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Correlation between Raman wavenumbers and P—O bond lengths in crystalline inorganic phosphates

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A linear empirical correlation was established between Raman stretching wavenumbers of phosphorus–oxygen bonds and their bond lengths in inorganic crystalline phosphates. Although established on samples of inorganic crystalline phosphates, the correlation can be applied to glassy and amorphous phosphate materials (GAMs). Their unpolarized vibrational spectra are often similar because they are determined largely by short-range order. The correlation was used to predict P—O bond length in the α-form of Li_3PO_4, which is stable over only a small range of temperatures below the melting-point. It can also be used to estimate the length of P—O single bonds, terminal P—O and O—P—O chain bonds and terminal double bonds in many technologically important amorphous materials containing phosphate groups. This correlation is expected to offer invaluable insight into the structures of phosphate species for which diffraction or other spectroscopic techniques provide incomplete structural information. That would enhance the value of Raman spectroscopy as a complementary technique in structural studies of phosphates. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: inorganic phosphates; bond lengths; force constant correlation; phosphorus–oxygen bonds

INTRODUCTION

Vibrational (infrared and Raman) spectroscopy can play a prominent role in the structural study of inorganic crystals. It is particularly useful in cases where diffraction methods fail to give unequivocal results as in glasses and amorphous materials. For these applications, correlation between diffraction results and vibrational spectroscopy becomes of practical importance.

In practical application, it is necessary first to investigate the possibility of establishing a relationship between crystallographically determined bond lengths and observed stretching wavenumbers assigned to localized diatomic units in molecules. Such a direct relationship is expected from a diatomic approximation which assumes that each distinct bond is vibrationally independent of the crystalline lattice. This approach is widely applied in bond length-wavenumber correlations and, despite its simplicity (complicated analytical expressions do not contribute to a better theoretical understanding of the correlations), is of great practical value. Recently, the diatomic approximation has been used to justify the observed relationship between molybdenum–oxygen,[1] vanadium–oxygen,[2] niobium–oxygen,[3] bismuth–oxygen,[4] tungsten–oxygen,[5] chromium–oxygen[6] and boron–oxygen[7] bond lengths and their corresponding Raman stretching wavenumbers.

Raman spectroscopy is more sensitive and in general displays narrower bands than infrared spectroscopy. Different molecular structures typically have different types of bonds and this, in turn, leads to a different set of Raman spectral features. Raman spectroscopy is an effective structural tool because it can be used to discriminate or 'fingerprint' between alternative structures proposed for chemical species. Spectroscopic assignments of observed wavenumbers take into account the mixing of all vibrational modes and this approach is different from assigning a specific wavenumber to the deformation of an isolated diatomic unit.

Within these constraints, an empirical correlation between Raman stretching wavenumbers of phosphorus–oxygen (P—O) bonds and their bond lengths in inorganic crystalline phosphates is possible. The resulting empirical relationship is discussed in the light of similar correlations developed for other systems and its applicability in the structural evaluation is shown on some examples.

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EXPERIMENTAL

The phosphates which were used in the correlation included ortho-, pyro- and metaphosphates of mono- and divalent elements. Crystallographic and Raman spectral data were taken from the literature only where good-quality matching data were available. The criterion for good-quality crystallographic data is estimated standard deviations (ESD) of <1 pm (except in $Cd_2P_2O_7$, where three of its bond lengths were given with ESD as high as 2 pm in the most recent refinement). Good spectral resolution in the case of Raman spectra was chosen to be limited to values better than 3 cm^{-1}. These data were supplemented by our experimental measurements on samples prepared by solid-state techniques and characterized by powder x-ray diffraction (Rietveld method)[8,9] and Raman spectroscopy.[10]

THEORY

Approximations

Solid-state vibrational spectra represent internal vibrations, characteristic of the complex anion, and external librations and translations of both anion and cation. Such a separation of the internal modes of the molecular unit contained within the crystal from the external modes of the crystalline lattice is an assumption of the site symmetry approximation.[11] This approximation is easily justified by the fact that, in a number of cases, the force constants (and the resulting vibrational wavenumbers) are significantly higher for the internal than for external vibrations. Internal vibrations are further separated into stretching (during which bond lengths change) and bending vibrations (during which bond angles change). Their mutual interaction is usually negligible, even though allowed by symmetry properties. For salts containing light or high-valency cations, translational wavenumbers may be of the same order of magnitude as the bending wavenumber of the complex anion. Owing to the resulting vibrational interactions and band overlap, characteristic features are restricted to the high-wavenumber part of the spectrum, corresponding to the stretching vibrations of the anion.

Whereas the site symmetry approximation assumes that each polyhedron is separated from the crystal lattice, the diatomic approximation assumes that each distinct bond is vibrationally independent of the crystalline lattice. Consequently, each isolated bond exhibits a unique stretching wavenumber which is assumed to be characteristic of its bond length. Since vibrational interactions between neighbouring chemical bonds are neglected, the Raman spectrum is a superposition of the stretching wavenumbers from an assembly of diatomic oscillators.

Correlation studies

There have been many attempts to relate physical parameters such as bond lengths, force constants and bond orders. The best-known semi-empirical equation for diatomic molecules is Badger's rule,[12,13] expressed by the general equation

$$k(R - d_{ij})^n = c_{ij} \tag{1}$$

that relates stretching force constant (k) and equilibrium interatomic distance (R), via empirical parameters (d_{ij} and c_{ij}, which depend on the position of the constituent atoms in the periodic table) and $n = 2$–6, usually 3. Since Badger's rule does not apply to polyatomic molecules, two new families of equations are used to relate stretching wavenumbers (ν) and equilibrium bond lengths (R). One of them assumes the exponential form[1–6] with experimentally derived fitting parameters A and B:

$$\nu = A\exp(BR) \tag{2}$$

whereas the other is a linear fit.[7]

Some bond length–bond order and bond order–stretching wavenumber or force constant correlations are applicable to P—O bonds. Brown–Shannon's 'power formula':[14,15]

$$S = S_0(R/R_0)^{-N} \tag{3}$$

and Brown–Altermatt's 'exponential formula':[16,17]

$$S = \exp\left(\frac{R^0{}_{ij} - R}{B}\right) \tag{4}$$

relate bond strength (S), usually referred to in the biochemical literature as bond order, defined so that it represents the average number of electron pairs involved in a bond, so that the summed bond strengths for an atom is equal to its oxidation state or valence [Eqn (5)], to bond length (R) via empirically determined parameters S_0, R_0, N, $R^0{}_{ij}$ and B.[15,17] The parameter S_0 is assigned arbitrarily by the user and if chosen to be unity, then R_0 is (1.62 Å) the length for a P—O bond of unit valence. The parameters (Brown and Wu exponent for P—O bond $N = 4.29$ and universal constant $B = 0.37$) are usually determined by fitting Eqn (5) to the environments found around a number of cations. Pauling's concept of bond strength is derived from an ionic model of chemical bonding, but may also be used in covalent bonding. Therefore, 'cation' and 'anion' do not necessary imply any separation of charge, but only qualify atoms of the opposite formal charge. According to Pauling's electrostatic valence principle,[18] each bond of length R_{ij} around a central atom (i), which has n_i atoms bound to it, is assigned a bond valence S_{ij}, such that

$$\sum_j^{n_i} S_{ij} = V_i \tag{5}$$

the sum of the bond valences around an atom (i) is equal to its atomic valence (V_i), i.e. formal oxidation state (the 'valence sum rule').

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Robinson[19] has established an approximately linear relation between $\log R_{P—O}$ and $\log k_{P—O}$ for a whole range of oxygen compounds of phosphorus:

$$\log k_{P—O} = -8.0 \log R_{P—O} + 7.30 \quad (6)$$

where $R_{P—O}$ is the bond length in Å and $k_{P—O}$ is an approximate force constant in dyn cm^{-1}. $k_{P—O}$ is calculated directly from the appropriate stretching wavenumbers using an equation for diatomic molecules:

$$k = 5.888 \times 10^{-2} \mu \nu^2 \quad (7)$$

where μ is the reduced mass of a PO (or POH) group and ν is average vibrational (IR or Raman) wavenumber.[20] The fundamental wavenumber, ν_ω, is an average wavenumber defined as[20]

$$(n_{as} + 1)\nu_\omega^2 = \nu_s^2 + n_{as}\nu_{as}^2 \quad (8)$$

where n_{as} is the degeneracy of the antisymmetric modes (when these are present, otherwise the symmetric stretching mode is a fundamental mode). A troubling aspect of this correlation (besides relatively old information used) is that each type of the oxyanion (ortho-, pyro-, hydrogeno-, halogeno-, peroxydiphosphate, phosphonate, phosphite, etc.) is represented by one example with average wavenumber of terminal P—O stretches and average bond length only.

Ray *et al.*[21] combined Eqns (3) and (2) to obtain the following relationship between ν and S with two adjustable parameters (exponent $N = 4.29$ for phosphorus–oxygen bonds):

$$S = [a \ln(b/\nu)]^{-4.29} \quad (9)$$

The parameters a and b are adjusted so that the 'valence sum rule' is satisfied for phosphorus in a series of phosphates (including HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4 and their ester ions) in aqueous solution. However, there were some doubts on the following:

1. Which wavenumber should be used in Eqn (8): the symmetric, ν_s, the antisymmetric, ν_{as}, stretch of the P—O bonds or some specific combination?
2. Do wavenumber–bond strength relationships for P—O and P—OH bonds differ since $\mu^{1/2}$ for P—OH is about 2% larger than for P—O?[21]

Deng, *et al.*[22] showed by normal mode analysis and *ab initio* calculations that:

1. ν_ω depends almost entirely on the force constant and reduced mass of a P—O bond in phosphoric acid or its anions, whereas ν_s and ν_{as} individually depend also on the molecular geometry. Therefore, they concluded that the P—O bond order is more closely related to the fundamental than to the symmetric or antisymmetric stretching wavenumber.
2. P—OH and P—O stretching wavenumbers should not be combined in constructing bond order–wavenumber correlations because the wavenumber of P—OH stretching modes is more sensitive to motional coupling with P—O and other P—OH groups than that of the P—O stretching mode. Moreover, the effect of coupling on P—O and P—OH stretching modes is opposite.

The previous relationship for phosphates in aqueous solutions [Eqn (9)] was derived using a very limited number of compounds (though very well chosen, as, for example, with regular structure or with only one P—O bond). Although broad in their scope [Eqns (6), (7) and (9)] and very accurate for regular structures [especially Eqn (9)], these relationships do not take into account distortion observed within inorganic solid-state phosphates, because they use average values.

It is not only bond lengths which were correlated with spectroscopic quantities, but also bond angles (θ). Rulmont *et al.*[23] correlated the P—O—P angles with the bridging vibrational (mainly IR) wavenumbers in a series of pyrophosphates. They tested two types of relationships in their study. Brown's relationship:

$$\nu_{as} - \nu_s = f(\theta) \quad (10)$$

does not take possible variations of the force constant of the bridging bond (which is not really constant, especially in solids) into account. Lazarev's relationship:[24]

$$\Delta = \frac{\nu_{as} - \nu_s}{\nu_{as} + \nu_s} = f(\theta) \quad (11)$$

originally applied to pyrosilicates, eliminates the contribution of the force constant and was therefore expected to be more satisfactory than Brown's. However, both relationships give similar curves and deviations from them, attributed to vibrational interactions between the P—O—P bridge and the external PO_3 groups, and also to the disturbing influence of the cation (which are neglected by the approximation of the P—O—P bridge as an independent vibrating unit).[23]

RESULTS

On the assumption that P—O stretching wavenumbers of the phosphates are primarily determined by the values of the P—O bond lengths, it is possible to assign a given pattern of bands to a definite structural type (ortho, pyro, chain or ring structure).[23] This type of correlation between structure and spectra is generally applicable to phosphates of mono- and divalent cations, but less so to phosphates of tri- or tetravalent elements, and to hydrogeno-phosphates. The cation–oxygen bond strengths of the latter are large enough to alter the P—O vibrational wavenumbers, thus leading to spectra which, in some cases at least, are not characteristic of the structural type of interest. Characteristic features in the Raman spectra of

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phosphates are therefore restricted to the high-wavenumber part of the spectrum (600–1400 cm^{-1}), corresponding to the stretching vibrations of the anion (Table 1).[23,25–27] For the condensed phosphates, an additional approximation may be considered, in relation to the existence of two types of P—O bond. The external distance, the P—O_{ext} (either terminal PO_3 in pyro- or PO_2 in metaphosphates) is shorter (and stretching wavenumber accordingly higher) than the internal (bridging O—P—O) distance within the P—O—P chain or ring (Table 1); hence the separation of P—O stretching vibrations into P—O external (higher) and P—O bridging (lower) wavenumbers.

In order to investigate possible correlations, it is necessary to assign P—O bond lengths to their corresponding stretching wavenumbers. The procedure for making these assignments here is as follows:

1. In general, shorter bonds vibrate at higher wavenumbers than longer bonds.
2. A trial bond length–stretching wavenumber trend is defined on the basis of a solid solution series (barium–strontium and strontium–calcium for orthophosphates[8,9,28] and calcium–cadmium for pyrophosphates[29]) (see [b] in Tables 2[30–48] and 3[29,49–66] for explanation of initial assignments in each data set).
3. Further assignments are made with the assumption that bonds of comparable length give rise to comparable stretching wavenumbers.

These guidelines help to overcome complications that arise in cases where not all Raman bands present in the spectrum can be assigned to P—O functionalities, or not all P—O bonds exhibit stretching modes which are observable in the Raman spectrum.

In terms of these guidelines, an empirical correlation that relates Raman stretching wavenumbers of the P—O bonds to their bond lengths in inorganic solid-state phosphates was established. Tables 2–4[26,67–78] contain the assignment of bond lengths to stretching wavenumbers for ortho-, pyro- and metaphosphates. Figure 1 shows a correlation graph that relates bond lengths to stretching wavenumbers for inorganic phosphates. While searching for a simpler empirical correlation between bond lengths and Raman wavenumbers, a satisfactory linear fit:

$$\nu = a + bR \tag{12}$$

as shown in Fig. 1 was found. Least-squares analysis gives $a = 6.3 \times 10^3\ cm^{-1}$ and $b = -34.3\ pm^{-2}$ and results in a correlation coefficient of −0.972.

In the case of condensed phosphates, the P—O terminal (P—O_{ext}) stretching wavenumbers correlate well with their bond lengths whereas the bridging ones (P—O_{int}) show some scatter (on the other hand, P—O—P bond angles correlate well with bridging vibrational wavenumbers, albeit without any analytical description[23]). This may be related to:

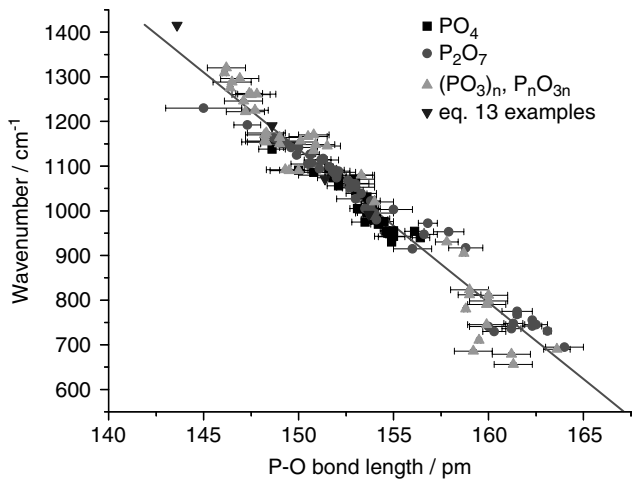

Figure 1. Empirical correlation between crystallographically determined P—O bond lengths and Raman stretching wavenumbers for inorganic phosphates. 133 data points from Tables 2–4 are fitted according to Eqn (12). For details on the accuracy of the bond length and Raman wavenumber determinations, see the text (error bars seem to be noticeable in the direction of bond length axis only, because absolute wavenumber errors are comparatively small).

1. the greater sensitivity of the P—O terminal stretching wavenumbers to the nature of cations, compared with bridging groups; cations may cause distortion of the PO_4 tetrahedra;
2. bridging (P—O_{int}) stretching wavenumbers having some bending character for medium-wavenumber vibrations (<750 cm^{-1}) (Table 1).

DISCUSSION

This is the second linear correlation established in this type of study; the first was observed in borate crystals.[7] It is interesting that all transition metal–oxygen bond lengths and their corresponding Raman stretching wavenumbers studied up to now are exponentially related,[1–6] whereas non-metal–oxygen bonds show a linear relationship.

By combined use of the bond order–stretching wavenumber correlation for phosphates in aqueous solution[21,22] [Eqn (9)] and bond length–bond order correlation of Brown and Wu[15] [Eqn (3)], the following relationship may also be derived between the fundamental (average) wavenumber of P—O stretches and P—O bond lengths (in pm):

$$\nu_\omega = 224500 \exp\left(\frac{-R}{28.35}\right) \tag{13}$$

P—O bond lengths calculated from appropriate wavenumbers by using Eqns (12) and (13) are compared mutually and with the experimental values (when available) in Table 5.

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Table 1. Characteristic features of phosphates studied: external (terminal) and internal (bridging) P—O bond lengths (pm), with average (mean) value in parentheses, and P—O stretching wavenumbers[a]

Parameter (au)	Orthophosphates PO_4^{3-}	Pyrophosphates $P_2O_7^{4-}$	Metaphosphates $(PO_3^-)_n$ chain	Metaphosphates $P_nO_{3n}^{n-}$ ring
R(P—O_{ext})/pm (average)	150–158 (156.3)	145–156 (151.3)	145–154[23] (148.9)	(148.0)
ν(P—O_{ext})/cm^{-1}	900–1100 $\nu_{as} > \nu_s$	975–1250	IR: 1250–1300 ν_{as}[23] (1 or several, s) (P═O: 1220–1360, chain < ring)[25] R: 1150–1200 ν_s[25] (1 vs)	
	IR: ~1050 vs	IR: ν_{as} ~ 1100 s (gr. bands)	IR, R: 1050–1150 ν_{s+as}[23] (var. int. bands)	
	R: ~950 vs	R: ν_s ~ 1000 s		IR: P_4O_{12}[26] 1330–1180 ν_{as} 1180–1080 ν_s
R(P—O_{int})/pm (average)	— —	156–165 (158.4)	158–165[23] (159.4)	(160.8)
ν(P—O_{int})/cm^{-1}	—	675–975 IR, R: s, br 900–950 ν_{as}	IR: 860–946 ν_{as}[23] (1 s, br)	IR: ν_{as}[23] (1 s, br): ~1000 ($n = 3$) 960–1060 ($n = 4$) ~950 ($n = 6$) 910–920 ($n = 8$)
		IR: w, R: s ~750 ν_s doublet? Linear P—O—P: no bands	650–800 ν_s Intensity: $IR_{chain} < IR_{ring}$ No. of bands = chain periodicity[25] (No. of tetrahedra in repeating unit of a chain) NA for large repeat unit	ν_s 765–780 ($n = 3$) IR: vs for planar ring (doublet: low ring sym.) R: vw or missing IR: ($n = 4$) ring sym.:[26] S_4: (2 m) ~800 + ~700 (doublet?) C_{2v}: (2 m, 1 vw) As for S_4 + 660–690 vw C_i/C_{2h}: 700–750 (doublet) C_1: (3 m, 1 vw) ~800 + 730–700 (doublet) + ~670 vw
			R: 650–750 ν_s (1 vs)[23,27b]	R: <700 ($n = 3, 4$) 705–720 ($n = 6$) 725–760 ($n = 8$) 620–650 ($n = 3$) (2nd peak, m)

[a] w, Weak; m, medium; v, very; s, strong; sh, shoulder; br, broad; var. int., variable intensity; NA, not applicable; IR, infrared; R, Raman; gr. bands, group of bands; doublet, always doublet; doublet?, possible doublet; s + as, vibration with mixed symmetric and antisymmetric character.

[b] Medium-wavenumber vibrations have some bending character.

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The average wavenumber [by means of Eqn (13)] gives the average bond length, which is more appropriate for regular structures such as those used by Deng *et al.*[22] ($Na_2CH_3PO_4$, F_3PO, Ph_3PO, for example, also incorporated in Fig. 1 together with free PO_4^{3-} in aqueous solution). Individual stretching wavenumbers [by using Eqn (12)] give individual bond lengths and it is not necessary to distinguish between symmetric and antisymmetric stretching modes [since the diatomic approximation, on which Eqn (12) is based, does not differentiate between them]. This is especially difficult when several types of phosphates present in the structure preclude any assignments to ν_s and ν_{as} modes [as shown for $Na_5Ti(PO_4)_3$ crystal[79,80]]. In the case of some glasses [as illustrated on $Na_5Ti(PO_4)_3$ glass[79]] where stronger symmetric stretching modes are usually observed, both equations give similar predictions.

Since Eqn (9) was fitted with the help of the data with short P—O bonds only (in PO_4^{3-} and double bond in F_3PO), it is expected that the predictions of Eqns (12) and (13) will be comparable in this region. In addition, the linear Eqn (12) incorporated pyrophosphates and metaphosphates with some longer P—O bridging bonds for which the predictions of these two equations should differ significantly. Indeed, the predictions differ in the long bond length range, although both equations greatly overestimate the value for bridging bonds of polycrystalline $Ga(PO_3)_3$,[81,82] with a slightly closer match to experimental bond lengths obtained by the linear equation.

In order to evaluate these two equations more accurately, with respect to their different origins, a tedious comparative study with the method for matching ν_s and ν_{as} pairs for solid-state examples having large but different numbers of symmetric and antisymmetric stretching wavenumbers is necessary. The comparison given here shows that the newly established linear correlation is:

1. statistically more sound (133 data points were used for its derivation) than the aqueous solution equation (fitted by means of two data points only, although very well chosen);
2. more versatile because ortho-, pyro- and metaphosphates were not well represented in the previous correlations;

Table 2. Bond lengths and assigned stretching wavenumbers for P—O bonds in orthophosphate compounds[a]

Compound	R/pm (ESD)	ν/cm^{-1}
β-Li_3PO_4[30]	154.9(7)	942 vs
γ-Li_3PO_4[31]	154.7(2)	950 vs
$Ba_3(PO_4)_2$[32b]		1045 m
	154.1(7)	982 w
	154.9(2)	930 vs
$Sr_3(PO_4)_2$[32b]	152.1(4)	1073 m
		998 m
	155.0(2)	955 vs
$Mg_3(PO_4)_2$[33,34]	150.8(8)	1086
	152.7(5)	1065
	153.5(7)	975 vs
$Cu_3(PO_4)_2$[34,35]	153.8(5)	981 vs
β-$Ca_3(PO_4)_2$[36–38b]	150(1)	1091 w
		1084
	151.8(4)	1074 w
		1059 w
	153.0(4)	1046 m
	153.2(4)	1038 w
	153.6(5)	1031 w
	153.7(4)	1016
	153.9(4)	1005 w
	154.2(4)	970 vs
		961 sh
	154.8(4)	949 s
		946
α-$Ca_3(PO_4)_2$[38–40]	148.6(7)	1138 vw
	151.6(4)	1095 w
	152.1(4)	1075 w
	152.8(5)	1060 w
	153.6(6)	998
	154.5(5)	976 vs
	156.1(5)	954 sh
$Pb_3(PO_4)_2$[41,42]	154.6(3)	955 s
$Zn_3(PO_4)_2{\cdot}4H_2O$[43,44]	152.1(6)	1056 m
	153.6(5)	996 vs
	156.4(5)	940 m
α-Na_3PO_4[45,46]	153(1)	1071 s
	155(1)	943 vs
$Na_3PO_4{\cdot}12H_2O$[47,48]	153.1(4)	1005 w

[a] w, Weak; m, medium; v, very; s, strong; sh, shoulder.

[b] Initial assignments for orthophosphates: longer bonds in $Ba_{3-x}Sr_x(PO_4)_2$ ($0 < x < 3$) solid solution series stay constant throughout the series[9] [from 154.9 for $Ba_3(PO_4)_2$ to 155.0 pm for $Sr_3(PO_4)_2$], whereas the shorter ones decrease [from 154.1 for $Ba_3(PO_4)_2$ to 152.1 pm for $Sr_3(PO_4)_2$]. This decrease in bond length is followed by an overall upward wavenumber shift,[8] so the shortest bond in $Sr_3(PO_4)_2$ can be assigned to the highest wavenumber (at 1073 cm^{-1}), and the longest bond to the lowest wavenumber (at 955 cm^{-1}). Accordingly, the longer bond in $Ba_3(PO_4)_2$ is assigned to lowest wavenumber (at 930 cm^{-1}), whereas its slightly shorter bond is assigned to next higher wavenumber (at 982 cm^{-1}). Similarly, strontium–calcium solid solution series[28] show an overall increase in degeneracy of the PO_4^{3-} bands and a spectral shift towards higher wavenumbers. This indicates that the shortest bond, 150 pm in β-$Ca_3(PO_4)_2$, can be assigned to 1091 cm^{-1} band.

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Table 3. Bond lengths and assigned stretching wavenumbers for P—O bonds in pyrophosphate compounds[a]

Compound	R/pm (ESD)	ν/cm^{-1}
$Na_4P_2O_7$[49,50]	151.3(2)	1115 w
	163.1(2)	731 m
$Na_4P_2O_7 \cdot 10H_2O$[51,52]	151.2(5)	1115 m
	151.9(5)	1091
	153.8(5)	996
	161.2(5)	736 m
α-$Zn_2P_2O_7$[53,54]	149(1)	1156 w
	151.2(9)	1114 m
	152.0(5)	1078 m
	152.8(9)	1061 vs
	153(1)	1053 sh
	154.1(6)	980 vw
	156.6(7)	947 vw
	160.3(6)	730 m
α-$Mg_2P_2O_7$[55,56]	147.3(7)	1192
	150.6(5)	1126
	152.1(6)	1089 vs
	153.5(4)	1005
	156.8(5)	972
	161.3(5)	748 vs
β-$Mg_2P_2O_7$[56,57]	153(1)	1060 vs
α-$Sr_2P_2O_7$[58,59]	150.7(2)	1128 m
	151.6(2)	1099 w
	152.6(1)	1068 vs
	161.5(2)	768 s
$Ca_2P_2O_7 \cdot 2H_2O$[60,61]	149.9(1)	1125 m
	151.3(1)	1117 m
	151.9(1)	1084 m
	153.8(1)	990 w
	162.3(1)	755 s
α-$Ca_2P_2O_7$[59,62]	149.3(8)	1152
	150.5(9)	1105
	152(1)	1074 vs
	154(1)	995
	157.9(8)	953
	161.5(8)	775
β-$Ca_2P_2O_7$[63,64b]	148.7(4)	1163
	149.6(4)	1142
	150.7(4)	1107
	151.1(5)	1094
	151.8(4)	1087
	152.7(4)	1051vs
	153.8(4)	1006
	162.3(5)	742 s
$Cd_{1.25}Ca_{0.75}P_2O_7$[29,65b]	149(1)	1152 sh
	150(1)	1142 m
	152(1)	1086 sh
	153.3(8)	1039 vs
	158.8(9)	917 w
	162.5(6)	745 m
$Cd_2P_2O_7$[29,66b]	145(2)	1230 w
	149(2)	1154 m
	152(2)	1080 w
	153(1)	1027 vs
	155(1)	1003 sh
	156(1)	915 w
	160(1)	741 s
	164(1)	695 m

[a] w, Weak; m, medium; v, very; s, strong; sh, shoulder.
[b] Initial assignments for pyrophosphates: the shortest bond in $Cd_{1.25}Ca_{0.75}P_2O_7$ solid solution (149 pm) can be assigned without doubt to its highest wavenumber (1152 cm^{-1}), and longest terminal to the lowest P—O terminal stretching wavenumber (1039 cm^{-1}). Accordingly, β-$Ca_2P_2O_7$ and $Cd_2P_2O_7$ short bonds are assignable to comparable high wavenumbers. Further shortening of the bond in $Cd_2P_2O_7$ (145 pm) is accompanied by higher wavenumber (1230 cm^{-1}). Bridging bonds shorter than 160 pm are assignable to higher bridging wavenumbers (usually above 900 cm^{-1}), and longer ones to lower wavenumbers (below 800 cm^{-1}).

3. easy to apply since it is not necessary to differentiate between symmetric and antisymmetric stretches, which would require more detailed structural and vibrational analysis.

Therefore, the simple linear equation is more suitable for representing the actual bond lengths in solid-state phosphates.

Although most bond length–wavenumber correlations can be derived from appropriate diatomic potentials, their practical importance appears to be independent of such a derivation.[83] Even though correlations are carried out graphically without any analytical description in some cases, their diagnostic value is well documented.[84] An advantage of the bond length–wavenumber correlation compared with other structural techniques is the sensitivity of the Raman band shifts to small changes in bond length. A small difference in bond length (1 pm) at the limit of x-ray measurements produces a relatively large shift (34 cm^{-1} here) of the appropriate Raman band. Using laser excitation, Raman data acquisition at 5 cm^{-1} resolution and $\pm$1 cm^{-1} accuracy is commonplace for very small crystalline samples. This value corresponds to an optimum resolution in calculated bond length of better than 0.1 pm. In practice however, even for effectively decoupled bonds, factors other than a variation in bond length (such as group symmetry or counter-cation mass) can cause a Raman wavenumber shift of the order of 30–50 cm^{-1}. Such a large wavenumber variation merely corresponds to a 1 pm error in the determination of bond lengths. A limitation of the correlation function lies in the fact that it is empirical and therefore cannot

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Table 4. Bond lengths (ESD where available, otherwise assumed to be <1 pm for graph purposes) and assigned stretching wavenumbers for P—O bonds in metaphosphate compounds[a]

Compound	R/pm (ESD)	ν/cm^{-1} (intensity)
$(NH_4)_4P_4O_{12}$[26,67]	147.1	1246
	148.3	1154
	160.0	811
	161.3	656
α-$Na_2P_4O_{12}\cdot 4H_2O$[26,68]	146.9	1296
	147.8	1261
	149.0	1150
	160.0	798
	161.2	679
β-$Na_2P_4O_{12}\cdot 4H_2O$[68,69]	147.2	1222 (1)
	148.2	1156 (10)
$Cu_2P_4O_{12}$[70,71]	147.4(7)	1263 vs
	150.8(8)	1170 vs
	151.5(7)	1145 s
	153.3(6)	1088 m
	157.8(6)	930 w
	159.0(6)	812 w
	163.6(7)	690 vs
$Mg_2P_4O_{12}$[26,72]	146.2	1320(3)
	146.5	1288(3)
	150.5	1166(8)
	150.9	1148
	159.0	823
	159.9	745
$Co_2P_4O_{12}$[71,73]	146.1(1)	1309 s
	146.4(1)	1275 s
	150.1(1)	1156 vs
	150.8(1)	1135 w
	158.7(1)	905 w
β-$Ca(PO_3)_2$[74,75]	147.5(2)	1260 (1)
	148.2(1)	1170 (10)
	149.3(1)	1092(1)
	159.2(1)	686(1)
β-$Sr(PO_3)_2$[75,76]	148.3	1174 (10)
	149.5	1090 (1)
	159.9	790
$Zn(PO_3)_2$[75,77]	147.7 (7)	1225 (10)
	150.0 (1)	1090 (1)
	158.8 (1)	780
	159.5 (1)	710 (8)
$Ba(PO_3)_2$[75,78]	149	1164 (10)
	154	1020 (1)

[a] w, Weak; m, medium; v, very; s, strong; sh, shoulder.

give better predictions than the techniques from which it is derived. The precision in the estimation of P—O bond length from a measured Raman wavenumber using the bond length–stretching wavenumber correlation is 1 pm. The standard deviation in the estimate of a Raman stretching wavenumber from an absolute P—O bond length is 37 cm^{-1}.

Application

The correlation was used to predict P—O bond lengths in the highest temperature polymorph of Li_3PO_4 which is here labelled as α. The α-form is stable for a small range of temperatures (1170–1220 °C) below the melting-point. Owing to the irreversible nature of a second phase transition, it is not possible to obtain good quality PXRD data for structural determination. A model structure obtained by tripling one of the parameters in the unit cell of the low-temperature form (β)[85] gives P—O bond lengths far outside the normal expected range for orthophosphates. Valence bond calculation showed that the structure was not reliable;[10] bond valence sums at the P atoms were in good agreement with expected formal oxidation state of P^{5+} for the first two forms (β and γ), but not for the third form (α).

In order to gain an insight into its structure, phase transitions of Li_3PO_4 were monitored by Raman spectroscopy.[10] The previously established correlation [Eqn (11), Fig. 1] was then used to predict the P—O bond length in the highest temperature form of Li_3PO_4. The predicted average bond length of 156 ± 1 pm agrees well with the values found for other orthophosphates.

Some more applications of the previously established correlation are envisaged:

1. In the field of glassy and amorphous phosphate materials (GAMs) to estimate the length of P—O single bonds, terminal P—O and O—P—O chain bonds and terminal double bonds (as shown in the discussion for some examples in Table 5). The unpolarized vibrational spectra for crystals and GAM analogues are often similar because vibrational spectra are determined largely by short-range order. That justifies using vibrational assignments based upon an analysis of a crystal to describe spectral features of their GAM analogues.[86]
2. In molecular mechanics (MM), which can optimize molecular structure[87] with high accuracy and relatively little computational expense. The chemical bond between a pair of atoms is a function of the electron density distribution between the atoms. In MM this function is quantified in terms of bond order (N), equilibrium bond distance (R) and force constant (k). These parameters are interrelated and Raman spectroscopy may be used to obtain an independent estimate of k, as demonstrated here.

CONCLUSIONS

A linear empirical correlation was established between Raman stretching wavenumbers of phosphorus–oxygen bonds and their bond lengths in inorganic crystalline phosphates. The correlation was used to predict the P—O

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Table 5. Comparison of the results of P—O bond length calculations by using Eqns 12 ($\nu = 6.3 \times 10^3 - 34.3R$) and 13 [$\nu_\omega = 224\,500 \exp(-R/28.35)$] with available experimental values

Compound	Parameter	ν_s	ν_{as}	ν_ω				
$Na_2CH_3PO_4$[22]	Wavenumber/cm^{-1}	974	1117	1071				
	$R_{calc.}$ [Eqn (13)]/pm	154.2	150.3	151.5				
	$R_{calc.}$ [Eqn (12)]/pm	155	151	152				
	$R_{exp.}$/pm	151.2	151.2	151.4				
Ph_3PO[22]	Wavenumber/cm^{-1}	1190						
	$R_{calc.}$ [Eqn (13)]/pm	148.6						
	$R_{calc.}$ [Eqn (12)]/pm	149						
	$R_{exp.}$/pm	148.2						
F_3PO[22]	Wavenumber/cm^{-1}	1415						
	$R_{calc.}$ [Eqn (13)]/pm	143.6						
	$R_{calc.}$ [Eqn (12)]/pm	142						
	$R_{exp.}$/pm	143.6						
			$\nu(PO_4)$					
$Na_5Ti(PO_4)_3$ cryst.[79,80]	Wavenumber/cm^{-1}	1158	1060	891				
	$R_{calc.}$ [Eqn (13)]/pm	149.3	151.8	156.8				
	$R_{calc.}$ [Eqn (12)]/pm	150	152	157				
	$R_{exp.}$/pm	150.5	150.9	156.0				
		$\nu_s(PO_2)$	$\nu_s(PO_3)$					
$Na_5Ti(PO_4)_3$ glass[79]	Wavenumber/cm^{-1}	1149	1028					
	$R_{calc.}$ [Eqn (13)]/pm	149.5	152.7					
	$R_{calc.}$ [Eqn (12)]/pm	150	153					
		$\nu_{as}(PO_2)$			$\nu_s(PO_2)$			$\nu_s(POP)$
$Ga(PO_3)_3$ polycryst.[81,82]	Wavenumber/cm^{-1}	1242	1214	1184	1171	1064	1023	675
	$R_{calc.}$ [Eqn (13)]/pm	147.3	148.0	148.7	149.0	151.7	152.8	164.6
	$R_{calc.}$ [Eqn (12)]/pm	147	148	149	149	152	153	163
	$R_{exp.}$/pm		148.6		149.5		156.7	157.9

bond length in the α-form of Li_3PO_4, which is stable for only a small range of temperatures below the melting-point. The emphasis was not so much on applications (although they certainly justify the correlation) but on finding the method which will reflect distortions observed within inorganic solid-state phosphates, since averaging cannot do that. The correlation method is expected to offer invaluable insight into the structures of species for which diffraction or other spectroscopic techniques provide incomplete structural information (as for example GAMs). That would enhance the value of Raman spectroscopy as a complementary technique in structural studies of phosphates.

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