On the Structure and Symmetry of the Phosphate Ions in Some Calcium Phosphates

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The infrared spectra, recorded at room-temperature and at 77^0K, of some calcium orthophosphates (anhydrous dicalcium phosphate, dicalcium phosphate dihydrate and octacalcium phosphate) have been analysed, particularly with respect to the site symmetry of the phosphate ions.

Whereas the free phosphate ion exhibits T_d symmetry, C_{3v} symmetry could be expected for the hydrogen phosphate ion, HPO_4^{2-}. However, in the solid state the site symmetry of the phosphate ions of the analysed compounds is apreciably lowered as inferred from the fact that the degeneracies of all vibrational modes have been removed and all modes are infrared active. This could correspond to the C_s or C_1 symmetry groups for which the selection rules and activities are identical. It was concluded that, on the basis of the present information, it is not possible to distinguish between these two symmetry groups.

INTRODUCTION

The free phosphate ion, PO_4^{3-}, is known[1] to have tetrahedral symmetry. Its nine vibrational degrees of freedom give, under T_d symmetry, four vibrational modes: the non-degenerate ν_1 stretching mode, the doubly degenerate ν_2 bending mode and the two triply degenerate modes, ν_3 and ν_4, of which the former is a stretching and the latter is a bending mode. The symmetry of these four vibrational modes are A_1, E, F_2 and F_2 respectively. Only the modes of the F_2 class are infrared active.

The frequencies of the four modes have been established from the Raman spectra of dilute aqueous solutions and are 980, 363, 1082 and 515 cm.$^{-1}$ respectively[2]. Nakamoto[3], quoting the Landolt-Börnstein Tables[4], gives slightly different values, namely 970, 358, 1080 and 500 cm.$^{-1}$ for the frequencies of the ν_1, ν_2, ν_3 and ν_4 modes respectively.

For the HPO_4^{2-} ion, the highest possible symmetry is C_{3v} but in the solid state the symmetry can be (and usually is) reduced still further. This has an effect on the degeneracies of the vibrations (see, for example, the correlation Table in Ref. 1, p. 237; the trivial point group C_1 under which all the degeneracies are removed and all vibrations become of the symmetry class A, is not included in that table). The activity of the vibrations also changes: under the C_{3v} point group all relevant species are both infrared and Raman active; of the relevant species of the C_{2v} point group, A_2 are infrared inactive, whereas all are Raman active; the A_1 and B_1 species are infrared inactive under the

point group D_{2d}, and all vibrations are both infrared and Raman active for the symmetry groups C_s and C_1^1.

Several possible factors may act towards the lowering of the symmetry in the solid state. Ross and his co-workers[5-9] list three such factors:

(1) Co-ordination to the metal through one or more of the oxygen atoms;

(2) Perturbation of the anion due to the non-uniform field created by the water molecules (where present) and

(3) Lowered site symmetry of the anion in the crystal lattice.

Another important factor, which Ross and his collaborators did not have to consider in their studies of perchlorates, sulfates, phosphates and carbonates[5-9], but which should be important in hydrogen phosphates is the type and extent of hydrogen bonding.

The symmetry of the phosphate ion in various phosphates (in solution and, in some instances, in the solid state) has been discussed by a number of authors, among them Ryskin and Stavitskaya[10], Chapman and Thirlwell[11], Stutman et al.[12], Fowler et al.[13], Baddiel and Berry[14] and Hezel and Ross[9]. In their calculation of the force constants of the phosphate ions, Chapman et al.[15]
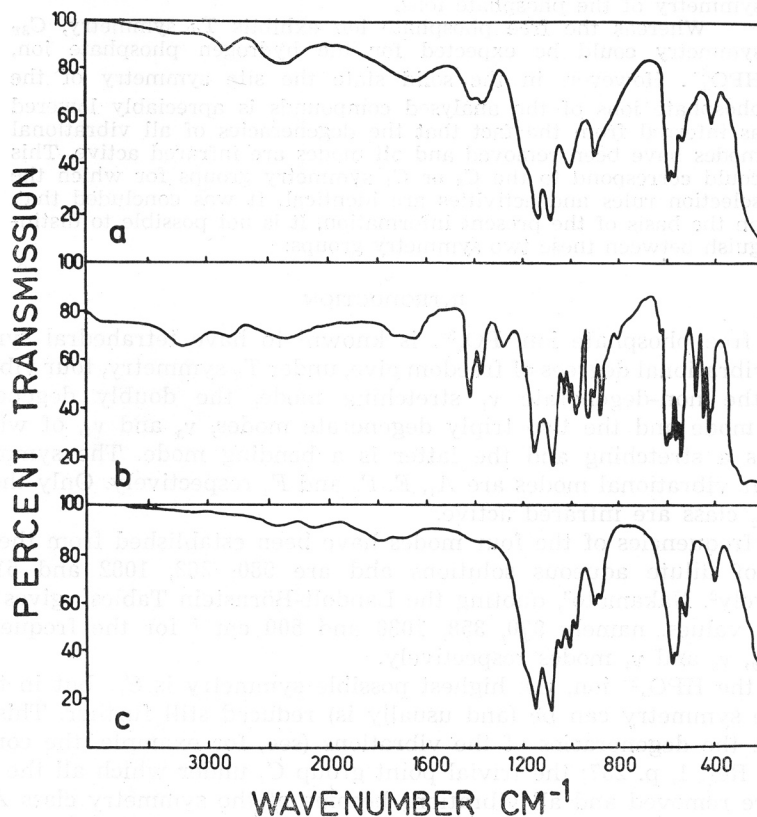

Fig. 1. Infrared spectra of DCPA:
a. Room-temperature (300⁰K) spectrum of CaHPO₄
b. Low-temperature (77⁰K) spectrum of CaHPO₄
c. Room-temperature (300⁰K) spectrum of CaDPO₄

assumed T_d symmetry for the PO_4^{3-} ion, C_{3v} symmetry for the P—O skeleton of the HPO_4^{2-} ion and C_s symmetry for the P—O skeleton of the $H_2PO_4^-$ ion. In our investigation of some calcium phosphates[16,17] we also made some conclusions with respect to the symmetry of the HPO_4^{2-} ion in anhydrous dicalcium phosphate (DCPA), $CaHPO_4$ and dicalcium phosphate dihydrate (DCPD), $CaHPO_4 \cdot 2H_2O$ but there still remained some unanswered questions concerning the exact site symmetry of the phosphate ion and its structure in the crystal lattice. We therefore undertook this more detailed investigation of the two above-mentioned compounds and of octacalcium phosphate (OCP), $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, hoping to throw some more light on this interesting problem.

EXPERIMENTAL

The methods for the preparation of DCPA, DCPD and OCP have been described elsewhere[18,19]. The spectra were of Nujol and hexachlorobutadiene mulls and of KBr and CsI pressed discs recorded on a *Perkin-Elmer* 521 spectrophotometer. The low-temperature spectra were run on a *Beckman* IR 12 instrument using a low-temperature cell of conventional design with AgCl windows and cooled with liquid nitrogen. These latter spectra are not reliable below 400 cm.$^{-1}$ because of the use of AgCl as window material.
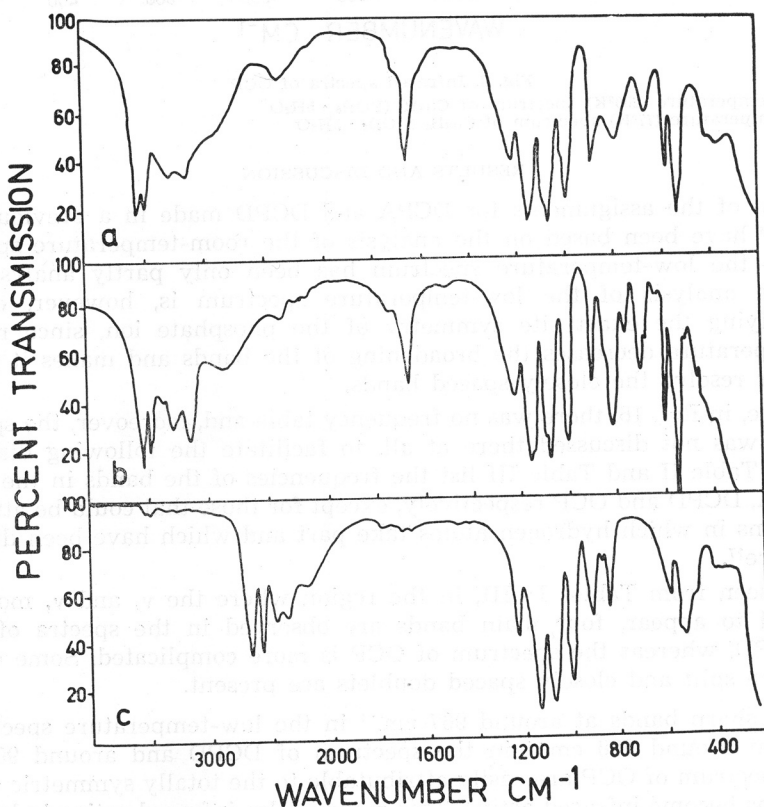

Fig. 2. Infrared spectra of DCPD

a. Room-temperature (300°K) spectrum of $CaHPO_4 \cdot 2H_2O$
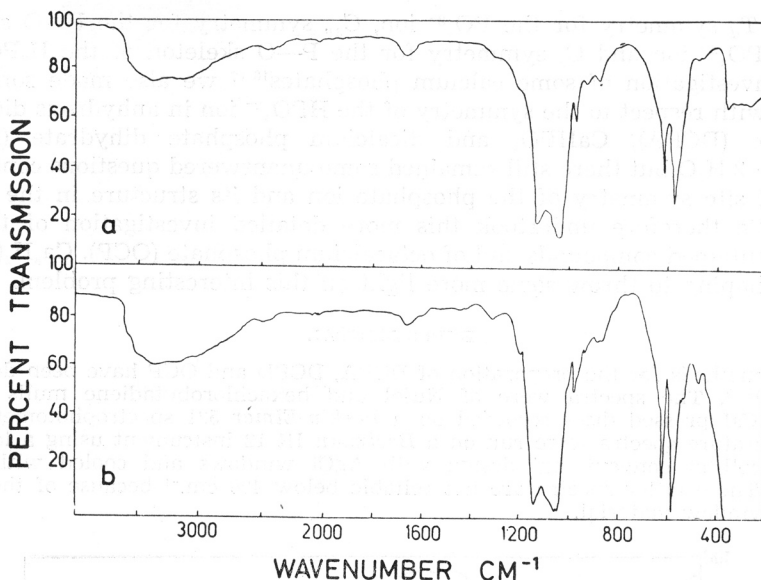b. Low-temperature (77°K) spectrum of $CaHPO_4 \cdot 2H_2O$
c. Room-temperature (300°K) spectrum of $CaDPO_4 \cdot 2D_2O$

Fig. 3. Infrared spectra of OCP
a. Room-temperature (300°K) spectrum of $Ca_8H_2(PO_4)_6 \cdot 5H_2O$
b. Low-temperature (77°K) spectrum of $Ca_8H_2(PO_4)_6 \cdot 5H_2O$

RESULTS AND DISCUSSION

Most of the assignments for DCPA and DCPD made in a previous paper of ours[16] have been based on the analysis of the room-temperature spectrum, whereas the low-temperature spectrum has been only partly analysed. The complete analysis of the low-temperature spectrum is, however, essential in clarifying the exact site symmetry of the phosphate ion, since reducing the temperature decreases the broadening of the bands and makes it possible to better resolve the closely spaced bands.

Since, in Ref. 16, there was no frequency table and, moreover, the spectrum of OCP was not discussed there at all, to facilitate the following discussion, Table I, Table II and Table III list the frequencies of the bands in the spectra of DCPA, DCPD and OCP respectively, except for those that could be attributed to motions in which hydrogen atoms take part and which have been discussed elsewhere[17].

As seen from Tables I—III, in the region where the v_3 and v_1 modes are expected to appear, four main bands are observed in the spectra of DCPA and DCPD, whereas the spectrum of OCP is more complicated. Some of these bands are split and closely spaced doublets are present.

The sharp bands at around 967 cm.$^{-1}$ in the low-temperature spectrum of DCPA, at around 988 cm.$^{-1}$ in the spectrum of DCPD and around 962 cm.$^{-1}$ in the spectrum of OCP are easily attributable to the totally symmetric v_1 mode which has become infrared active. This mode is also infrared active in hydroxy-apatite, fluoroapatite[14] and chlorapatite[12], where it is found in the same region. This immediately rules out the site symmetry D_{2d} (and also D_2), under which the totally symmetric mode should be infrared inactive (cf. Ref. 1, p. 113).

TABLE I.

Phosphate bands in the spectrum of DCPA*.

DCPA (300° K)		DCPA (77° K)		DCPA-d (300° K)		Assignment
ν	I	ν	I	ν	I	
1170	sh	1180	w	1180	sh	ν_3'
1130	s	1135	s	1140	s	
1070	s	1060	s	1073	s	ν_3''
		1015	w			$\nu_2' + \nu_4'$
1000	m	996	w	969	m	$\nu_2' + \nu_4''$
		967	m			ν_1
		950	w			$\nu_2' + \nu_4'''$
900	m	910	s	896	m	ν_3''' : P—O(H) stretch
		890	m	877	m	
		868	s			
		849	sh			
581	m	585	s	576	s	ν_4'
		578	s			
566	sh	566	s	562	sh	ν_4''
		545	s			?
		540	sh			?
530	m	528	s	523	m	ν_4'''
480	sh	470	s	?		combination?
428	vw	429	s	420	w	ν_2'
405	m	405	s	403	m	ν_2''
398	sh	394	s	398	sh	

* ν : frequency (cm.⁻¹); I : intensity; vw : very weak; w : weak; m : medium; s : strong; sh : shoulder

The bands around 1170/1130, 1070 and 900 cm.⁻¹ in the spectrum of DCPA and around 1135, 1075/1060 and 875 cm.⁻¹ in the spectrum at DCPD undoubtedly belong to the three components (ν_3', ν_3'' and ν_3''') of the ν_3 mode. The situation is less clear for OCP, mainly due to the lack of the spectrum of deuterated OCP[17]. Because of that, the phosphate bands could not be distinguished with certainty from the O—H bending vibrations and the librational modes of the water molecules. In any case, at least three of the bands in this region certainly belong to the components of the ν_3 mode.

Two of the components of the ν_3 mode are close together and the third is far removed from them (see Tables I—III). This third component (around 900 cm.⁻¹ in the spectrum of DCPA and around 875 cm.⁻¹ in the spectrum of DCPD) has been attributed[11,15,16] to the P—O (H) stretching and some of the bands in this region in the spectrum of OCP are apparently also due to such a vibration. The observed splitting of this band in the low temperature spectrum of DCPA and possibly also of some of the bands in the 950—850 cm.⁻¹ region of the spectrum of OCP, can be interpreted in terms of a distribution of the acidic proton and formation of several types of hydrogen bonds, as proposed earlier[16,17,23]. It should, however, be borne in mind that in this same

TABLE II

Phosphate bands in the spectrum of DCPD*.

DCPD (300° K)		DCPD (77° K)		DCPD-d_3 (300° K)		Assignment
ν	I	ν	I	ν	I	
1135	s	1140	s	1143	s	ν_3'
		1128	s			
1075	s	1083	s	1083	s	ν_3''
1060	s	1061	s			
1005	sh	1008	m	1005	sh	ν_1
988	s	990	s	986	s	
875	m	885	s	837	s	ν_3''' : P—O(H) stretch
577	m	579	s	582	s	ν_4'
526	m	542	sh	535	s	ν_4''
		527	s	515	s	ν_4'''
		445	m			?
418	sh	420	sh			ν_2' ?
400	m			400	m	ν_2''

* ν : frequency (cm.$^{-1}$); I : intensity; vw : very weak; w : weak; m : medium; s : strong; sh : shoulder

region of the spectrum of OCP, one could expect to find the frequencies of the librational modes of the co-ordinated water molecules.

The ν_4 mode is also split into three components, readily detectable in all three phosphates (*cf.* Tables I—III) except in the room-temperature spectrum of DCPD. However, the low-temperature spectrum of DCPD and the spectrum of DCPD-d_3 show that such a splitting (into three components) of the ν_4 mode also takes place in the hydrated dicalcium phosphate.

The detection of the components of the ν_2 mode is very difficult. The components of this mode (forbidden under T_d symmetry) are weak and may be obscured by the lattice vibrations (or their combinations) and/or by the Ca—O$_w$ stretching vibrations (»translations«) of the co-ordinated water molecules (in DCPD and OCP). The assignments are more reliable for DCPA, are tentative for DCPD and impossible for OCP (the deuterated analogue of which, as noted earlier, could not be prepared[17]). It should be mentioned that the components of the ν_2 mode in hydroxyapatite and fluoroapatite were assigned[14] lower frequencies than those proposed here. The assignments in this region are, therefore, still open to discussion.

The appearance of doublets instead of single bands, observed in many instances, may be caused by several factors. First of all there is, because of the existence of more than one phosphate group per unit cell, the so called correlation field splitting, associated with the site-group-to-factor-group transformation[24]. The non-equivalence of all phosphate groups in the unit cell (indicated by the crystallographic data[21-23,25]) may be another possible cause. Overtones and/or combination frequencies, reinforced by Fermi resonance may further complicate the picture. The marked difference between the room-temperature and the low-temperature spectra of DCPA might be,

TABLE III
Phosphate bands in the spectrum of OCP*.

OCP (300° K)		OCP (77° K)		Assignment
ν	I	ν	I	
1175	sh	1180	w	?
1120	s	1128	s	
		1113	sh	
1080	sh	1080	s	ν_3
1045	s	1043	s	
1018	s	1025	s	
		990	sh	
962	m	970	m	ν_1
		955	sh	
910	w	922	w	ν_3 : P—O(H) stretch
		900	sh	and/or H₂O libration
868	sh	870	w	
855	w	850	w	
600	s	603	s	ν_4'
561	s	580	sh	ν_4''
		564	s	ν_4'''
465	vw	468	w	?
		420	sh	
		400	sh	
355	sh			ν_2 and Ca—O$_w$ stretch
340	m			(H₂O »translation«)
305	m			
285	m			

* ν : frequency (cm.$^{-1}$); I : intensity; vw : very weak; w : weak; m : medium; s : strong; sh : shoulder

as pointed out by one of the referees, due to a change in the crystal structure of this compound, although no indication for the existence of two crystallographic forms of CaHPO₄ could be found in the literature (the related, isostructural, SrHPO₄, however, has a high-temperature and a low-temperature modification[26]).

It should be noted that the general appearence of the spectra suggests that the deuterated analogues of DCPA and DCPD are better crystallized than their protonated counterparts and that DCPD is better crystallized than DCPA.

Another point worth-while mentioning is the frequency change in some of the components of the ν_3 mode on deuteration. It can be seen (cf. Table I and Table II) that the ν_3' and ν_3'' bands have higher and the ν_3''' band lower frequencies in the deuterated compound spectrum than in that of the protonated species of DCPA and, more so, of DCPD. The reason for this must be the interaction of the P—O vibrations with the in-plane O--H (O—D) bending

mode. In the protonated species this later mode has a frequency of about
1400 cm.$^{-1}$ (two bands are actually found: at 1400 and 1356 cm.$^{-1}$) in DCPA
and about 1217 cm.$^{-1}$ in DCPD. It is thus conceivable that the interaction will
be stronger in the latter compound and it would displace to lower frequencies
the P—O frequencies more in DCPD than in DCPA. When, on deuteration,
the O—H (O—D) in-plane vibration shifts to about 1000 cm.$^{-1}$ in DCPA
and to about 900 cm.$^{-1}$ in DCPD it »pushes« aside the neighbouring bands and
again the closer the frequency, the stronger the interaction is expected to be,
if only allowed by symmetry restrictions. The fact that almost all bands
are affected by such an interaction shows that the restrictions are not
rigorous and, hence, the symmetry of the phosphate ion is very low.

The X-ray data also do not explicitly show the site symmetry of the
phosphate ion and only the space groups (that is, the symmetry) of the whole
unit cell is given. It was established that the space group of the DCPA unit
cell is $P1$[27], that of DCPD is Ia[22], whereas the space group of OCP, according
to Brown[25] is either $P1$ or $P\bar{1}$. The site symmetry of the phosphate ion can only
be inferred from the P—O distances. Only C_1 symmetry is compatible with
the unequally long P—O distances in the crystal unit of DCPA[21], whereas C_s
symmetry is possible for DCPD, if the P—O distances given by Jones and
Smith[22] are taken or on their face values. Our calculation of the interatomic
distance in OCP[23], based on the atomic parameters by Brown[25], revealed the
non-equivalence of the phosphate tetrahedra in the crystal unit of this
compound and, whilst some of them may have symmetry close to C_s, the
others show no symmetry at all.

The appearence of the ν_1 mode, the splitting of the triply degenerate ν_3
and ν_4 modes each into three components and the likely splitting of the ν_2
mode as well, show, on the other hand, that the site symmetry of the phosphate
ion in DCPA, DCPD and OCP is definitively lower than C_{3v} (the symmetry
of different phosphate ions in OCP is probably different). The presence of
one P—O bond longer than the rest (due to the fact that the acidic hydrogen
is attached to the oxygen in question) rules out the symmetry groups C_{2v}
and C_2 (in which a two-fold axis is present) at least for DCPA and DCPD.
Thus the symmetry groups compatible with the infrared data (as well as
with the crystallographic ones) are C_s and C_1, under which all the degeneracies
are removed and all modes are infrared active. The present information does
not permit one to distinguish between these two groups and polarisation
measurements at low temperatures are required to uniquely determine the
exact site symmetry of the phosphate ions.

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ИЗВОД

За структурата и симетријата на фосфатните јони кај некои калциумови фосфати

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Анализирани се инфрацрвените спектри, снимени на собна температура и на 77^0 K, на некои калциумови ортофосфати (безводен дикалциум фосфат, дикалциум фосфат дихидрат и октакалциум фосфат), особено во поглед на симетријата на фосфатните јони.

Слободниот фосфатен јон има симетрија T_d, а за хидроген фосфатниот јон, HPO_4^{2-} би можела да се очекува C_{3v} симетрија. Мег'утоа, во тврда состојба симетријата на фосфатните јони кај сите испитувани соединенија е знатно снижена, како што може да се заклучи од фактот дека дегенерациите на сите вибрациони начини се отстранети и сите начини се активни во инфрацрвениот спектар. Ова би можело да одговара на симетриските групи C_s или C_1 за кои правилата за избор и активноста на вибрационите начини се идентични. Заклучено е дека само врз основа на податоците со кои сега располагаме не е можно разликувањето на овие две симетриски групи.

ХЕМИСКИ ИНСТИТУТ
ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ