Relationship between Bond Stretching Frequencies and Internal Bonding for [^{16}O$_4$]- and [^{18}O$_4$]Phosphates in Aqueous Solution

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A normal-mode analysis is used to show that the fundamental stretching frequency, defined as $\nu^2 = (\nu_s^2 + n_a\nu_a^2)/(n_a + 1)$ where ν_s and ν_a are the symmetric and asymmetric modes, respectively, and n_a the degeneracy of the asymmetric modes, depends almost entirely on the force constant and reduced mass of a P⋯O (or P−OH) bond in phosphoric acid or its anions to a good approximation. On the other hand, ν_s or ν_a, separately, depend not only on these parameters but also on molecular geometry. Thus, P⋯O (or P−OH) bond order is more closely related to the fundamental frequency than to the symmetric or asymmetric stretching frequencies. Similar conclusions apply to V⋯O (or V−OH) bonds in vanadate molecules. The frequencies for the four different P⋯O bonds and three different P−OH bonds in [^{18}O$_4$] phosphoric acid and its three anions were measured by Raman and FT-IR spectroscopy. The measured values, plus those for [^{16}O$_4$] phosphates, were correlated with P⋯O valence bond order, by using a modification of the Hardcastle−Wachs procedure (Hardcastle, F. D.; Wachs, I. *J. Phys. Chem.* **1991**, *95*, 5031). The bond order/stretching frequency correlations thus produced are expected to hold accurately over a wide range, for both [^{16}O] and [^{18}O] phosphates. Thus, P⋯O bond order and bond length in phosphates can be determined from vibrational spectra by using the derived bond order/stretching frequency correlation and the bond length/bond order correlation of Brown and Wu (*Acta Crystallogr.* **1976**, *B32*, 1957). The accuracy is very high. The error in these relationships is estimated to be within ±0.04 vu and ±0.004 Å for bond orders and bond lengths, respectively, as judged by examining the affects of neglecting small terms in normal-mode analysis and by comparisons of derived bond lengths of P⋯O bonds from frequency data to the results from small-molecule crystallographic data.

There have been several studies relating valence bond order of chemical bonds to vibrational frequecies. In fact, a linear relationship between valence bond order and ν^2, the square of the stretching frequency of a bond, was posed[1] shortly after Pauling's[2] work relating valence electrons to bond strength appeared. This ν−s relationship has gained acceptance among spectroscopists because of its accuracy correlating s and ν for a variety of simple molecules.[3] However, Gordy's original parameter set fails to provide a satisfactory measure of valence bond order for some tetrahedral molecules, especially those that contain multiply bonded atoms, e.g. phosphates and vanadates. The bond length, r, also is a measure of bond order (subsequently we drop the adjective, valence) although s−r relationships tend to be entirely empirical. Defining s in terms of bond lengths so that Σs for all chemical bonds to a given atom are equal to its formal valence,[4] the s−r relationship developed by Brown and associates[5,6] (eq 1), holds for a much wider variety

$$s = (r/r_1)^{-p} \quad (1)$$

of bonds than Gordy-type s−ν relationships. In fact, eq 1 can be applied to bonds with a nonintegral bond order in asymmetric environments, i.e., the relationship is independent of bond angles. The parameters r_1 and p of eq 1 have been assigned on the basis of extensive compilations of atomic distances obtained via crystallography, and unique values are available for most elements more electropositive than oxygen. These assignments were made by treating a crystal as a continuous network such that Σs for each atom in the network is as close as possible to its valence or formal oxidation state. Hence, s is expressed in "valence units", vu, and specifies the average number of electron pairs that participate in a bond. This approach is particularly useful for describing the bonds within molecules that can be considered as resonance hybrids.

Recently Hardcastle and Wachs[7] showed that the vibrational frequency of V⋯O bonds also can be related to bond length, r, in their examination of the correlation between stretching frequency and the summed vanadium−oxygen bond order, Σs_{VO}, using 14 different crystalline V(IV) and V(V) vanadium oxides that exhibit a variety of bonding patterns and geometries. The basic assumption in this treatment is that V⋯O bonds in crystalline vanadium oxides can be treated as independent oscillators and that the frequency of the symmetric stretching

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mode can be related to bond order. The relationship that provides a reasonable fit for their extensive data set takes the form

$$s = [a \ln(\nu_0/\nu)]^{-p} \qquad (2)$$

where a and ν_0 are adjustable parameters and the value of p is the same as in eq 1 and thus is the Brown and Wu exponent for a bond between two specified atoms. Both a and ν_0 were adjusted by curve-fitting so that each value of s_{VO} is close to the value calculated via the Brown–Wu relationship on the basis of a direct bond-length measurement. Hence, in this system, stretching frequency can be used as a direct measure of the average number of electron pairs per VO bond *and* bond length. The same approach also has been used successfully to analyze the bonding within a group of molybdenum oxides.[8] Ray et al.[9] applied a variant of this approach to aqueous solutions of natural-abundance phosphoric acid and its anions in an attempt to relate bond order to stretching frequency in solution. However, in all these studies, it has been unclear what should be used for frequency, ν, in eq 2: the symmetric, ν_s, or the asymmetric, ν_a, stretch of the PO (or VO) bonds or some specific combination.

The present paper begins where the study of Ray et al.[9] ends and provides a validation of the frequency selection in that paper as well as a modification of the s–ν equation described therein. To accomplish this, a simple normal-mode analysis was used to assess the relative importance of the parameters upon which PO frequencies in phosphates depend. Ab initio calculations were used in conjunction with this analysis to check the validity of various approximations that simplify the analytical expressions. This combined approach shows that the symmetric and asymmetric stretching frequencies of phosphates (and related compounds such as vanadates) depend not only on the stretching force constant of the bonds between the central atom and the surrounding oxygens but also on molecular geometry. In addition, it shows that in the case of phosphates (and vanadates) appropriate combinations of the symmetric and asymmetric stretching frequencies can be used to obtain both the stretching force constant and the angular geometry of the PO (or VO) bonds. In fact, the fundamental frequency, ν, defined as below, depends almost entirely on the force constant and thus is indeed the appropriate parameter to be used to develop frequency-bond order relationships. In addition, the symmetric and asymmetric stretching frequencies for the four different P⋯O bonds and three different P–OH bonds in [${}^{16}O_4$] and [${}^{18}O_4$] phosphoric acid and its three anions were measured in solution under the same conditions by Raman and FT-IR spectroscopy. The derived s–ν relationship from these data is expected to hold quite accurately for P⋯O bonds with differences in bond order at least as large as those encountered in aqueous solutions of phosphates.

Such ν–r relationships are quite powerful in determining molecular structure and establishing structure–reactivity relationships. The relationships for simple phosphates and vanadates described here are quite accurate and yield bond lengths to an accuracy of better than 0.01 Å. In addition, the absolute determination of the structures of these compounds in solution and in other environments, such as the binding sites of protein, is feasible. For example, changes in P–O bond length of phosphates in range of 0.05 Å or less may occur during binding to phosphoryl-transfer enzymes. Such small changes may reflect the substantial changes in the energy of the transition state and thus can be used to correlate with the mechanism and catalytic power of the enzyme and/or elucidate the forces responsible for binding (cf. Jones and Kirby;[10] Tonge and Carey;[11] Deng et al.[12]). The present study shows that the stretching frequencies of phosphates and vanadates bound to proteins (cf. Callender and Deng;[13] Deng et al.[14]) can be used to assess changes in the P⋯O bonding of such compounds that could accompany the binding process with a substantially greater accuracy than by use of diffraction data from such systems.

Materials and Methods

[${}^{16}O_4$]- and [${}^{18}O_4$]phosphates were prepared from PCl_5 using normal and [${}^{18}O$]H_2O, respectively, via a modification of a previously reported procedure[15] in which the reaction time was increased from 0.5 to 72 h and the diethylamine treatment omitted. For reasons that we do not understand, several attempts to repeat the previous procedures, as described, produced unacceptably low conversions of PCl_5 to phosphate (and thus poor utilization of [${}^{18}O$]H_2O). The indicated modification provides yields comparable to those reported previously. After ion-exchange chromatography (to eliminate traces of polyphosphates), followed by lyophilization (to eliminate the (Et_3NH)-(HCO_3) buffer), the phosphate was converted to phosphoric acid by passing it through a short column of freshly recycled Dowex-50-H+ resin (2% cross-link). Four equal aliquots were removed from matching samples of 0.25 M [${}^{16}O$]- and [${}^{18}O$]phosphate. After adding 3, 2, or 1 equiv of NaOH to three of these and nothing to the fourth, the samples were evaporated under vacuum. Water was then added to the residue to produce matched pairs of [${}^{16}O$] and [${}^{18}O$] samples at a concentration close to 0.5 M. ([${}^{18}O_4$]H_3PO_4 treated in this manner undergoes oxygen exchange at a slow but significant rate, and was used shortly after preparation.) Raman spectroscopy on the phosphoric acid, its anions, and the ${}^{18}O$-labeled derivatives was conducted in the manner described previously.[9] Symmetric and asymmetric modes were distinguished by polarization studies (cf. Ray et al.[9]). FT-IR spectroscopy was performed using a Bruker IFS66 spectrometer.

Force constants used to evaluate the influence it has on a stretch frequency were obtained by ab initio quantum mechanical methods employing the Gaussian 94 program[16] at various levels, including HF/3-21G*, and blyp/6-31G** levels. The Cartesian force fields are then converted to internal force field by the program REDONG[17] in subsequent frequency calculations so that the effect of a particular force constant or coupling constant to a vibrational frequency can then be tested by varying its value, keeping all others constant.

Results

Vibrational Normal-Mode Anaysis. The following conventions are used in our calculations: PO is used to designate either P⋯O or P–OH bonds unless a distinction between these is necessary. The fundamental stretching frequency for P⋯O or P–OH bonds, ν, is an average frequency defined as $\nu^2 = (\nu_s^2 + n_a\nu_a^2)/(n_a + 1)$, where ν_s and ν_a are the symmetric and asymmetric modes for these bonds, respectively, and n_a the degeneracy of the asymmetric modes. A superscript 16 or 18 is used when a distinction between bonds in normal and [${}^{18}O_4$]-phosphates is necessary. PO bond order is designated by s, although $s_{P⋯O}$ and s_{P-OH} sometimes are used for clarity. To determine which of the vibrational frequencies of a phosphate, ν_a, ν_s, or ν, is the most appropriate for constructing a bond order–frequency relationship, a vibrational analysis of phosphoric acid and its anions was conducted using the Wilson-FG method.[18] Our analysis shows that ν, as opposed to ν_s or ν_a, depends almost entirely on the force constant and is largely

independent of bond angles when coupling can be ignored. Although the analysis presented here focuses on the nonbridging P⋯O bonds of phosphoric acid and its anions, a simple variation of this analysis can be used for the P−OH bonds in these compounds. In addition, the same analysis holds for V⋯O and V−O bonds in vanadate molecules.

Phosphoric Acid. Since there is only one P⋯O bond in H$_3$PO$_4$, $\nu = \nu_a = \nu_s$. If one can ignore coupling between P⋯O stretching modes and other vibrational modes that involve P−OH groups (see below) and if the stretching frequency of the P⋯O bond can be considered as localized (i.e., a strict diatomic oscillator), its frequency is given by the following equation:

$$\nu^2 = f_s/\mu \qquad (3)$$

where f_s is the stretching force constant for the P⋯O bond and μ is the reduced mass of the P⋯O group. For $f_s^{18} \equiv f_s^{16}$, ν^{16}/ν^{18} would equal 1.039. The observed ratio, 1.032 (± 0.002) (see below), is consistent with the assumption that the P⋯O stretching mode is localized to a sufficient extent to the P⋯O bond.

Monoanionic Phosphate. There are two P⋯O bonds in H$_2$PO$_4$. The frequencies of their stretching modes can be computed analytically by the Wilson-FG method and simplified considerably if the coupling terms between the P⋯O stretching modes and the O⋯P⋯O bending mode (cf. Bansil et al.[19]) as well as the vibrational interactions with the two −OH groups can be ignored. The unimportance of these interactions for our purposes was verified by vibrational analysis using a complete force field derived from the ab initio methods described below. Thus, according to the Wilson-FG method, the effect of O⋯P⋯O bending on P⋯O stretching can be formulated as in eqs 4 and 5 if the coupling constant for the two stretching modes is C_{ss}, and the bending force constant and bond angle for the O⋯P⋯O group are f_b and θ, respectively. (Note that since $\theta > 90°$ for H$_2$PO$_4^-$, cos $\theta < 0$).

$$\nu_s^2 = \left\{ \left(\frac{1}{\mu} + \frac{\cos \theta}{M_p} \right) (f_s + C_{ss}) \sqrt{1 + \Delta(f_s, C_{ss}, f_b, \theta)} \right\} \qquad (4)$$

$$\nu_a^2 = \left(\frac{1}{\mu} - \frac{\cos \theta}{M_p} \right) (f_s - C_{ss}) \qquad (5)$$

Here, μ, is the reduced mass of the P⋯O bond, M_p is the mass of the phosphorus, and Δ is a function of the bending and stretching force constants, the atomic masses, the P⋯O bond length, and θ. Subsequent ab initio calculations (see below) provide values for the force constants and bond lengths of H$_2$PO$_4^-$ that are required to evaluate the function Δ, which comes to about 0.1 (see below). Hence, for this system the bending of the O⋯P⋯O constellation contributes little to the symmetric stretching of the P⋯O bonds, and eq 4 may be rewritten as

$$\nu_s^2 = \left(\frac{1}{\mu} + \frac{\cos \theta}{M_p} \right) (f_s + C_{ss}) \qquad (6)$$

Another way to validate the accuracy of eqs 5 and 6 is to assess how systematic changes in the bending force constant affect ν_a and ν_s, again using ab initio procedures. As will be seen below, ν_a exhibits virtually no dependence on the bending force constant, in accord with eq 5, whereas the symmetric stretching is reduced by only 10 cm^{-1} from 1249 cm^{-1} when f_b is set to zero in these calculations (Table 1). Hence, for the

TABLE 1: P⋯O Stretching Frequencies for Isolated [^{16}O$_4$]Phosphate Molecules, Calculated by an ab Initio Procedure, plus the Effect on These Frequencies of Setting the Values of Various Force Constants to Zero[a]

species	force field[b,c]	frequency (P=O)[d]			force field[e]	frequency (P−O)[d]		
		ν_s	ν_a	ν		ν_s	ν_a	ν
H$_3$PO$_4$	full set	1471		1471	full set	963	957	959
	$f_{b=0}$	1463		1463	$f_{b=0}$	964	956	960
	$f_{s(P=O)=0}$	1455		1455	$f_{s(P=O)=0}$	1007	957	982
H$_2$PO$_4^-$	full set	1249	1489	1374	full set	905	953	929
	$f_{b=0}$	1239	1489	1370	$f_{b=0}$	905	953	929
	$f_{s(P=O)=0}$	1247	1488	1373	$f_{s(P=O)=0}$	953	954	954
HPO$_4^{2-}$	full set	1070	1325	1246	full set	788		788
	$f_{b=0}$	1066	1310	1234	$f_{b=0}$			
	$f_{s(P=O)=0}$	1073	1325	1247	$f_{s(P=O)=0}$	808		808
CH$_3$PO$_4^{2-}$	full set	1068	1327	1247	full set	729		729
	$f_{b=0}$	1067	1315	1238	$f_{b=0}$			
	$f_{s(P=O)=0}$	1085	1326	1251	$f_{s(P=O)=0}$	744		744
PO$_4^{3-}$	full set	963	1146	1103				
	$f_{b=0}$	963	1123	1085				

[a] Calculations performed at the HF/3-21g* level; see Experimental Section. [b] In this table, P=O is used for P⋯O. [c] In this column, f_b refers to the O⋯P⋯O bending force constant except in H$_3$PO$_4$, where it refers to O⋯P−O bend. [d] All values are in cm^{-1}. [e] In this column, f_b refers to the HO−P−OH bending force constant.

TABLE 2: V⋯O Stretching Frequencies for Isolated [^{16}O$_4$]Vanadate Molecules, Calculated by an ab Initio Procedure, plus the Effect on These Frequencies of Setting the Values of Various Force Constants to Zero[a]

species	force field[b,c]	frequency (V=O)[d]			force field[e]	frequency (V−O)[d]		
		ν_s	ν_a	ν		ν_s	ν_a	ν
H$_3$VO$_4$	full set	1310		1310	full set	879	983	948
	$f_{b=0}$	1301		1301	$f_{b=0}$	877	971	941
	$f_{s(V=O)=0}$	1317		1317	$f_{s(V=O)=0}$	888	983	952
H$_2$VO$_4^-$	full set	1200	1214	1207	full set	779	845	813
	$f_{b=0}$	1190	1214	1202	$f_{b=0}$	777	845	812
	$f_{s(V=O)=0}$	1206	1214	1210	$f_{s(V=O)=0}$	797	845	821
HVO$_4^{2-}$	full set	1068	1088	1081	full set	648		648
	$f_{b=0}$	1055	1070	1065	$f_{b=0}$			
	$f_{s(V=O)=0}$	1073	1088	1083	$f_{s(V=O)=0}$	657		657
CH$_3$VO$_4^{2-}$	full set	1057	1086	1076	full set	582		582
	$f_{b=0}$	1045	1067	1060	$f_{b=0}$			
	$f_{s(V=O)=0}$	1050	1069	1063	$f_{s(V=O)=0}$	593		593
VO$_4^{3-}$	full set	944	894	907				
	$f_{b=0}$	944	858	880				

[a] Calculations performed at the HF/3-21g* level; see Experimental Section. [b] In this table, V=O is used for V⋯O. [c] In this column, f_b refers to the O⋯V⋯O bending force constant except in H$_3$VO$_4$, where it refers to O⋯V−O bend. [d] All values are in cm^{-1}. [e] In this column, f_b refers to the HO−V−OH bending force constant.

present system eqs 5 and 6 provide sufficiently accurate descriptions of ν_a and ν_s for our purposes. Alternatively, ab initio procedures can be used, together with known values of μ and M_p plus measured values of ν_a and ν_s, to calculate values for θ and f_s/C_{ss}, about 123° and 10, that seem reasonable. Or, conversely, eqs 5 and 6 plus reasonable values of the above parameters provide a rationale for the observed ν_a/ν_s ratio (Table 3).

Equations 5 and 6 also show that both ν_s and ν_a are functions of molecular geometry, and that an altered geometry, i.e., a change in θ, will change these two frequencies *in opposite directions*. However, their average or "fundamental" frequency, as determined by $\nu = [(\nu_s^2 + \nu_a^2)/2]^{1/2}$, will be essentially independent of geometry if the coupling constant for the two P⋯O groups, C_{ss}, is much smaller than the force constant for stretching, f_s. In such a case, the square of the average or fundamental frequency will approach f_s/μ, i.e., the expression for ν^2 in the case of H$_3$PO$_4$ (eq 3), where there is only a single

TABLE 3: Raman Stretching Frequencies for [$^{16}O_4$]- and [$^{18}O_4$]Phosphates

species	bond type	[$^{16}O_4$]phosphate[a]			[$^{18}O_4$]phosphate[a]			ν^{16}/ν^{18}
		ν_s	ν_a	ν	ν_s	ν_a	ν	
H_3PO_4	P⋯O	1177		1177	1143		1143	1.030
$H_2PO_4^-$	P⋯O	1078	1159	1119	1040	1129	1085	1.031
$D_2PO_4^-$	P⋯O	1084	1190	1138	1048	1155	1103	1.033
HPO_4^-	P⋯O	990	1084	1054	950	1053	1020	1.033
DPO_4^{2-}	P⋯O	989	1085	1054	952	1055	1022	1.031
$MePO_4^{2-}$	P⋯O	983	1097	1060	945	1070	1030	1.030
$MePO_4^{2-}$ (crystal)	P⋯O	974	1117	1071	931	1090	1040	1.031
PO_4^{3-}	P⋯O	938	1010	992	882	982	958	1.036
							av	1.032 ± 0.002
H_3PO_4	P−OH	891	1010	972	849	979	938	1.036
$H_2PO_4^-$	P−OH	878	943	911	838	918	879	1.036
HPO_4^{2-}	P−OH	858		858	833		833	1.030

[a] All values are in cm^{-1}.

P⋯O bond. Thus, although the stretching force constant f_s is numerically smaller in $H_2PO_4^-$ because the P⋯O bond strength is lower than in the monoanion, the fundamental frequency of the P⋯O stretching mode in $H_2PO_4^-$ is primarily a function of the same reduced mass as in H_3PO_4, and the ν^{16}/ν^{18} ratio should be essentially the same for both species. This expectation is consistent with ab initio calculations and with experimental observations (see below).

Dianionic Phosphate. The Wilson-FG equations for the P⋯O stretching modes in dianionic phosphoric acid HPO_4^-, which contains three P⋯O bonds, are similar to those above. Ab initio calculations again show that f_b exerts a small influence on the stretching frequencies. Setting $f_b = 0$ simplifies the equation enormously. The following expressions thus are obtained for ν_s and the doubly degenerate ν_a of a $-PO_3^{2-}$ group with symmetry C_{3v} symmetry (HPO_4^{2-}), or C_{3d} symmetry (PO_3^{2-}):

$$\nu_s^2 = \left(\frac{1}{\mu} + 2\frac{\cos\theta}{M_p}\right)(f_s + 2C_{ss}) \tag{7}$$

$$\nu_a^2 = \left(\frac{1}{\mu} - \frac{\cos\theta}{M_p}\right)(f_s - C_{ss}) \tag{8}$$

The expression for ν_a (eq 8) is the same as that for the monoanion (eq 5), whereas the contribution of the angle-dependent term to ν_s (eq 7) is increased by a factor of 2 compared with that in monoanion (eq 6). Hence, ν_s likely is more sensitive to a geometrical change in the $-PO_3^{2-}$ moiety than is ν_a. However, the average P⋯O stretching frequency ν, given by $\nu = [(\nu_s^2 + 2\nu_a^2)/3]^{1/2}$, is much less dependent on geometry than ν_s, and ν^2 will approach f_s/μ in the limiting case when $f_s \gg C_{ss}$. As in the case for phosphate monoanion, the ratio of f_s/C_{ss} can be estimated from eqs 7 and 8 using the observed values of ν_s and ν_a (Table 3) and the bond angle θ calculated by ab initio methods. Here θ is about 110°, which yields an f_s/C_{ss} ratio of about 15. Since in this case

$$\nu^2 = \frac{f_s}{\mu}\left(1 + 2\cos\theta\frac{C_{ss}}{f_s}\frac{\mu}{M_p}\right)$$

the effect on ν^2 produced by the increased degeneracy of the asymmetrical mode, relative to that for $H_2PO_4^-$, is largely compensated for by a larger f_s/C_{ss} ratio and a smaller value of $|\cos\theta|$. The change in frequency of ν by setting C_{ss} to zero is calculated to produce a downshift in frequency of about 6 cm^{-1}. This is a measure of the accuracy of employing the fundamental

frequency in $\nu-r$ correlations and corresponds to a calculated difference of about 0.002 Å in P⋯O bond length as determined by the relationships below.

Trianionic Phosphate. A treatment for tetrahedral PO_4^{3-} similar to that for HPO_4^{2-} yields the following expression for ν_s and triply degenerated ν_a:

$$\nu_s^2 = \left(\frac{1}{\mu} + 3\frac{\cos\theta}{M_p}\right)(f_s + 3C_{ss}) \tag{9}$$

$$\nu_a^2 = \left(\frac{1}{\mu} - \frac{\cos\theta}{M_p}\right)(f_s - C_{ss}) \tag{10}$$

Although the angle, θ, between each O⋯P⋯O constellation is the same for a molecule with perfect T_d symmetry, most of the geometric dependence of the stretching modes will be eliminated in the fundamental stretching mode, defined by $\nu = [(\nu_s^2 + 3\nu_a^2)/4]^{1/2}$, even for PO_4^{3-} with imperfect T_d symmetry. As above, ν^2 will approach f_s/μ if $f_s \gg C_{ss}$, but an even larger f_s/C_{ss} ratio is required. The f_s/C_{ss} ratio estimated by eqs 9 and 10 using the observed values ν_s and ν_a (Table 3) is about 12, i.e., somewhat smaller than for HPO_4^{2-}. This means that eq 3 applies slightly less well to PO_4^{3-} as to the other phsophates. However, the change in frequency of ν by setting C_{ss} to zero is calculated to produce a downshift in frequency of only about 10 cm^{-1}, which corresponds to a change of about 0.003 Å in derived bond length. Hence, in constructing a $\nu-s$ relationship (see below), PO_4^{3-} remains a choice reference molecule because not only is its P⋯O bond order unusually low (and thus is an appropriate reference for low-frequency P⋯O bonds) but its P⋯O bond order is defined by its structure.

Ab Initio Vibrational Analysis of the P⋯O Stretching Modes of Phosphoric Acid and Its Anions. Ab initio frequency calculations were performed on phosphoric acid and its three anions, as well as on metaphosphate (PO_3^-) to evaluate the contribution of O⋯P⋯O bending motion and P−OH stretching motion to the frequencies of P⋯O stretching modes. Such calculations also were used to determine whether the ν^{16}/ν^{18} ratio for the various P⋯O bonds can be considered as a constant and thus to assess how extensively the normal stretching mode is localized. The results of the calculations at HF/3-21 g* level is shown in Table 1 for phosphate molecules and Table 2 for vanadate molecules.

The calculated values of ν_s and ν_a for P⋯O stretching modes are about 20% higher than the corresponding experimental values for phosphoric acid and its anions (see below). This difference arises partly because frequency calculations at the HF level overestimate the stretching force constant and partly because calculations are performed on isolated molecules, whereas the experimental values are influenced by the interactions between P⋯O bonds and water molecules. However, these differences do not affect our inquiry about the validity of using the simple relationship between the fundamental frequency and the force constant for the P⋯O stretching mode concerning coupling effects among stretching and bending modes because all that is needed for our purposes are approximate relative values. As seen below, the results from HF/3-21G* satisfactorily reproduce the ^{18}O isotope shifts observed experimentally. Calculations employing the more extensive blyp/6-31G** basis set yielded the same results with regard to the relative size of the various terms. Thus, the simpler HF/3-21G* are used in this analysis.

The data in Table 1 indicate that the dependence of the P⋯O stretching modes on O⋯P⋯O bending and P−OH stretching motions in a series of phosphates is quite small, as reflected by

[$^{16}O_4$]- and [$^{18}O_4$]Phosphates

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the small effect on the P⋯O stretching mode frequencies when the relevant force constants are set equal to zero. When the bending force constant is set equal to zero, the fundamental P⋯O stretching frequency changes only by 0.1–2% within this series. Similarly, when the force constant for P−OH stretching is set to zero, the frequency of the P⋯O stretching mode changes by no more than 1.5%. Thus, ignoring the force constants for O⋯P⋯O bending and P−OH stretching in the analytical analysis of the phosphate P⋯O stretching normal modes is justified. Our results also indicate that, while P−OH stretching modes are reasonably well behaved (i.e., not particularly influenced by HO−P−OH and O⋯P⋯O bending modes), they are somewhat more sensitive to P⋯O stretching modes. Thus, for comparison, when the force constants for the P−OH stretching modes are set to 0, the average frequency of the P⋯O stretching modes shifts to *lower* frequencies by less than 5 cm^{-1} for mono- and dianionic phosphate although the shift is about 16 cm^{-1} for phosphoric acid; in contrast, when the force constants for the P⋯O stretching modes are set to 0, P−OH stretching frequencies shift to *higher* frequencies for phosphoric acid and its anions by 20 cm^{-1} or more (Table 1). The ab initio calculations yield the ν^{16}/ν^{18} fundamental frequency ratio as 1.033 for H_3PO_4, 1.033 for $H_2PO_4^-$, 1.032 for HPO_4^{2-}, 1.035 for $CH_3PO_4^{2-}$, and 1.034 for PO_4^{3-} (and 1.038 for metaphosphate, PO_3^-). These ratios range from 1.032 to 1.038 and thus are close to the uncoupled value, i.e., the value expected on the basis eq 4 (1.039). Interestingly, the ratios calculated by ab initio methods are intermediate between the uncoupled and observed values (see below). Setting the bending force constant to zero, the ab initio calculations yield the ν^{16}/ν^{18} fundamental frequency ratio as 1.035 for H_3PO_4, 1.033 for $H_2PO_4^-$, 1.035 for HPO_4^{2-}, 1.038 for $CH_3PO_4^{2-}$, and 1.039 for PO_4^{3-}, closer to the uncoupled values. It appears that the ab initio results slightly underestimate the stretch/bend coupling.

Table 2 shows similarly for vanadates that the dependencies of the V⋯O stretching modes on the O⋯V⋯O bending and V−OH stretches are small, varying the fundamental frequency by only 0.5–3.0% when they are set to zero. Thus the simplifications made in the analytical analysis of the P⋯O stretch normal modes for phosphates hold equally well for vanadates. The ab initio calculations show that the ν^{16}/ν^{18} ratio is 1.044 for H_3VO_4, 1.043 for $H_2VO_4^-$, 1.042 for HVO_4^{2-}, 1.043 for VO_4^{3-}. The experimentally observed ν^{16}/ν^{18} ratios for $H_2VO_4^-$, HVO_4^{2-}, and VO_3^- are 1.041, 1.050, and 1.050, respectively. The value calculated for a VO diatomic oscillator is 1.045. Thus, like the phosphate results, the fundamental frequency associated with vanadate molecules behaves quite well as an isolated oscillator. All these results show, interestingly, that the relatively large difference between ν_s and ν_a for the phosphates versus the relatively small difference for vanadates arises mostly from the smaller coupling constant C_{ss} in phosphate, although the different angles between the nonbridging bonds of the vanadate and phosphate and the different masses of vanadium and phosphorus also make some contribution.

Bond Order/Stretching Frequency Correlation for Normal and Isotopic Phosphates

Values of ν_s, ν_a, and ν for the P⋯O bonds in aqueous solutions of [$^{16}O_4$]- and [$^{18}O_4$]phosphoric acid and the various anions of both are recorded in Table 3. The symmetric stretching modes are well defined, but asymmetric modes are rather broad and exhibit somewhat different values in Raman and IR spectra. Hence, the values in Table 3, some of which differ slightly from previously reported values, are the average

TABLE 4. P⋯O Bond Order and Bond Length Calculated from Raman Stretching Frequencies

species	ν (cm^{-1})	bond order[a]	bond length (Å)[b]
H_3PO_4	1177	1.44 (1.44)	1.48$_9$
$H_2PO_4^-$	1119	1.38 (1.37)	1.50$_3$
$D_2PO_4^-$	1138	1.40 (1.40)	1.49$_8$
HPO_4^{2-}	1054	1.31 (1.30)	1.52$_0$
DPO_4^{2-}	1054	1.31 (1.30)	1.52$_0$
$MePO_4^{2-}$	1060	1.32 (1.31)	1.51$_8$
$MePO_4^{2-}$ (crystal)	1071	1.33 (1.32)	1.51$_5$

[a] Calculated according to eq 11 from values of ν(P⋯O) in Table 3 (and reproduced in column 2). Numbers in parentheses are calculated by eq 4 in Ray et al. (1992). [b] Calculated according to eq 1 with $r_1 = 1.62$ Å and $p = 4.29$.

of several measurements. The last column of Table 3 gives the measured value of the fundamental frequency ratio, ν^{16}/ν^{18}, for the different P⋯O bonds in the database. The standard deviation of the individual values, ±0.002, from the average value of this ratio, 1.032, is what would be obtained for a ±2 cm^{-1} error in measuring the appropriate vibrational frequencies. This is the precision of the measured frequencies.

In an earlier study,[9] a correlation between bond order and PO stretching frequencies for phosphates in aqueous solution was formulated by defining bond order so that $\sum s_{PO}$ for the four PO bonds of phosphoric acid and its anions is 5 and assuming that when $s = 1$ the stretching frequency of P−OH and P⋯O groups is the same, i.e., that the parameters a and ν_0 in eq 2 are the same for P−OH and P⋯O groups. (In that study (valence) bond order was referred to as bond strength.) However, the current study shows that P−OH and P⋯O stretching frequencies should not be combined in constructing a bond order/frequency correlation. Not only is the frequency of P−OH stretching modes more sensitive to motional coupling with P⋯O and other P−OH groups than that of the P⋯O stretching mode, the effect of coupling on P⋯O and P−OH stretching modes is *opposite* (Table 1). Thus, at least small differences can be expected between the apparent force constants for P⋯O and P−OH bonds at $s = 1$ when f_s is calculated via eq 2, and these differences should be reflected by differences in parameters a and ν_0 in eq 2.

Therefore, the previously determined a and ν_0 parameters, eq 2 (eq 4 in Ray et al.[9]), are modified, herein. This modification involves using only P⋯O bonds to evaluate parameters. Since there are only a limited number of compounds where both the structure and the P⋯O stretching frequency have been determined, only two reference compounds seemed appropriate for use in this process. These represent extremes for a structure−frequency relationship involving phosphates. One is the phosphate trianion, with a low stretching frequency (Table 3), and a defined bond order, 1.25 vu; the other is F_3PO, with short PO bonds (1.436 Å[20]) and the highest known P⋯O stretching frequency (1415 cm^{-1} [21]). Using eq 1 with $r_1 = 1.62$ Å and $p = 4.29$, the P⋯O bond order in F_3PO is calculated as 1.68 vu. Equation 2 thus becomes

$$s^{16}_{P⋯O} = [0.175 \ln(224{,}500/\nu^{16}_{P⋯O})]^{-4.29} \qquad (11)$$

The P⋯O bond order for several phosphates, calculated according to eq 11, is listed in Table 4 and compared with that calculated previously (using eq 4 in Ray et al.[9]). The differences actually are quite small but would become significant if an extrapolation to substantial larger or smaller bond orders was used. Also listed in Table 4 are P⋯O bond lengths for the same phosphates calculated from $s_{P⋯O}$ by using eq 1 with $r_1 = 1.62$ Å and $p = 4.29$ (cf. Brown and Wu[6]).
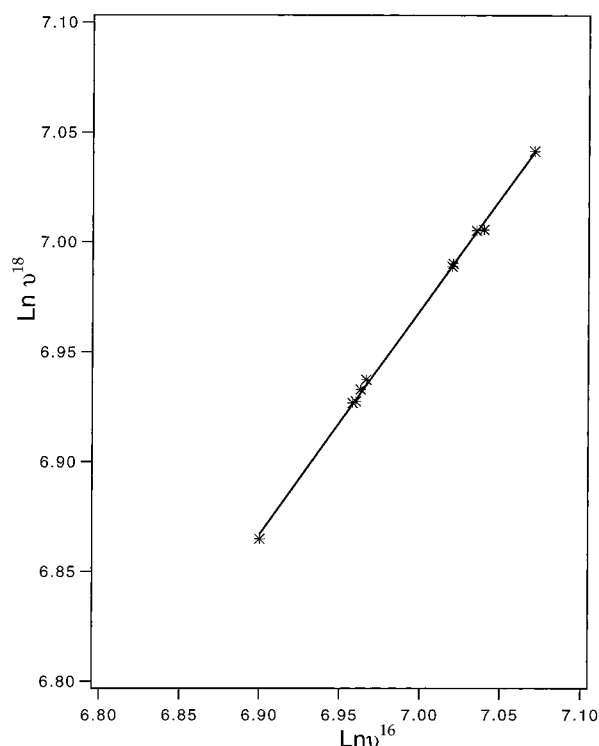
Figure 1. Logarithmic plot (base e) of fundamental stretching frequencies for the P⋯O groups of [$^{18}O_4$]phosphates versus those for the corresponding [$^{16}O_4$]phosphates. The experimental data in Table 3 are shown. Two additional data points are from FTIR measurements; the straight line is the least-squares fit.

The P⋯O bond lengths in crystalline disodium methyl phosphate are 1.512, and 1.512, 1.514 Å,[22] in excellent agreement with the length determined from vibrational data (entry 7, Table 4; difference ≈ 0.002 Å). Similarly, the reported P⋯O stretching frequency of triphenylphosphine oxide (1190 cm^{-1}, Aldrich Library of FT-IR spectra), yields a P⋯O bond length of 1.486 Å, also in good agreement, difference ≈ 0.004 Å, with the reported P⋯O bond length of 1.482 Å determined by X-ray crystallography.[23]

The bridging P−OH or P−OR bond order in an anion of phosphoric acid or a phosphate ester, or the bond-order sum, can be estimated by using the P⋯O stretching frequency to estimate s_{P-O} (eq 11) and subtracting $\sum s_{P-O}$ from 5.0 vu, the sum defined by the approach used herein. (When eq 11 is used to calculate s_{P-OH} or s_{P-OR}, the results are about 5% too high or 5% too low, respectively.)

As discussed in previous sections for isolated bonds, the ratio ν^{16}/ν^{18} should be a constant at 1.039. Although both the calculated and measured values of this ratio are somewhat lower, about 1.033 and 1.032 (Tables 1), if this difference is ignored, a correlation between the bond order and P⋯O stretching frequencies from ^{18}O-labeled phosphate can be derived by substituting $1.032\nu^{18}$ for ν^{16} in eq 11. However, although $\nu^{16}/\nu^{18} = 1.032$ is a reasonable approximation for 1.039, there appears to be a slight trend in the data of Table 3; this ratio seems to decrease in the series from phosphate trianion to phosphoric acid. Thus, parameter a in eq 2 for ν^{16} may differ slightly from that for ν^{18}. One the other hand, Figure 1 shows a plot of ln ν^{18} against ln ν^{16} plus the least-squares line calculated for these data points:

$$\ln \nu^{18} = 1.0195 \ln \nu^{16} - 0.1647$$

When this result is used, the bond order-frequency correlation

for the ^{18}O labeled phosphate is given by the following equation.

$$s_{P-O}^{18} = [0.1717 \ln(241360/\nu^{1818}_{P-O})]^{-4.29} \qquad (12)$$

Bonding Compensation within the PO$_4$ Moiety. According to the data in Table 3, as the P⋯O bond order decreases within the series, (HO)$_3$PO to HOPO$_3^{2-}$, the P−OH bond order increases, as it must if $\sum s_{PO} = 5.0$ vu. In other words, a change in the bonding of one PO group in the PO$_4$ moiety is compensated by opposite changes in the bonding of the other three PO groups. This conclusion together with the observation that ν^{16}/ν^{18} is essentially constant within the above series, i.e., that $\nu^{16} - \nu^{18} \approx 0.032\nu^{16}$, provides an insight into the origin of the [$^{18}O_4$] equilibrium isotope effect (EIE) that accompanies the successive protonation of the oxygens of PO$_4^{3-}$.[24] Thus, the binding of a proton to PO$_4^{3-}$ produces a decrease in the bond order of one P⋯O group and a corresponding increase in $\sum s_{PO}$ for the other three PO bonds. To the extent that zero-point energy (ZPE) differences, which are related to $\nu^{16} - \nu^{18}$, dominate the expression for the [$^{18}O_4$] equilibrium isotope effect (EIE) on proton binding (cf. Cook[25]), altered PO bonding should make only a minor contribution to this isotope effect. Thus, weakening of the P⋯O bond that is protonated (decreased P⋯O bond order) should produce a direct EIE, whereas the strengthening of the remaining P⋯O bonds (increased P⋯O bond order) should produce an inverse EIE that largely compensates the direct EIE. In fact, the net ZPE difference calculated by use of eqs 11 and 12, <1 cm^{-1}, would contribute a factor of only 0.001 to the EIE. The small size of the calculated contribution relative to the observed EIE, 0.019,[24] suggests that the observed effect is produced by differences in ^{16}O−H and ^{18}O−H stretching modes. This suggestion is in accord with our ab initio calculations (to be published).

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