304. The Vibrational Spectra and Structures of Dithionate, Hypophosphate, and Related Ions.

By W. G. Palmer.

Complete assignment of the vibrational frequencies observed in the spectra of dithionate and hypophosphate reveals the close structural similarity of these ions and appears to demand the symmetry D_{3d} for hypophosphate as well as for dithionate. The spectra of the acid ion $H_2P_2O_6^{2-}$ and of diphosphate $P_2O_7^{4-}$ are compared with those of hypophosphate. The relation of vibrational frequencies to bond strengths and orders in the oxy-anions of sulphur and phosphorus is briefly discussed.

Although the formula $H_4P_2O_6$ has long been accepted for hypophosphoric acid, there is still some doubt about the structure of the corresponding ion $P_2O_6^{4-}$. No examination by *X*-ray diffraction leading to definite atomic positions in a hypophosphate has yet appeared, although a preliminary study of the salt $(NH_4)_2H_2P_2O_6$ resulted in tentative suggestions about the structure of the ion $H_2P_2O_6^{2-}$.[1] Raman spectra of aqueous solutions of the pure acid and of the salts $K_2H_2P_2O_6$ and $(NH_4)H_3P_2O_6$ have been observed but the polarization properties were not recorded.[2,3] It has been proved [4,5] that on controlled oxidation of hypophosphate by halogens the sole product is diphosphate. Although it is possible to explain this observation on the basis of structure (II),[5] yet structure (I) seems the more natural deduction for the hypophosphate ion. On the other hand, examination of hypophosphate by the method of nuclear magnetic resonance has strongly supported the symmetrical formula (II).[6]

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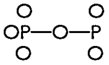
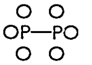
[1] Raistrick and Hobbs, *Nature*, 1949, **164**, 113.
[2] Gupta and Majumdar, *J. Indian Chem. Soc.*, 1942, **19**, 286.
[3] Baudler, *Z. anorg. Chem.*, 1955, **279**, 115.
[4] Blaser and Halpern, *Z. anorg. Chem.*, 1933, **215**, 33; Blaser, *Chem. Ber.*, 1953, **86**, 563.
[5] Palmer, *J.*, 1961, 1079.
[6] Callis, Van Wazer, Schoolery, and Anderson, *J. Amer. Chem. Soc.*, 1957, **79**, 2719.

It is plain that structure (I) or (II) could be excluded if both the infrared and Raman spectra of the ion were adequately known. The structures correspond to two extreme relations between the two types of spectra: all fundamentals of (I) will in principle be active in both spectra, while the two spectra of (II), if as is most probable it has the symmetry D_{3d}, will contain no frequencies in common (Table 1). Further evidence can be sought in the relations between the spectra of $P_2O_6^{4-}$ and $S_2O_6^{2-}$, which has been conclusively assigned the structure analogous to (II) by *X*-ray methods.[7] Although the experimental difficulty of observing a complete Raman spectrum of $P_2O_6^{4-}$ frustrated this simple and direct approach, it can at least be claimed that the present investigation has produced no support for (I) and much evidence in favour of (II).

(I) 

$$\overset{O}{\underset{O}{OP}}\text{—O—}\overset{O}{\underset{O}{P}}$$

 (II)

$$\overset{O}{\underset{O}{OP}}\text{—}\overset{O}{\underset{O}{PO}}$$

In general, the observation and analysis of the infrared and Raman spectra of a compound afford a means of discovering its structure ranking in power with diffraction methods (if the structure has a fair degree of symmetry), but some disturbing features enter when the compound is an oxy-anion. It is then probably impossible to observe spectra of which the frequencies are entirely specific to the ion, and owe nothing to its environment, which may include the chemical nature, size, and charge of the cation, and the presence of water of hydration when observations are made upon crystal powders or " mulls; " nor can the effect of an environment of water in the concentrated solutions employed for the Raman effect be excluded. Such influences upon frequencies appear to be sporadic and usually vary both in sign and magnitude over the range of frequencies concerned, so that corrections for shift, from one salt to another, from solution to crystal, or even from a Nujol mull preparation to that of a KBr disc, are valid over only short ranges.

It appears wise to rely, for structural purposes, mainly on salts of the alkali metals, and to employ them, when normally hydrated, in anhydrous condition whenever the removal of water of hydration can be isolated from further possible decomposition. In spite, however, of such obvious precautions, it is not to be expected that absolute frequencies can be assigned to fundamentals and combination bands of such ions as are concerned in the present investigation with the precision attainable in the study of volatile, electrically neutral compounds. For such reasons correlation with the behaviour of a neutral compound of parallel type and comparable force constants, such as C_2F_6, the spectra of which have been fully analysed,[8] has proved helpful during the present work.

Of the 18 possible fundamentals of a molecule or ion A_2X_6 of symmetry D_{3d}, eight of type *u* and nine of type *g* are allowed only in the infrared and Raman spectra respectively (Table 1). In each set of fundamentals, six, being doubly degenerate (E_u and E_g) yield only three frequencies. Therefore, if $P_2O_6^{4-}$ has structure (II) with symmetry D_{3d} a full assignment of its spectra must show in all 11 distinct frequencies, five in the infrared and six in the Raman spectrum. It is to be expected that the highest four frequencies [one doubly degenerate (*E*) and one single (*A*) in each spectrum] will correspond to $P-(O)_3$ stretching vibrations, followed at a much lower average frequency by the four $P-(O)_3$ deformation frequencies (also one doubly degenerate and one single in each spectrum). Lastly, at the lowest frequencies will come the vibrations in which PO_3 acts principally as a single, heavy unit: PO_3-PO_3 stretching and rocking. For ions related in structure to $P_2O_6^{4-}$, such as the acid ion $H_2P_2O_6^{2-}$, diphosphate $P_2O_7^{4-}$, and phosphite HPO_3^{2-}, the lower symmetry permits all (or nearly all) of the vibrations to be active in the infrared spectrum, which for all these ions is more readily accessible than the Raman spectrum.

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[7] Barnes and Wendling, *Z. Krist.*, 1938, **99**, 153; Stanley, *Acta Cryst.*, 1953, **6**, 187; Martinez, Garcia-Blanco, and Rivoir, *ibid.*, 1956, **9**, 145.

[8] Nielson, Richards, and McMurry, *J. Chem. Phys.*, 1948, **16**, 67; Nielson and Gullikson, *ibid.*, 1953, **21**, 1416.

In the task of assigning frequencies to $P_2O_6^{4-}$ it is therefore very helpful to consider related frequencies in the infrared spectra of these other ions.

EXPERIMENTAL

Infrared spectra were observed on a Perkin–Elmer spectrophotometer No. 21, in the range 5000—400 cm.$^{-1}$ (2—25 μ, NaCl and KBr prisms) for alkali-metal dithionates and hypophosphates, and in the NaCl range (5000—625 cm.$^{-1}$) for the latter salts of a number of other cations. As far as possible, hydrated salts were rendered anhydrous before being " mulled " in Nujol or hexachlorobutadiene, or distributed in a KBr disc. An infrared spectrum in the NaCl range for a saturated solution of $K_4P_2O_6$ was successfully obtained from a film between silver chloride plates. The Raman spectrum of the same concentrated solution was examined in the Laboratory of Inorganic Chemistry at Oxford by the most generous co-operation of Dr. L. A. Woodward, who reported that the ion $P_2O_6^{4-}$, like the corresponding di-acid ion,[3] proved to be an intrinsically weak scatterer, and only three frequencies (out of a possible six for symmetry D_{3d}) could be identified. Fortunately, the well-defined combination frequencies observable in the infrared spectra allowed the remaining Raman frequencies to be calculated satisfactorily, and those observed to be confirmed.

Raman spectra of sodium dithionate have been fully explored for aqueous solution,[9] and sufficiently for the crystalline powder,[10] to ascertain the shift in frequencies on passing from the dissolved to the crystalline state. The infrared spectra of sodium and potassium dithionates have been re-examined, as doubt existed about the absolute frequencies previously published.[11]

Preparation and Purity of Materials.—(a) *Dithionates.* The sodium salt $Na_2S_2O_6,2H_2O$ and the anhydrous potassium salt were obtained by oxidation of sulphite with silver nitrate.[12] When finally purified neither of the salts gave any qualitative indication for nitrate or sulphate, nor did the infrared spectra reveal any known frequency of these ions. At 115° *in vacuo* the sodium salt lost 14·88% as water, and the resulting solid 31·2% as SO_2 on ignition (Calc.: 14·87 and 31·1%, respectively). The potassium salt lost 27·0% as SO_2 on ignition (Calc.: 27·0%).

(b) *Hypophosphates.* The salts required were obtained by standard operations from an initial stock of sodium hypophosphate prepared as described elsewhere,[5] where will also be found the methods by which purity was confirmed. Particular care was taken to ascertain that salts requiring dehydration suffered thereby no chemical change other than loss of water. To observe the Raman spectrum of $P_2O_6^{4-}$ three nearly saturated aqueous solutions of $K_4P_2O_6$ were prepared from pure $K_2H_2P_2O_6,2H_2O$ and potassium hydroxide, containing respectively 10, 25, and 50% excess of potassium hydroxide over that required stoicheiometrically. All three solutions gave identical spectra.

RESULTS AND DISCUSSION

The terminology to be used is set out in Table 1.

Dithionate, $S_2O_6^{2-}$.—For dithionate ion it has been possible to assign all eleven frequencies allowed for the symmetry D_{3d} and to amplify the *X*-ray analysis. The fundamentals listed in Table 9 are referable to the anhydrous sodium salt, although for $S_2O_6^{2-}$ the frequency shifts between the anhydrous sodium and potassium salts, and between preparations of the sodium salt under various conditions, are slight and no corrections were attempted. In assigning the combination frequencies (Table 2), which for symmetry D_{3d} follow the $g \times u$ rule, fundamentals, with the exception of ν_{12}, have been taken from observations on the powdered dihydrate, $Na_2S_2O_6,2H_2O$. Assignments of the six Raman frequencies, which fall into the expected three pairs, follow almost automatically from their polarization properties. The totally symmetrical breathing frequency ν_1 is, as in most other cases, by far the most intense in the Raman spectrum, especially when observed in aqueous solution, and as usual the degenerate frequencies E_g are all notably weaker than their non-degenerate counterparts A_{1g}.

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[9] Gerding and Eriks, *Rec. Trav. chim.*, 1950, **69**, 724.

[10] Eucken and Wagner, *Acta Phys. Austrica*, 1947—48, **1**, 339.

[11] Lecomte and Duval, *Compt. rend.*, 1943, **217**, 42; *Bull. Soc. chim. France*, 1944, **11**, 376.

[12] Baubigny, *Ann. Chim. Phys.*, 1910, **20**, 5; Palmer, " Experimental Inorganic Chemistry," Cambridge, 1954, p. 361.

TABLE 1. *Classification of infrared and Raman fundamental frequencies.*

	Type of vibation	Infrared spectrum		Raman spectrum	
A_2X_6: D_{3d}	A–X stretching	ν_5, A_{2u}	ν_7, E_u	ν_1, A_{1g}	ν_{10}, E_g
	AX_3 deformation	ν_6, A_{2u}	ν_8, E_u	ν_2, A_{1g}	ν_{11}, E_g
	A–A stretching			ν_3, A_{1g}	
	AX_3 rocking		ν_9, E_u		ν_{12}, E_g
	AX_3–AX_3 torsion	ν_4, A_{1u} *			

* Inactive as a fundamental.

A_2X_6: D_{3h} Frequencies as for D_{3d}, with the addition that ν_7, ν_8, and ν_9 may also occur in the Raman spectrum (as depolarized radiation).

Vibrations of species A_{1g} give polarized radiation, and those of species E_g depolarized radiation, in the Raman spectrum.

HAX_3: C_{3v}	Infrared and Raman spectra	
(HA)–X stretching	ν_2, A_1	ν_5, E
$(HA)X_3$ deformation	ν_3, A_1	ν_6, E

(The numbering of the fundamentals follows that of Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," New York, 1946.)

TABLE 2.*

Dithionates *Observed frequencies* (*cm.*$^{-1}$)

Infrared spectra (preparation in Nujol mull unless otherwise stated).

$Na_2S_2O_6,2H_2O$	$Na_2S_2O_6$	$K_2S_2O_6$	Assignment
2320 (w)	2326 (w)	2326 (m)	$\nu_1 + \nu_7$ (2337)
2198 (m)	2203 (s)	2208 (s)	$\nu_{10} + \nu_5$ (2216)
2083 (s)	2088 (m)	2083 (m)	$\nu_1 + \nu_5$ (2102)
1240 (10, v sp)	1235 (10, v sp)	{1240 (10, v sp) {1212 (4, v sp)	ν_7, E_u
1000 (9, v sp)	1000 (9, v sp)	996 (7, v sp)	ν_5, A_{2u}
760 (s)	760—700 (sh)	{760—770 (sh) {707 (s) [1], 710 (m) [2], {711 (w) [3]	$\nu_{11} + \nu_9$ $\nu_5 - \nu_3$ (707)
N.I.	N.I.	{584 (10, v sp) [1] {570 (10, v sp)	ν_6, A_{2u}
N.I.	N.I.	{514 (5, v sp) [1] {518 (8, v sp)	ν_8, E_u

Raman spectra

$Na_2S_2O_6$ (aqueous solution)	$Na_2S_2O_6,2H_2O$ (crystal powder)	Assignment
1206 (1, dp)	1216 (4, dp)	ν_{10}, E_g
1092 (10, p)	1102 (7, p)	ν_1, A_{1g}
710 (6, p)	710 (6, p)	ν_2, A_{1g}
550 (1, ?)	556 (0, dp ?)	ν_{11}, E_g
320 (4, ?)	—	ν_{12}, E_g
281 (8, p)	293 (4, p)	ν_3, A_{1g}

* Maximum of intensity scale for fundamentals, 10: v sp, very sharp. Intensities of combination frequencies: s, strong; m, medium; w, weak; sh, shoulder.

[1] Preparation in KBr disc: spectrum in KBr range. [2] Preparation in hexachlorobutadiene mull: spectrum in KBr range. [3] Preparation in Nujol mull: spectrum in NaCl range: combination frequency completely resolved from Nujol frequency at 720 cm.$^{-1}$.

Raman spectra: p, polarized; dp, depolarized. N.I.: Not investigated.

In the infrared spectrum of sodium dithionate and its dihydrate two sharply defined fundamentals are observed in the NaCl range, and the higher of these is sharply resolved into a doublet in the corresponding spectrum of potassium dithionate. Such splitting is taken to mean that the frequency is that of a degenerate vibrational mode and may be assigned as ν_7, E_u, leaving the lower frequency, at about 1000 cm.$^{-1}$, as ν_5, A_{2u}. The corresponding fundamental ν_7 from the hydrated sodium salt is not resolved but definitely shows indications of a shoulder. Both the potassium and the hydrated sodium salt have 4 molecules per unit cell, with complicated but quite different crystal structures from which a specific cause of the removal of degeneracy is not easily discerned. Although neither of the very sharply defined fundamentals round 577 and 516 cm.$^{-1}$ in the spectrum of potassium dithionate in the KBr range reveals degeneracy in a similar way, they are assigned respectively to the deformation frequencies ν_6, A_{2u} and ν_8, E_u by analogy with corresponding frequencies in hypophosphate spectra, where, as will appear later, the reasons for the particular assignment are rather clearer.

The three high combination frequencies, well defined in all the spectra observed, are easily and unambiguously assigned as shown in Table 2. If the two lower frequencies at 760 and 710 cm.$^{-1}$ are both regarded as binary summation terms their possible Raman constituents are ν_3, ν_{11}, and ν_{12}. Since there are certainly no infrared-active fundamentals in the observed range from near the lower limit of the KBr range at 400 cm.$^{-1}$ to ν_8 at 518 cm.$^{-1}$, we derive the possible frequencies 154, 204, and 390 cm.$^{-1}$ from which to select the two remaining fundamentals ν_9 (symmetrical SO_3 rocking) and ν_4 (torsion round the S–S axis). The frequency ν_9 will very probably be lower than that of the unsymmetrical rocking ν_{12} observed in the Raman spectrum at 320 cm.$^{-1}$; moreover the assignment of ν_9 as 204 cm.$^{-1}$ falls appropriately into the group of degenerate frequencies E_u:

E_u	C_2F_6	$S_2O_6^{2-}$
ν_7	1251	1240
ν_8	523	518
ν_9	216	204

As ν_4 will certainly enter as the minimal fundamental, we could select for this 154 cm.$^{-1}$, and assign the frequency at 710 cm.$^{-1}$ as ν_{11}, $E_g + \nu_4$, A_{1u}, a combination allowed in both symmetries D_{3d} and D_{3h}. However, it is equally possible to assign this frequency as the *difference* term $\nu_5 - \nu_3$, as shown in Table 2. In spite of careful search,[8] no combination frequency involving ν_4 could be traced in the whole extent of the infrared spectrum of C_2F_6, nor do any such occur with certainty in the spectrum of C_2H_6. Since the term $\nu_5 - \nu_3$ does occur unambiguously (though weakly) in the C_2F_6 spectrum, it may be presumed to represent the most probable interpretation of the $S_2O_6^{2-}$ frequency at 710 cm.$^{-1}$. The corresponding summation term would be masked by its proximity to the very intense fundamental ν_7.

The coincidence of the infrared frequency round 710 cm.$^{-1}$ with the Raman frequency assigned as ν_2 is certainly fortuitous. In the three separately observed infrared spectra in which fundamentals as well as the frequency 710 cm.$^{-1}$ occur, the last, although always very sharply defined, has only the secondary intensity appropriate to a combination frequency. If $S_2O_6^{2-}$ possessed the ("eclipsed") symmetry D_{3h} then the fundamentals ν_7, ν_8, and ν_9 could appear in both the infrared and the Raman spectra, but in all three cases as depolarized radiation in the latter. On the contrary, the radiation of the frequency ν_2, which shows high intensity in both Raman spectra, is quite certainly polarized.

Diphosphate, $P_2O_7^{4-}$.—From a Nujol mull of the anhydrous sodium salt, obtained from the pure decahydrate by heating it *in vacuo* at 115°, the following fundamentals were observed in the NaCl range of the infrared spectrum:[13]

cm.$^{-1}$	cm.$^{-1}$
1152 (10) 1121 (10) } partially resolved, sp	987 (5, v sp) 917 (10, m)
1030 (5, v sp)	735 (10, v sp)

(Maximum of intensity scale, 10: v sp, very sharp; sp, sharp; m, medium definition.)

The ion $P_2O_7^{4-}$ has symmetry C_{2v}[14] and none of the possible stretching vibrations of the PO_3 groups is degenerate. Consequently, six distinct frequencies are to be expected ($2A_1$, $2B_1$, A_2, and B_2) of which only one, A_2, is forbidden in the infrared spectrum. It seems clear that at least four of the remaining five frequencies are included in the infrared range 987—1152 cm.$^{-1}$. The frequencies at 917 and 735 cm.$^{-1}$ may plausibly be assigned to two of the three possible P–O–P vibrations, all of which are active in the infrared region.

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[13] Cf. Corbridge and Lowe, *J.*, 1954, 493.

[14] MacArthur and Beevers, *Acta Cryst.*, 1957, **10**, 428.

Hypophosphate Ions.—(1) *The di-acid ion* $H_2P_2O_6^{2-}$. It must be assumed in view of the dissociation constants of hypophosphoric acid [15] that the Raman spectra of concentrated solutions of the free acid and of the salts $(NH_4)H_3P_2O_6$ and $K_2H_2P_2O_6$ previously observed [2,3] relate to the ion $H_2P_2O_6$ and not to $P_2O_6^{4-}$. The relation of the infrared spectrum of $Na_2H_2P_2O_6$ to these Raman spectra fully bears out this assumption (Table 3).

TABLE 3.* *Sodium dihydrogen hypophosphate*, $Na_2H_2P_2O_6$.

Infrared (cm.$^{-1}$) $Na_2H_2P_2O_6$ (nm.) (NaCl and KBr ranges)	Raman * (cm.$^{-1}$) $(NH_4)H_3P_2O_6$ aq. solution	Interpretation	Related frequencies in $P_2O_6^{4-}$ (cm.$^{-1}$)
2252 (3, b)		O–H–O stretching	
1695 (4, v b)		O–H–O deformation	
1339 (5, v sp)			
1186 (10, v sp)	1175 (2, b)	$PO_2(OH)$ stretching	ν_{10}, E_g, 1168
1050 (8, sp)	1069 (6, b)		ν_7, E_u, 1090
1026 (6, sp)			ν_1, A_{1g}, 1060
943 (7, sp)	957 (2, b)		ν_5, A_{2u}, 942
867 (5, sp)			
676 (5, v sp)	651 (5)	$PO_2(OH)$ deformation	ν_2, A_{1g}, 666
513 (7, m)			ν_8, E_u, 495
475 (3, m)	461 (3, b)		
455 (7, m)			
N.I.	278 (6, d)	P–P stretching	ν_3, A_{1g}, 275

* Maximum of intensity scale, 10; v sp, very sharp; sp, sharp; m, medium definition; b, broad; vb, very broad; d, diffuse (Baudler [3]). N.I., not investigated. nm. Nujol mull.

The infrared spectrum of $Na_2H_2P_2O_6$, as anhydrous salt in Nujol mull, reveals no trace of absorption at frequencies above the sharp Nujol band at 2950 cm.$^{-1}$, and hence in the crystal both OH groups must be involved in hydrogen bonding, as they are well known to be in the diacid salt KH_2PO_4. In fact the frequencies (cm.$^{-1}$) of $H_2PO_4^{-1}$ and $H_2P_2O_6^{2-}$ run parallel in the region concerned:

KH_2PO_4 *	2320	1640	1300
$Na_2H_2P_2O_6$	2252	1695	1339

* Miller and Wilkins, *Ind. Eng. Chem. Analyt.*, 1952, **24**, 1253.

If the highest frequency 2252 cm.$^{-1}$ is taken to be due to O–H–O stretching then, according to Lord and Merrifield,[16] the O–O distance should be close to 2·52 Å, as found by neutron diffraction [17] in potassium dihydrogen phosphate.

The frequency at 1186 cm.$^{-1}$ and those below are reasonably to be assigned to modes of vibration within the ion itself. In the last column of Table 3 the frequencies in $P_2O_6^{4-}$ most closely related in type to those of the acid ion are indicated.

It will be seen from Table 3 that at least four of the fundamentals in the infrared and Raman spectra severally lie within 10—20 cm.$^{-1}$ of one another. This close relation can hardly be fortuitous, and when account is taken of the shift of frequency so often consequent upon the change from solution to crystal, and encountered again in the work on $S_2O_6^{2-}$ and $P_2O_6^{4-}$ with proved values of the shifts, it becomes highly probable that the symmetry of the acid ion is such as to allow most of the frequencies to be common to both spectra. It is unfortunate that no polarization properties were recorded for the Raman frequencies.

(2) *The normal ion* $P_2O_6^{4-}$. In normal hypophosphates, containing a quadruply charged anion, the interionic crystal field must be much stronger than that in the dithionates, with only a doubly charged anion. Consequently, the cationic influence upon anionic vibration frequencies is more emphatic in the former salts, and in analysing their spectra and assigning the anionic frequencies to fundamental types it becomes essential

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[15] Schwarzenbach and Zure, *Monatsh.*, 1950, **81**, 202.

[16] Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166.

[17] Bacon and Pease, *Proc. Roy. Soc.*, 1953, *A*, **220**, 397.

always to refer them to the same cation: the sodium cation, in the anhydrous salt $Na_4P_2O_6$, has been so chosen in the present investigation.

Table 4 shows the influence of a variety of cations in salts examined in Nujol mulls upon the non-degenerate infrared active P–O stretching frequency ν_5, which was also observed for the potassium salt $K_4P_2O_6$ in 50% aqueous solution. Cations intrinsically large, or smaller cations enlarged by much water of hydration (Section A), shift the frequency only slightly from its value in solution. The frequencies in Sections B and C, which comprise cations of rare-gas configuration, appear to illustrate mainly increasing frequency caused by decreasing cation radius and therefore increasing crystal field strength; but the actual crystal structure (at present unknown), as well as the possibility of hydrogen bonding between anion and hydration water, no doubt also play their parts. On the contrary, large cations not of rare-gas configuration (Section D) depress the frequency substantially below that observed in solution, possibly owing to incipient covalent linking.

We shall at first assume that the anion $P_2O_6^{4-}$, like dithionate, has the symmetry D_{3d}, and then show that this assumption leads to a consistent scheme of assignments. Of the eleven possible active frequencies, seven have been directly observed, although, as mentioned before, two of the three Raman frequencies observed from an aqueous solution of the potassium salt needed confirmation, which, as well as the missing frequencies, was forthcoming from well-defined combination frequencies (Table 5).

TABLE 4. *Frequency shifts for* $P_2O_6^{4-}$ *with change of cation.* $K_4P_2O_6$, *in* 50% *solution,* $\nu_5 = 909$ cm.$^{-1}$.

Cation, and water of hydration of the salt (Nujol mulls)	ν_5, A_u (cm.$^{-1}$)	Cation, and water of hydration of the salt (Nujol mulls)	ν_5, A_u (cm.$^{-1}$)
(A) $Co(NH_3)_6Na,4H_2O$	911	(C) Ba_2, anhydrous	917 † 901
$K_2Na_2,10H_2O$	911 *	$Ca_2,2H_2O$	922 *
Ce(IV),H_2O	915	Mg_2,H_2O	940
$Na_4,10H_2O$	916 *	(D) Tl_4, anhydrous	873
(B) K_4, anhydrous	923	Ag_4, anhydrous	877
$Li_4,7H_2O$	929	Pb_2, anhydrous	896
Li_4,H_2O	935		
Na_4, anhydrous	942		

* From Corbridge and Lowe, *J.*, 1954, 4555. † See text.

Of the highest three frequencies observed in aqueous solution that at 1023 cm.$^{-1}$ is certainly the strongest in the full Raman spectrum and may therefore be at once assigned as ν_1, A_{1g}, the totally symmetric breathing frequency. The infrared frequencies at 1064 and 909 cm.$^{-1}$ are clearly the two stretching frequencies ν_5 and ν_7. In the spectra of solid hypophosphates (Tables 5 and 6) there is abundant evidence (splitting or broadening) that a double degeneracy is removed from the vibrational mode corresponding to the higher frequency, while the lower remains single and sharply defined. The spectrum of barium hypophosphate, $Ba_2P_2O_6$, provides a unique exception to this regularity. Two separate specimens of this salt, one prepared in crystalline condition by adding barium chloride to a mixture of $Na_2H_2P_2O_6$ and sodium acetate in aqueous solution, and the other by neutralizing the acid sodium salt with aqueous barium hydroxide, gave as Nujol mulls, identical spectra, which entirely confirmed the results of Corbridge and Lowe.[18] In these spectra the higher frequency is sharply resolved into a *triplet*, and the lower equally sharply into a *doublet* (Table 6). Without a knowledge of the crystal structure of the salt an explanation can hardly be attempted, but it is not possible for the spectra of a *free* molecule or ion of the composition A_2X_6 to contain a frequency corresponding to a genuine triply degenerate vibrational mode. A large balance of evidence thus favours the assignment of the higher frequency to ν_7, E_u, and of the lower to ν_5, A_{2u}, as in the case of dithionate.

With the aid of the frequencies observed for ν_5 and ν_7 in the infrared spectra of solid

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[18] Corbridge and Lowe, *J.*, 1954, 4555.

Table 5. *Hypophosphates: Alkali-metal salts. Observed frequencies* (*cm.*$^{-1}$).

Infrared spectra.

$K_4P_2O_6$ aq. soln.	$K_4P_2O_6$ Nujol	$Na_4P_2O_6$ (1) Nujol (2) KBr disc	$Li_4P_2O_6,7H_2O$ Nujol	$Li_4P_2O_6,H_2O$ Nujol	Assignment
		2208 (vw)			$\nu_7 + 2\nu_6$ (2214)
		2208 (w)			
		2150 (m)			$\nu_7 + \nu_1$ (2152)
		2150 (m)			
		2114 (m)			$\nu_{10} + \nu_5$
		2105 (m)			
		2010 (s)			$\nu_1 + \nu_5$ (2004)
		2000 (s)			
		1961 (vw)			$\nu_5 + 2\nu_{11}$ (1958)
		1961 (w)			
		—			
		1450 (s)			$\nu_{11} + \nu_5$
		—			
		1420 (s)			$\nu_7 + \nu_{12}$
1064 (10, b)	1075 (10, sp)	1085 (10, b)	1093 (8, v sp)	1080 (10, vb)	ν_7, E_u
	1037 (8, sh)	1083 (10, sp)	1064 (10, sp)		
909 (8, sp)	923 (5, v sp)	942 (8, v sp)	929 (8, v sp)	935 (8, sp)	ν_5, A_{2u}
		942 (7, v sp)			
	879 (sh)		877 (s)	870 (w)	$\nu_2 + \nu_9$
		770 (sh) [1]			$\nu_3 + \nu_8$
		—			
		—			
		710 (m)			$\nu_9 + \nu_{11}$
		568 (10, sp)			ν_6, A_{2u}
		557 (10, sp)			
N.I.		517 (s)	N.I.		$\nu_9 + \nu_{12}$
		—			
		493 (8, v sp)			ν_8, E_u
		495 (8, v sp)			

Raman spectrum.

$K_4P_2O_6$, aq. soln.	Assignment
1023 ± 5	ν_1, A_{1g}
666 ± 10	ν_2, A_{1g}
ca. 320	ν_{12}, E_g

General notes: see earlier Tables. [1] Observed in both the NaCl and the KBr range.

Table 6.

Hypophosphates: Other rare-gas cations.

Salt, examined in Nujol mull	ν_7, (E_u)	ν_5, (A_{2u})
$Mg_2P_2O_6,H_2O$	1094 (10, vb) 1042 (8, sh)	940 (8, m)
$Ba_2P_2O_6$	1111 (10, v sp) 1081 (10, v sp) 1058 (7, v sp)	917 (10, v sp) 901 (10, v sp)
CeP_2O_6,H_2O	1080 (10, vb)	915 (5, sp)
Hypophosphates: Non-rare-gas cations.		
$Tl_4P_2O_6$	1053 (7, m) 1000 (10, m)	873 (10, v sp)
$Pb_2P_2O_6$	1081 (8, sh) 1047 (10, sp)	896 (5, v sp)
$Ag_4P_2O_6$	1031 (10, vvb)	877 (9, m)
$Co(NH_3)_6NaP_2O_6,4H_2O$ *	1058 (10, m)	911 (5, sp)

* Observation of the spectrum of $Co(NH_3)_6PO_4,4H_2O$ enabled cationic frequencies to be eliminated from the spectrum of the hypophosphate salt.

$Na_4P_2O_6$ or $K_4P_2O_6$, together with well-defined combination frequencies interpreted by the $g \times u$ rule, we calculate the Raman frequency ν_1 as it would be observed by using the solid salts (Table 7). The substantial upward shift of this Raman frequency is similar to that shown directly by ν_7 (1064 to 1085 cm.$^{-1}$ in the sodium salt) and ν_5 (909 to 942 cm.$^{-1}$ in the sodium salt) in the change from $K_4P_2O_6$ solution to $Na_4P_2O_6$ solid. In seeking the remaining stretching frequency ν_{10}, which is commonly of weak intensity and is obscured in the observed Raman spectrum, we notice, first, that in the infrared spectrum of $H_2P_2O_6^{2-}$, in addition to frequencies obviously corresponding to ν_5 and ν_7, another occurs (in both infrared and Raman spectra) at 1175—1186 cm.$^{-1}$. Secondly, the highest stretching frequency registered in the infrared spectrum of $P_2O_7^{4-}$ lies at 1152 cm.$^{-1}$. If from the well-defined high-frequency combination terms at 2150, 2110, and 2000 cm.$^{-1}$, each occurring in at least two of the spectra of $P_2O_6^{4-}$, as shown in Table 5, we deduct the infrared frequencies ν_5 and ν_7, we obtain for ν_{10} by the $g \times u$ rule, the possible Raman frequencies 1208 and 1168 cm.$^{-1}$. Of these the latter has been preferred.

The frequencies at 568, 567, and at 493, 495 cm.$^{-1}$ observed in the infrared spectrum of sodium hypophosphate in Nujol mull and KBr disc preparations respectively are without doubt the P–O deformation frequencies ν_6, A_{2u}, and ν_8, E_u. In the infrared (or Raman) spectrum of phosphite HPO_3^{2-} the pair of corresponding deformation frequencies are as shown in Table 8.[19] Since the constitution of phosphite ion in respect to its P–O vibrations must be close to that of a " monomerized " $P_2O_6^{4-}$ ion, it appears reasonable, in the absence of other evidence, to assign ν_6 and ν_8 of the latter to the mean frequencies 562 and 494 cm.$^{-1}$, respectively.

TABLE 7.* *Shifts of the Raman frequency* ν_1, A_{1g}.

	$K_4P_2O_6$		$Na_4P_2O_6$	
Frequencies (cm.$^{-1}$)	50% aq. soln.	Xl. nm.	Xl. nm.	KBr disc
ν_7, obs. IR	1064	1075	1090	1088
ν_5, obs. IR	909	923	942	942
ν_1, obs. R	1023 (±5)			
$\nu_1 + \nu_7$, obs. IR			2150	2150
$\nu_1 + \nu_5$, obs. IR		1976	2010	2000
ν_1		1053	1060	1062
(Corrected values)			1068	1058

* Xl. nm., crystals in Nujol mull; obs. IR (or R), observed in the infrared (or Raman) spectrum.

TABLE 8.

	Raman	Infrared	
	Na_2HPO_3 in aq. soln. (cm.$^{-1}$)	K_2HPO_3 in aq. soln. (cm.$^{-1}$)	$BaHPO_3$ in Nujol mull (cm.$^{-1}$)
ν_6, E *	459 (m, dp)	465 (m, b)	471 (m) 498 (m)
ν_3, A_1	550 (vw)	567 (m)	591 (m)

* For terminology see Table 1.

In the Raman spectrum of $K_4P_2O_6$ one of the symmetrical deformation frequencies ν_2, A_{1g} and ν_{11}, E_g is revealed at 666 (±10) cm.$^{-1}$, and this from its magnitude is almost certainly the higher of the two possible frequencies. The magnitude of the strong combination frequencies at 1450 and 1420 cm.$^{-1}$ in the infrared spectrum of $Na_4P_2O_6$ (as KBr disc preparation) shows without doubt that a stretching frequency must be a constituent of each. Since only the symmetrical rocking frequency ν_9 remains to be assigned in the infrared spectrum and this can hardly lie much higher than 200 cm.$^{-1}$ (in analogy with $S_2O_6^{2-}$), we deduce, in view of the $g \times u$ rule, that the stretching frequencies concerned are limited to ν_5 and ν_7, giving the choice 330 or 487 cm.$^{-1}$, 350 or 508 cm.$^{-1}$ from which to assign the Raman frequencies ν_{11} and ν_{12}. Of these frequencies, the first is evidently ν_{12} observed in the Raman spectrum round 320 cm.$^{-1}$, and we choose the last and highest as the most probable value for the deformation frequency ν_{11}.

The two remaining assignments, the P–P stretching frequency ν_3 in the Raman spectrum, and ν_9 in the infrared spectrum, follow easily from lower summation frequencies,

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[19] Masamichi Tsuboi, *J. Amer. Chem. Soc.*, 1957, **79**, 1351.

as indicated in Table 5. A second, and lower, estimate for ν_{12} at 317 cm.$^{-1}$ is deducible from the combination frequency at 517 cm.$^{-1}$ observed only in the spectrum of a Nujol mull preparation of sodium hypophosphate (which gives ν_6 as 568 cm.$^{-1}$) and not in the KBr disc preparation (which gives ν_6 as 557 cm.$^{-1}$). The shift so illustrated between the two modes of observation may reasonably account for the apparent disparity in the values for ν_{12}: Table 9 shows a mean value.

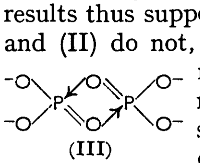
TABLE 9.* *Vibration frequencies* (cm.$^{-1}$).

	$S_2O_6^{2-}$	$P_2O_6^{4-}$		$S_2O_6^{2-}$	$P_2O_6^{4-}$
A_{1g} (Raman)			E_u (Infrared)		
ν_1	1102	1062	ν_7	1240	1085
ν_2	710	670	ν_8	516	494
ν_3	293	275	ν_9	204	200
A_{1u}			E_g (Raman)		
ν_4	—	—	ν_{10}	1216	1168
A_{2u} (Infrared)			ν_{11}	556	508
ν_5	1000	942	ν_{12}	320	323
ν_6	577	562			

In view of the *X*-ray investigations of dithionate the only question about that ion concerns the alternative symmetries D_{3h} and D_{3d}. It appears certain that there are no frequencies common to both Raman and infrared spectra, and all the observed combination frequencies have proved assignable under the $g \times u$ rule. For the symmetry D_{3h} six binary combination terms, active in the infrared, are allowed which are forbidden for D_{3d}, namely, $\nu_{7,8,9} + \nu_{8,9,7}$ and $\nu_{10,11,12} + \nu_{11,12,10}$. Of these terms four are calculable from directly observed frequencies: $\nu_7 + \nu_9$ (1756), $\nu_{10} + \nu_{11}$ (1772), $\nu_{11} + \nu_{12}$ (876), and $\nu_{10} + \nu_{12}$ (1536), but no sign of these frequencies occurs, although none of them would be masked by Nujol, water, or fundamental frequencies. The results of the spectral examination thus point strongly to the (staggered) D_{3d} symmetry for dithionate.

While the incompleteness of the observed Raman spectrum of hypophosphate must diminish the force of spectral evidence for its structure, it appears certain that the Raman frequencies ν_1 and ν_2 are absent from the infrared spectrum. In respect to ν_1, this point is made particularly clear by the observation of both spectra (in the NaCl range) on a 50% aqueous solution of potassium hypophosphate, wherein the very intense frequencies ν_1 (1023 cm.$^{-1}$), ν_7 (1064 cm.$^{-1}$) and ν_5 (909 cm.$^{-1}$) are sharply distinguished. In the KBr range there is certainly no fundamental between ν_6 at 562 cm.$^{-1}$ and the usual observational upper limit of the range at 800 cm.$^{-1}$. Structure (I) for $P_2O_6^{4-}$ is thus discredited.

As in the case of dithionate all observed combination terms in the infrared spectrum of hypophosphate conform to the $g \times u$ rule. Of the six combination terms allowed for D_{3h} but not for D_{3d} only one, $\nu_7 + \nu_8$ (1584 cm.$^{-1}$), can be calculated from directly observed frequencies, and it certainly does not occur in the infrared spectrum. However, the value of the Raman frequency ν_{10} (1168 cm.$^{-1}$) appears so firmly supported that the absence of the term $\nu_{10} + \nu_{12}$ (near 1500 cm.$^{-1}$) is very probably also significant. The experimental results thus support structure (II) with symmetry D_{3d} for hypophosphate. The forms (I) and (II) do not, however, quite exhaust the structural possibilities for $P_2O_6^{4-}$. There remains a bond diagram (III) (symmetry C_{2h}), which on account of mesomerism could develop a structure of symmetry $D_{2h}(V_h)$. Neither symmetry allows degeneracy, of which for hypophosphate the spectral evidence gives ample proof; it is also very improbable that the two additional fundamentals certain to lie in the infrared NaCl–KBr range would not have been observed.



(III)

It will be seen from Table 9 that while, as is to be expected, the rocking frequencies ν_9 and ν_{12} are practically identical in dithionate and hypophosphate, and the deformation frequencies are only moderately higher for dithionate, the P–O and S–O stretching frequencies are widely separated. This could be attributed to two major causes: inequality in the intrinsic strengths of P–O and S–O links, and the varying effect of mesomerism acting on the " single " and " double " links in the classical formulæ. The extent of the mesomeric influence can be qualitatively assessed from Table 10, where there is a comparison between the totally symmetrical (breathing) frequencies of oxy-anions of sulphur and phosphorus, which have all been observed under similar conditions in the Raman spectra of aqueous solutions. The formal bond orders, which are simply the ratios $(n_1 + n_2)/n_1$, where n_1 and n_2 are respectively the number of σ- and π-bonds to oxygen in the classical formula, ignore the increase in bond strength ensuing from mesomerism. The true bond orders should be somewhat greater, but will follow the same sequence. A general connexion between frequency and bond order may be inferred in each group of ions, and an inverse relation between frequency and bond length is implied. It is possible to see in the minor frequency differences between polythionate ions and between hypophosphate and phosphite some indications of an interaction between two X–O systems, leading to increasing mesomeric stabilization as the systems come closer together.

TABLE 10.

Anions	Totally symmetrical S,O stretching frequencies (cm.$^{-1}$)	Formal bond orders	Ref.	Anions	Totally symmetrical P,O stretching frequencies (cm.$^{-1}$)	Forma bond orders	Ref.
$S_2O_6^{2-}$ ...	1092	1·67	1	$H_2PO_2^-$...	1048	1·50	3
$S_3O_6^{2-}$ ...	1056		1	$P_2O_6^{4-}$ ...	1023		
$S_4O_6^{2-}$ ...	1042		1	HPO_3^{2-}...	993	1·33	3
SO_4^{2-}	981	1·50	2	PO_4^{3-} ...	936	1·25	4

(1) Gerding and Eriks, *Rec. Trav. chim.*, 1950, **69**, 724. (2) From closely agreeing results for sodium, potassium, and ammonium sulphates quoted in Kohlrausch, " Der Smekal-Raman Effekt," Springer Verlag, Berlin, 1931. (3) Tsuboi, *J. Amer. Chem. Soc.*, 1957, **79**, 1351. (4) Hoffman and Hanwick, *J. Chem. Phys.*, 1949, **17**, 1166.

On general grounds (*e.g.*, of electronegativity) it would be conjectured that, of P–O and S–O links of similar type and order, the former would be the stronger. The following thermal equations, taken from a recent study,[20] support such a view.

$$\text{(i)}\ SOCl_2(g) + \tfrac{1}{2}O_2 = SO_2Cl_2(g):\ \Delta H_{298^\circ} = -35{\cdot}6\ \text{kcal. mole}^{-1}$$

$$\text{(ii)}\ PCl_3(g) + \tfrac{1}{2}O_2 = POCl_3(g):\ \Delta H_{298^\circ} = -69{\cdot}1\ \text{kcal. mole}^{-1}$$

There is no significant difference in the S–Cl or S–O bond lengths on the two sides of equation (i), and the P–Cl lengths in PCl_3 and $POCl_3$ are equal.

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[20] Neale and Williams, *J.*, 1952, 4535; 1954, 2156.