instance, may be compared with the values already in the literature: 950 (dry), 965 (Nujol), 970 (Duval and Lecompte, *Bull. Soc. chim.*, 1947, 101), and 947 cm.$^{-1}$ (Bergmann, Littauer, and Pinchas, *J.*, 1952, 847). Silver pyrophosphate gives an absorption at 914 cm.$^{-1}$ in dry powder form and at 880 cm.$^{-1}$ as a Nujol mull, whereas Bergmann, Littauer, and Pinchas report 903 cm.$^{-1}$. A number of differences are found in the spectra of dibasic ammonium phosphate taken as a dry powder and as a Nujol mull, the latter agreeing closely with that recorded by Miller and Wilkins (*loc. cit.*). Differences were found in some other salts but the phenomena were not investigated further.

The spectra of powdered crystalline salts are liable to be influenced by a number of factors, which are usually less important in the case of liquids and solutions. Absorption bands can be broadened, split, or shifted by mutual interaction of adjacent ions or combination with long-wave lattice vibrations. The influence of local crystal structure and the positive ions may also be significant. Moreover, the presence of lattice water and hydrogen bonding may affect the internal modes of vibration of the anions.

Water of Crystallisation.—All the hydrated salts absorb in the 3300 and 1640 cm.$^{-1}$ regions, which presumably correspond to O–H stretching and O–H bending respectively. In most hydrates, frequencies higher than 3450 cm.$^{-1}$ are absent, which indicates that no completely free O–H stretching occurs and that extensive hydrogen bonding is probable. Although a few salts give only a broad absorption near 3300 cm.$^{-1}$, many give several sharp peaks between 3450 and 2860 cm.$^{-1}$ which may be ascribed to more than one type of hydrogen bonding in the crystals.

The hydrated cyclic metaphosphates are exceptional in that a general shift of the O–H stretching bands to higher frequencies occurs, with values as high as 3580 cm.$^{-1}$ in some salts. These absorptions are much sharper and probably correspond to free O–H stretching; moreover, the bands in the O–H bending region are stronger and sharper than in most other hydrated salts. It is apparent, therefore, that in these compounds, some, at least, of the water molecules are only loosely held in the crystal lattice, probably in an interstitial manner.

Another interesting exception is provided by sodium triphosphate hexahydrate $Na_5P_3O_{10},6H_2O$ which gives, in addition to two absorptions at 3350 and 3260 cm.$^{-1}$, a very sharp, strong band at 3630 cm.$^{-1}$. This again indicates that some of the water of crystallisation is probably only loosely held in the structure.

The spectra of the stable and the metastable form of sodium tetrametaphosphate tetrahydrate are interesting. The differences between the two crystalline forms (Topley, *Quart. Reviews*, 1949, **3**, 353) appear to be connected with the way some of the water molecules are held in the structure. In both compounds, some water appears to be loosely held (absorption at 3580 cm.$^{-1}$), but the peak at 3330 cm.$^{-1}$ which occurs in the stable form is almost entirely suppressed in the metastable salt. Moreover, in the latter compound the peaks in the O–H bending region are slightly shifted to lower frequencies with a marked reduction of intensity of one of them. The remaining absorptions of the two salts are practically identical.

No correlation was found between any property of the absorptions in the O–H bending and stretching regions, and the number of water molecules in a hydrate. The spectra produced by a hydrate and the corresponding anhydrous salt may be different for two reasons: the introduction of water molecules into the lattice usually results in rearrangement of the packing and the adoption of a different crystalline form, and the water molecules may form hydrogen bonds with some part of the anions and consequently affect their vibrational frequencies.

Comparison of the anhydrous salts with their hydrates reveals a number of differences in their spectra below 1500 cm.$^{-1}$. In many cases a general shift of peaks to lower frequencies occurs. This effect is most marked with peaks in the P–O stretching region (see below) and probably results from hydrogen-bonding of the water molecules on to the oxygen in the anions. A similar phenomenon has been noticed by Bellamy and Beecher (*J.*, 1952, 1701) who observed a shift of the P=O stretching frequency, normally at 1300—1250 cm.$^{-1}$, to considerably lower values in certain organophosphorus acids and amines where hydrogen bonding is very probable. A peculiar effect occurs with sodium hypophosphite. The very strong peak at 817 cm.$^{-1}$ in the monohydrate is split into a triplet in the anhydrous salt. Moreover, the single peak at 2330 cm.$^{-1}$ is also split, into a doublet, on conversion into the anhydrous form.

Polymorphism.—In cases where polymorphism implies merely slightly different packing schemes of similar anions, the differences in infra-red spectra would be expected to be small. On the other hand, when the polymorphism results from differently polymerised anions of the same empirical formula, or from relatively large differences in structural arrangement of similar ions, it is reasonable to expect considerable differences in spectra.

The sodium metaphosphates of general formula $(NaPO_3)_n$ are a case in point. Unfortunately, but few data are available on their internal crystalline structures, but structural differences are indicated by their varied physical properties (Topley, *loc. cit.*, p. 345). *X*-Ray studies of Kurrol salt, $(NaPO_3)_n$-IV (Plieth and Wurster, *Z. anorg. Chem.*, 1951, **267**, 49), show that the crystals contain long chains of linked PO_4 tetrahedra forming anions of high molecular weight. The infra-red spectra of four forms of sodium metaphosphate-II, -III, -IV, and glass * (nomenclature of Partridge, *Chem. Eng. News*, 1949, **27**, 214) are all of the same general type and different from the spectra of the cyclic metaphosphates. This may be an indication that all these compounds are composed of chain-like anions of high molecular weight, as in Kurrol salt. The spectra of forms II and III are almost identical except for one broad absorption which is at 878 cm.$^{-1}$ in the former and at 867 cm.$^{-1}$ in the latter. The somewhat larger divergences, however, among the spectra of the remaining compounds here considered as linear metaphosphates, presumably result from the chains' being polymerised to different extents or from greater differences of crystal structure.

P–O *Linkages.*—In the rock-salt region the PO_4^{3-} ion has two fundamental vibration frequencies, at about 1082 and 980 cm.$^{-1}$. Both these have been observed in Raman spectra, but the latter band, being the ν_1 symmetrical stretching frequency of an XY_4 molecule (Herzberg, " Infra Red and Raman Spectra of Polyatomic Molecules," New York, 1945, p. 167), should not normally appear in infra-red absorption. Colthup (*J. Opt. Soc. Amer.*, 1950, **40**, 397) records for phosphate ions a band at 1100—1040 cm.$^{-1}$ only. Bellamy and Beecher (*loc. cit.*), Miller and Wilkins (*loc. cit.*), and others have also observed absorption in this region.

* Glass obtained by melting NaH_2PO_4 at 700—725° for ½ hr., then chilling it by pouring it on to a stainless-steel plate.

TABLE 2. *Positions and intensities of infra-red absorption bands.*

Orthophosphates

(1) Li_3PO_4
~1100 vs
1050 vs
1035 vs

(2) Na_3PO_4
1125 s to 1028 vs, b
914 vw

(3) $Mg_3(PO_4)_2$
1140 s
1110 s, sh
1068 vs
~1030 m

(4) $Ca_3(PO_4)_2$
1093 vs, sh
1070 vs, sh
1045 vs

(5) $Sr_3(PO_4)_2$
~1140 m, sh
1068 vs
1040 vs
1015 vs

(6) $Ba_3(PO_4)_2$
1090 w, sh
1125 m
1043 s
1000 vs

(7) $Pb_3(PO_4)_2$
1056 vs
981 vs, b

(8) Ag_3PO_4
1037 s
950 vs, b

(9) $CrPO_4,6H_2O$
2915 vs, b
1610 m, b
1010 vs, vb

(10) $FePO_4,2H_2O$
3330 s, b
1600 s, b
1385 m ?
1255 vw ?
1105 vs
1068 vs
1005 vs
850 m ?

(11) $FeNH_4PO_4,H_2O$
3400 m
3210 m
2915 m
2760 m
1633 w, b
1470 m
1430 m
1105 ms
1047 s
~960 w
941 w

(12) $MgNH_4PO_4,6H_2O$
3400 m
3255 m
1700 w
1682 w
1475 m
1436 m
1236 m ?
1168 m
1105 m
1062 s
1024 s
990 s
953 w
890 w
767 w

(13) $NH_4H_2PO_4$
3200 s, b
3040 m, b
2860 w, b
~2700 w, b
~1640 m, b
1444 s
1406 s
1275 s
1084 vs, b
900 m, vb

(14) NaH_2PO_4
~2750 m, b
1650 m
1300 m
1282 m
1160 s
1125 s
1045 s
981 s, b
927 s, b
870 m
815 vw

(15) KH_2PO_4
1285 s, vb
1085 s, vb
890 s, vb

(16) $Ca(H_2PO_4)_2$
2850 w, b
1643 vw, b
~1300 vw
1128 s, vb
1072 m
990 w
935 w
877 w

(17) $Ca(H_2PO_4)_2,H_2O$
3425
3180
2910
1650 m
1240 m
1220 m, sh
1150 w
1090 s, b
~980 s, sh
963 vs
913 w
890 w

(18) $NaH_2PO_4,2H_2O$
3500
3420
3250 b
2700 w, b
1658 m
1280 m, sh
1245 m
1163 s
1100 s
1040 s
~990 w, sh
958 s
903 s
888 w, sh
820 vw

(19) $(NH_4)_2HPO_4$
3350 s
3225 s
3125 s
3025 s
~2700 vw, b
~1650 vw
1486 m
1468 m
1450 w
1409 m
1240 w
1070 vs, b
996 s
951 w
884 m

(20) Na_2HPO_4
2750 w, b
1240 w
1350 w
1310 w
1148 s
1125 s
1100 s
1065 s, b
991 s
973 m
940 b
~850 s, b
798 m

(21) K_2HPO_4
2900 m
2550 w
1650 w, b
1328 w
1110 vs, b
996 s
983 s
952 m
847 s, b
800 w ?

(22) $CaHPO_4$
~2800 w
~1620 w, vb
1390 w
1350 w
1170 m, sh
1130 s
1068 s
993 w
890 w, b

(23) $Na_2HPO_4,2H_2O$
3450 s
3360 s
3080 s
2700 w, b
1700 w, b
1257 m
1133 s
1120 s
1067 s
990 m
950 s
862 m
815 w

Pyrophosphates

(24) $Li_4P_2O_7,2H_2O$
~3350 m
2860 vw
~1640 m
1195 m
1170 vs
1150 vs
1128 vs
1107 vs
940 vs
896 m
738 w

(25) $Na_4P_2O_7$
1180 s, sh
1165 s, sh
1150 vs
1124 vs
1031 s
988 s
921 vs, b
895 m
735 vs

(26) $K_4P_2O_7$
1110 vs
1080 s, sh
1050 s, sh
1025 s
980 w
930 m
890 vs, b
720 m

(27) $Na_4P_2O_7,10H_2O$
3420 s
3230 s
3000 s
1655 m
1110 vs
1093 vs
1021 w
993 m
921 s, b
865 m
665 m, vb

(28) $Mg_2P_2O_7$
1161 vs
1122 vs
1049 m
1008 w
932 m
907 m
725 m

(29) $Ca_2P_2O_7$
1153 vs
to 1080 m
1035 w
1000 w
927 m, b
720 w

(30) $Sr_2P_2O_7$
1142 vs
1125 vs
1108 m, sh
1091 m, sh
1072 m
1030 m
981 w
888 s
722 m

(31) $Ba_2P_2O_7$
1135 vs
1110 vs
1021 w
977 w
912 s, b
718 m

32) $Pb_2P_2O_7$
1117 vs
1061 vs
1003 m
972 m
914 s
728 m

(33) $(NH_4)_4P_2O_7$
1460 s
1405 s
1164
1105 vs
~1070
~1045
868 vs, b
737 vw
702 w

(34) $Ag_4P_2O_7$
1093 vs
1063 vs
1046 vs
998 m
972 w
914 s, b
701 m

(35) $Na_2H_2P_2O_7$
~2700 w, b
1600 m, vb
1389 w
1333 w
1210 m
1191 s, sh
1155 s
1027 w
957 m
878 s, b
729 m

(36) $(NH_4)_2H_2P_2O_7,xH_2O$
3275 w
3150 w
3000 m
~2800 vw
~2600 vw
1465 m
1415 m
1292 m
1175 m, sh
1153 s
1118 s
1045 s, b
986 s
935 s, b
692 m

(37) $CaH_2P_2O_7$
~2700 vw
1280 vs
1212 m
1094 s
970 s
895 s, b
830 vw, b
735 m

Triphosphates

(38) $Na_5P_3O_{10}$-I
~1620 w, vb
1265 w
1215 s
1146 vs
1095 s
1022 w
989 w
912 s, b
798 vw, b
753 m
731 w
708 s

(39) $Na_5P_3O_{10}$-II
1214 s
1184 s
1165 vs
1145 vs
1098 s
1016 w
906 vs, b
737 m
665 s

(40) $Na_5P_3O_{10},6H_2O$
3630 s, sh
3350 m
3260 m
1651 w
1610 w
1410 w
1211 s
1157 s
1118 s
1100 s
1080 s
959 w
887 vs, b
768 w, b
710 m

(41) $K_5P_3O_{10}$
1208 s
1156 s
1130 vs, b
1090 s
874 vs, vb
726 m
683 m

TABLE 2. (*Continued.*)

(42) $Ag_5P_3O_{10}$

1306 vw	999 m
1170 m, sh	970 m
1097 s	893 s, b
1082 s	760 vw, b
1067 s	716 m
1047 s	701 s

(43) $Zn_2NaP_3O_{10},9H_2O$

3470 m	1044 m
3330 s, b	1026 m
1664 m	997 s
1625 m	916 vs, b
1243 s	781 m
1150 vs	710 w
1107 vs	

(44) $NiNa_3P_3O_{10},12H_2O$

~3175 s, vb	1088 s
1642 w	1025 m
1249 s	992 m
1141 s	913 m, b
1119 s	750 w, vb

Trimetaphosphates

(45) $Na_3P_3O_9$

1314 s, sh	1101
1298 vs	987 vs, b
1262 s	773 vs
1169 s	757 vs
1162 s	686 s
1120 s, sh	

(46) $Na_3P_3O_9,H_2O$

3465 m	1112 s
1680 w, b	1100 s
1610 w, b	970 vs, b
~1315 m	774 s
1292 vs	755 s
1260 vs	695 m
1158 m	

(47) $Na_3P_3O_9,6H_2O$

3485 s	1100 s
~1640 w, b	975 vs, b
1312 m	776 s
1294 vs	756 s
1270 s	698 m
1159 m	

(48) $Mg_3(P_3O_9)_2,10H_2O$

3480 s	1170 vw
3280 s. b	1100 vs
1680 s	1023 vs, vb
1642 s	977 m
1317 s	~900 vw
1271 vs	784 vs
1250 vs	690 vw, b

(49) $CaNaP_3O_9,3H_2O$

3580 w	1116 s
1655 m	1012 s, b
1625 s	900 vw
1320 m	772 vs
1303 vs	767 s
1275 vs	~700 w
1168 m	

(50) $Sr_3(P_3O_9)_2,7H_2O$

3560 m	1157 s
3510 m	1108 vs
3330 s, b	996 vs, b
1645 m	788 m
1620 m	765 s
1295 vs	697 m
1275 vs	
1256 vs	

(51) $Ba_3(P_3O_9)_2,4H_2O$

3560 m	1113 s
3340 s, b	1097 vs
1640 s	1085 vs
1612 s	1012 vs
1298 vs	983 vs
1265 vs	757 vs, b
1245 vs	685 m
1153 m	

(52) $Mn_3(P_3O_9)_2,11H_2O$

~3500 m	1170 w
3120 vs, b	1097 vs
1665 m	1012 vs, vb
1640 s	780 vs
1280 s	720 vw, b
1265 s	685 w, b
1235 vs	

(53) $Ag_3P_3O_9$

~1315 m	1132 m
1277 s	1106 s
1242 s	1085 s
1210 m	1068 s
1156 m	

Tetrametaphosphates

(54) $Na_4P_4O_{12}$

1306 s	1037 vs, b
1282 s	to 991 vs, b
1270 s	882 vw, b
1173 vw	794 m
1125 vs	710 m
1093 m	

(55) $Na_4P_4O_{12},4H_2O$

3580 w	1109 vs
3480 m	998 vs, vb
3330 m	880 vw ?
1693 w	748 m
1655 m	697 m
1290 vs	
1266 vs	
1122 vs	

(56) $Na_4P_4O_{12},4H_2O$
(metastable)

3580 w	1109 vs
3475 m	988 vs, vb
3330 vvw	880 vw ?
1670 w	750 m
1622 w	697 m
1284 vs	
1265 vs	
1117 vs, sh	

(57) $Ag_4P_4O_{12},2H_2O$

3415 w, vb	1087 s
1630 w, b	991 vs
1400 w, I ?	978 vs
1360 w, I ?	958 s
1250 s	797 m
1232 s	714 m
1206 s	693 m

(58) $Mg_2P_4O_{12},8H_2O$

~3600 s	1157 vs
3400 vs	1115 s
3330 vs	1030 vs, b
1665 s	797 m
1650 s	748 s
1315 vs	718 s
1253 vs	

(59) $Ca_2P_4O_{12},5H_2O$

3560 m	1120 s
3420 m	1108 m, sh
2980 w	~1030 vs, b
1655 w	1010 vs, b
1625 m	888 vw ?
1290 vs, b	800 m
1260 vs, b	732 m, b
1148 s	691 w

(60) $Sr_2P_4O_{12},5H_2O$

3630 s	1238 m
3580 vs	1153 vw
3380 vs	1125 m
1645 vs	1110 vs
1625 vs	1008 vs, vb
1285	755 s
1277 vs	720 m
1258 s	

(61) $Ba_2P_4O_{12},4H_2O$

3570 vs, sh	1108 vs
3400 vs	1073 s
3180 m	1030 vs
1645 s	1000 vs
1281 vs	987 vs
1258 vs	885 vw ?
1240 vs	798 s
1154 w	788 s
1120 vs	706 m

(62) $Pb_2P_4O_{12},4H_2O$

~3300 w	1147 w
1665 w	1095 s
1620 w	995 vs, b
1278 m	816 m
1260 vs	748 m
1235 vs	720 m, b

(63) $Mn_2P_4O_{12},9H_2O$

3400 vs, vb	1106 s
1625 s	1025 vs, vb
1290 vs	785 w
1238 vs	740 s
1140 vs	708 s

(64) $Cu_2P_4O_{12},8H_2O$

3550 s	1154 s
3400 vs	1105 s
3230 vs	1024 vs, vb
1645 s	910 vw
1298 vs	750 s
1250 vs	717 m

(65) $Al_4(P_4O_{12})_3$

1311 vs	1066 vs
1286 s	1029 vs
1230 w	808 m
1183 m	738 s
1143 m	718 m
1083 s	

Metaphosphates of high molecular weight

(66) $(NaPO_3)_n$-II

~1315 m, sh	1060 s
1298 vs	878 vs, vb
1160 m	742 w
1104 s	719 m
1097 s	702 m

(67) $(NaPO_3)_n$-III

~1315 m, sh	1060
1298 vs	867 vs, vb
1160 m	742 w
1104 s	719 m
1097 s	702 m

(68) $(NaPO_3)_n$-IV

~1630 w, b	996 s, b
1268 vs, vb	869 vs, b
1150 m	778 w
1110 s	724 w
to 1082 s	698 m

(69) $(NaPO_3)_n$(glass)

1262 vs, b	863 m
1150 w	770 vw, vb
1083 s, b	to 700 vw, vb
980 m, vb	

(70) $(KPO_3)_n$

1300 s	1015 w, b
1266 vs	851 vs, b
1150 s	760 m
1100 s, b	677 s

Orthophosphites

(71) Li_2HPO_3,H_2O

3450 s	1117 vs
3400 m	1096 vs
3250 m	1080 vs
2380 m	1045 w
2360 m	1038 w
1640 m	1005 w
1173 s	994 s

(72) Na_2HPO_3

2300 m, b	1037 w
1116 vs, b	993 m
to 1082 vs, b	972 w

(73) $Na_2HPO_3,5H_2O$

3225 vs, vb	1082 s, b
2320 w	1037 vs, b
1670 m	972 m

(74) $CaHPO_3,H_2O$

3360 m	1130 s, b
3300 m	1054 s, b
2430 m	1018 w
1665 m	996 s

TABLE 2. (*Continued.*)

(75) $SrHPO_3,H_2O$

3230 s, b	1068 vs
2382 m	1057 vs, sh
2340 m	1011 w
1680 w	993 s
1124 s	

(76) $BaHPO_3$

2400 m	1022 m
1130 s, sh	1006 m
1082 vs, b	978 s

(77) $PbHPO_3$

2373 w	1058 s
2340 m	1028 s
1126 s, sh	1012 m
1075 s	988 s
	963 s

(78) $NiHPO_3,H_2O$

3325 vs, vb	1088 vs
2400 w	1060 vs
2355 w	1020 s, sh
1640 m	995 s, sh
1120 s	

Hypophosphites

(79) LiH_2PO_2

2325 s	1100 s
1180 vs	1073 s
1148 s	817 vs

(80) NaH_2PO_2

2350 s	1092 s
2280 s	1080 vs
1966 vw	1065 s
1634 vw	1053 m
1190 vs	830 vs
1171 s	817 vs
1150 m	800 vs
1100 m	

(81) NaH_2PO_2,H_2O

3270 vs, vb	1098 w
2330 vs	1088 vs
1964 vw	1071 s
~1690 w	1060 w
1640 m	1045 w
1185 vs	817 vs
1167 s	

(82) KH_2PO_2

3400 m, b	1097 w
2295 s	1080 s
1964 vw	1065 s
1220 m	1050 s
1208 m	820 s
1195 s	810 s
1185 vs	800 s
1162 s	

(83) $Mg(H_2PO_2)_2,6H_2O$

3460 m	1110 s
3200 s, b	1075 m
2400 s	1020 m
2350 w	808 m
1665 m	760 m, vb
1153 m	

(84) $Ca(H_2PO_2)_2$

2360 s	1092 m
1184 vs	1063 m
1170 s	1042 m
1148 s	813 vs
1100 s	

(85) $Sr(H_2PO_2)_2$

2360 s	1054 s
1150 vs	834 vs
1082 s	824 s

(86) $Ba(H_2PO_2)_2$

2350 s	1078 s
1965 w	1040 s, b
~1170 s	822 vs
1147 s	811 vs
1090 s	

(87) $Pb(H_2PO_2)_2$

2355 s	1073 s
1950 w	1046 s
1191 m	1029 s
1128 vs, b	817 vs
1105 m	806 vs

(88) $Mn(H_2PO_2)_2$

2340 m	1093 w
1665 w, b	1081 m
1188 vs	1060 m
1160 vs	1051 m
1148 s	1043 m
1122 w	1033 m

Phosphoramidates

(89) $NaH(PO_3{\cdot}NH_2)$

2875 s, b	1615 m
2580 w	1158 vs, b
2470 w	994 s
2045 w	697 s

(90) $KH(PO_3{\cdot}NH_2)$

2890 m, b	1469 m
2585 w	1162 s
2475 w	993 m
2055 vw	691 m
1618 m	

(91) $NH_4H(PO_3{\cdot}NH_2)$

3260 m	1470 m, sh
3130 m	1457 m
2760 s, b	1415 s
2585 w	1143 vs, b
2445 w	994 m
2160 w	898 vw, b
1616 w	694 m

(92) $Ag_2(PO_3{\cdot}NH_2)$

2960 m, vb	1060 vs
1612 w, b	1011 m
1183 m	978 s
1154 m	952 m
1128 s	907 w
1100 s	824 w
1083 s	782 m, b

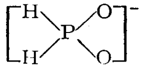
Amongst the tribasic orthophosphates, we have found strong absorptions between 1150 and 1000 cm.$^{-1}$ which we attribute to the ionic phosphate vibration. However, in all compounds which we have studied, strong absorptions, often consisting of multiplet peaks, occur over the range 1170—1000 cm.$^{-1}$, and these also are presumably connected with some kind of P–O ionic stretching. Although the ranges in which absorption occurs shown in Table 1 appear to be shifted to higher frequencies in some cases, no correlation could be found between the position of the absorption in each salt and the type of anion.

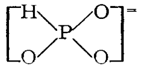
The P–O–P *Linkage.*—Our results show that compounds containing P–O–P links produce characteristic absorptions near 900 and near 700 cm.$^{-1}$. Limited studies with organophosphorus compounds have attributed bands near 700 cm.$^{-1}$ to P–O–P stretching (Holmstedt and Larson, *Acta Chem. Scand.*, 1951, **5**, 179) and bands at 950—930 cm.$^{-1}$ to P–O–P links (Bergmann, Littauer, and Pinchas, *loc. cit.*). The P–O–P stretching bands near 900 cm.$^{-1}$ appear to shift towards lower frequencies with increasing length of the P–O–P chain, in the pyrophosphate, triphosphate, and linear metaphosphate series of salts. The absorption near 700 cm.$^{-1}$, which also appears to be connected with P–O–P linkages, usually consists of two peaks in the triphosphates and metaphosphates, but only one peak in the case of pyrophosphates which contain a single P–O–P linkage. The cyclic metaphosphates show absorption near 700 cm.$^{-1}$ and also near 770 cm.$^{-1}$, the latter band replacing the one nearer 900 cm.$^{-1}$ in the chain compounds. The lower vibrational frequencies in the cyclic derivatives may be characteristic of P–O–P linkages in such ring systems.

The P–O–P stretching region at 940—850 cm.$^{-1}$ can be compared with Si–O–Si stretching at 1050—1025 cm.$^{-1}$ (Richards and Thompson, *J.*, 1949, 124) and P–O–$C_{\text{Aliphatic}}$ at 1070—1010 cm.$^{-1}$ (Bellamy and Beecher, *loc. cit.*). Wright and Hunter (*J. Amer. Chem. Soc.*, 1947, **69**, 803) attribute very strong absorption near 400 cm.$^{-1}$ to Si–O bending in Si–O–Si chains and suggest harmonics of this vibration near 800 cm.$^{-1}$ in several methylsiloxanes. The bands observed near 700 cm.$^{-1}$ in the phosphates containing P–O–P linkages may likewise be due to harmonics of P–O bending.

P–H *Linkage*.—Previous studies with phosphine (Herzberg, *op. cit.*, p. 164) and with organophosphorus compounds (Bellamy and Beecher, *J.*, 1952, 475; Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 883) have established a band at 2400—2300 cm.$^{-1}$ as due to P–H stretching. Our findings support this contention, absorptions being found at 2430—2300 cm.$^{-1}$ in phosphites and 2400—2280 cm.$^{-1}$ in hypophosphites. Moreover, when comparable specimens of a phosphite and a hypophosphite were used, the latter was invariably found to give a much stronger peak. This is to be expected if there are two P–H linkages in one instance and only one in the others, and is compatible with the formulæ (I) and (II) for the hypophosphite and phosphite ions respectively.

(I)





(II)

The P–H bending frequency is to be expected in the region 1150—950 cm.$^{-1}$, but it was not observed by Daasch and Smith (*loc. cit.*), who concluded that the absorption was probably very weak. The inorganic phosphites and hypophosphites give absorptions in this region, but these may be due to other causes which are discussed below.

P–O–H *Stretching*.—Characteristic of the acid orthophosphates and acid pyrophosphates is a weak, broad absorption near 2700 cm.$^{-1}$. Absorption in this region has been assigned to P–OH stretching (Daasch and Smith, *loc. cit.*; Bellamy and Beecher, *loc. cit.*).

P–N *Stretching*.—A strong absorption appears near 700 cm.$^{-1}$ in each of the phosphoramidates. Our attribution of this to P–N stretching is supported by the following calculation: For a simple harmonic oscillator,

$$\nu = 1307\sqrt{k/\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ν is the frequency in cm.$^{-1}$, μ is the reduced mass of the two atoms concerned, and k is the force constant $\times$ 10^{-5} in dynes/cm. From Gordy's relation (*J. Chem. Phys.*, 1946, **14**, 305) for the force constant, *viz.*,

$$k = 1{\cdot}67N\left(\frac{x_{\mathrm{A}}x_{\mathrm{B}}}{d^2}\right)^{\frac{3}{4}} + 0{\cdot}30 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k is the force constant $\times$ 10^{-5} dynes/cm., N is the bond order, $x_{\mathrm{A}}, x_{\mathrm{B}}$ are the electronegativities (P = 2·1, N = 3·0), d is the internuclear distance, P–N = 1·785 Å (Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621), this gives a value of $k = 3{\cdot}08 \times 10^{-5}$ dynes/cm., which, substituted in equation (1), gives a value of $\nu_{\text{calc.}} = 738$ cm.$^{-1}$. If the three hydrogen atoms (see below) are included in the expression for the reduced mass, $\nu_{\text{calc.}} = 692$ cm.$^{-1}$, whereas the experimental value in sodium phosphoramidate is $\nu_{\text{obs.}} = 697$ cm.$^{-1}$.

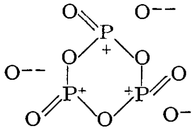
The monobasic phosphoramidates all exhibit absorption at 1618—1615 and 1470—1468 cm.$^{-1}$, which may be ascribed to zwitterion formation in this type of compound (cf. amino-acids). The existence of the phosphoramidate anion in the zwitterion form in the crystalline structure has recently been demonstrated (Hobbs, Corbridge, and Raistrick, *loc. cit.*).

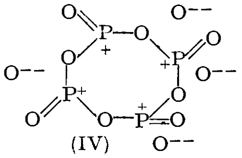
Ammonium Salts.—All the ammonium salts give two absorptions near 1400 cm.$^{-1}$, which can be ascribed to the NH_4^+ ion. Absorptions due to bonded N–H stretching appear around 3000 cm.$^{-1}$ in the phosphoramidates and in most ammonium salts.

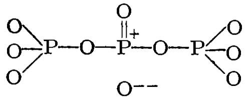
1050—850-cm.$^{-1}$ *Region*.—The assignment of P–O–P stretching at 940—850 cm.$^{-1}$ has already been discussed. Other absorptions in this region can be connected with several causes. The ν_1 symmetrical stretching frequency of the PO_4^{3-} ion might appear in special circumstances. The strong band at 950 cm.$^{-1}$ in silver orthophosphate is probably due to Ag–O covalent bond formation, as pointed out by Bergmann, Littauer, and Pinchas (*loc. cit.*). Distortion of the PO_4 tetrahedron in the silver salt has been inferred from bond-length measurements (Pauling, " The Nature of the Chemical Bond," Cornell University Press, New York, 1944, p. 243). A distorting effect might ensure from the presence of a heavy polarisable cation, as, *e.g.*, in lead orthophosphate, where a strong absorption is recorded at 981 cm.$^{-1}$.

A number of absorptions are found at 1050—850 cm.$^{-1}$ in the acid orthophosphates and acid pyrophosphates. Some of these are probably connected with the P–OH deformation frequency (Bellamy and Beecher, *loc. cit.*), while others may be due to modification of the symmetry of the PO_4 tetrahedra by the attached hydrogen atoms. Bands at about 1030 and 980 cm.$^{-1}$ in trialkyl phosphates have been attributed to antisymmetrical and symmetrical stretching, respectively, of the three P–OR groups (Bergmann, Littauer, and Pinchas, *loc. cit.*). Similar symmetrical stretching of the P–O linkages in the phosphite and phosphoramidate ions may account for the absorption observed in the 980-cm.$^{-1}$ region in these compounds.

Miscellaneous Bands.—The strong peaks observed in the 1100-cm.$^{-1}$ region in the metaphosphates have already been associated with ionic P–O stretching; the bands near 1000 cm.$^{-1}$ may also result from a stretching mode of the ionic phosphate groupings. The very strong bands in the 1300—1200 cm.$^{-1}$ region are not, however, easily explained. This region is normally assigned to P=O stretching and the P–O links outside the rings may be presumed to be of the same nature. The great strength of the absorption suggests a substantial ionic contribution in this linkage. Bond-length measurements on the crystal structure of ammonium tetrametaphosphate (Romers, Ketelaar, and MacGillavry, *Acta Cryst.*, 1951, **4**, 119) reveal significant shortening of the P–O bonds external to the ring. Structures such as (III), (IV), and (V) may make a significant contribution to the resonating state of these anions, thus accounting for both the short bonds and the strong absorption.


(III)


(IV)


(V)

The bands at about 1400—1220 cm.$^{-1}$, generally of medium intensity, in the acid phosphates may be due to a combination of the P–O stretching frequency with a lattice band, as suggested by Oberly and Weiner (*J. Chem. Phys.*, 1952, **20**, 740).

The very strong peaks near 820 cm.$^{-1}$ in the hypophosphites may be connected with torsional oscillations or rocking motions of the ion, since it is unlikely they are connected with P–H bending or P–O bending.

Effect of Positive Ions.—The influence of the cations on the spectra do not appear to be very marked, except in the case of the silver salts. In all silver salts, a pronounced shift of some peaks to lower frequencies is observed. This is particularly evident with those absorptions in the ionic P–O stretching region, as, *e.g.*, with the orthophosphate, pyrophosphate, and triphosphate salts. These shifts are probably bound up with the tendency for formation of silver–oxygen covalent bonds (see p. 501). Shift of peaks to lower frequencies in the case of some lead salts occurs, but is of a less marked extent.

With the remaining salts, a tendency for the shift of certain peaks to lower frequencies with increasing mass of the cation is noticeable in a few cases, but no systematic correlation between frequency and any property of the positive ion could be found. This progressive shift is most evident with the group of strong peaks in the ionic P–O stretching region, with the Mg, Ca, Sr, Ba, and Pb salts of the tribasic orthophosphates and pyrophosphates.

This work is being extended to other phosphorus compounds, and measurements will be made in the potassium bromide region. A more detailed correlation of absorption with molecular structure may be possible with the aid of Raman and polarised infra-red techniques. Particular interest lies in the crystalline and glassy metaphosphates, where infra-red absorption studies may throw some light on their constitution.

We thank Mr. J. E. Such and other members of the staff for providing some of the compounds used in the investigation.

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[*Received, May* 26*th*, 1953.]