

On the Problem of Hydrogen Bonding in some Calcium Phosphates

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With 3 Figures

Summary

The hydrogen bonding by the acidic protons of the HPO_4^{2-} ion and by the water hydrogens was studied in the case of anhydrous dicalcium phosphate, dicalcium phosphate dihydrate and octacalcium phosphate, mainly on the basis of the analysis of the infrared spectra. The O—H stretching, in-plane bending and out-of-plane bending regions, as well as the region where the librational and "translational" modes of water are expected to appear were investigated.

A distribution of the acidic hydrogen between more than two O's is indicated in the structure of CaHPO_4 , whilst this does not seem to be so in the case of $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$. It appears that several types of hydrogen bonds are present in the unit cell of CaHPO_4 . The water molecules in $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ are apparently of two types: some are coordinated onto Ca^{2+} and involved in rather strong hydrogen bonding, whereas the rest are only weakly hydrogen bonded. The water molecules in octacalcium phosphate are also differently bonded.

Inhaltsübersicht

Die Wasserstoffbindung der Protonen der HPO_4^{2-} -Ionen und des Wassers in den Verbindungen Dicalciumphosphat, Dicalciumphosphat-dihydrat und Oktacalciumphosphat wurde IR-spektroskopisch untersucht, wobei die Erwartungsbereiche sowohl der Valenz-, der ebenen und nichtebenen OH-Deformationsschwingungen als auch der Librations- und „Translations“-Eigenschwingungen des Wassers berücksichtigt wurden.

Eine Bindung des Protons an mehr als zwei Sauerstoffatome ist bei CaHPO_4 angezeigt, während dies bei $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ offenbar nicht der Fall ist. In der Elementarzelle des CaHPO_4 scheinen mehrere Arten von H-Bindungen vorzuliegen. Die Wassermolekeln des $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ sind einander nicht äquivalent: die einen sind an Ca^{2+} koordiniert und durch ziemlich starke H-Bindungen gebunden, während die anderen nur schwache Wasserstoffbindungen eingehen. Auch die Wassermolekeln des Oktacalciumphosphates sind verschiedenartig gebunden.

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The question of the nature of hydrogen bonding in calcium orthophosphates has been discussed in length³⁻⁸), but usually only the O—H stretching region has been considered. We re-examined the infrared spectra of anhydrous dicalcium phosphate CaHPO_4 (DCPA), dicalcium phosphate dihydrate $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ (DCPD), and of their deuterated analogues⁹), as well as those of octacalcium phosphate $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O}$ (OCP), in the spectral region between 4000 and 300 cm^{-1} , hoping that this may throw some new light on the interesting problem of hydrogen bonding in these phosphates. The experimental details, concerning the instrumentation, preparation of the samples (except for OCP, prepared by the method of BROWN et al.⁵) and recording the spectra are given elsewhere⁹).

1. Anhydrous Dicalcium Phosphate

JONES and co-workers⁸⁾¹⁰) have reported crystallographic and spectroscopic evidence that three types of hydrogen bonds were indicated in the crystal unit of DCPA. However, the correlation between the three shortest O...O separations found in the structure of DCPA¹⁰) and the three bands reported in the O—H stretching region of the spectrum of this compound⁸⁾¹⁰) is not straightforward because the positions of the hydrogen atoms are not known and because overtones of the O—H in-plane bending modes and/or combinations of these modes may fall in to the O—H stretching region. In fact, we were unable to detect the shoulder around 3010 cm^{-1} reported by JONES and co-workers⁸⁾¹⁰) and found instead a shoulder around 3200 cm^{-1} . The other two bands in this region (around 2820 and 2400 cm^{-1} ; cf. Table 1 and Fig. 1) undoubtedly correspond to those reported by JONES and his collaborators⁸⁾¹⁰).

³) A. S. POSNER, J. M. STUTMAN and E. R. LIPPINCOTT, *Nature* [London] **188**, 486 (1960).

⁴) J. M. STUTMAN, A. S. POSNER and E. R. LIPPINCOTT, *Nature* [London] **193**, 368 (1962).

⁵) W. E. BROWN, J. P. SMITH, J. R. LEHR and A. W. FRAZIER, *Nature* [London] **196**, 1050 (1962).

⁶) L. WINAND, M. J. DALLEMAGNE and G. DUYSKAERTS, *Nature* [London] **190**, 164 (1961).

⁷) L. WINAND and M. J. DALLEMAGNE, *Nature* [London] **193**, 369 (1962).

⁸) D. W. JONES and J. A. S. SMITH, *Nature* [London] **195**, 1090 (1962).

⁹) I. PETROV, B. ŠOPTRAJANOV, N. FUSON and J. R. LAWSON, *Spectrochim. Acta* [London] **23A**, 2637 (1967).

¹⁰) D. W. JONES and (in part) D. W. J. CRUICKSHANK, *Z. Kristallogr., Kristallgeometr., Kristallphysik, Kristallchem.* **116**, 101 (1961).

Table 1
Infrared frequencies
[cm^{-1}] of the bands affected
by deuteration in the
spectrum of DCPA^{a)}

DCPA	DCPA-d	R ^{a)}
3200	2390	1.34
2820	2100	1.34
2400	1800	1.33
1400	1030	1.36
1356	995	1.36
1265 ^{b)}		
790 ^{b)}		
760 ^{b)}	≈ 580	
700 ^{b)}		

^{a)} Ratio of the protonated to deuterated frequency.

^{b)} Seen in the low-temperature (77 °K) spectrum only.

The two bands around 1400 and 1355 cm^{-1} , as well as the low-temperature one around 1265 cm^{-1} , were attributed⁹⁾ to O—H in-plane bending modes. The O—H out-of-plane bending modes are difficult to detect in the room-temperature spectrum. However, the apparently single band, found there around 900 cm^{-1} , is split, in the low-temperature spectrum, into a complex feature of which three bands attributable to P—O(H) stretching and a clear maximum and two ill-defined shoulders (around 790, 760 and 700 cm^{-1} , respectively) attributable to O—H out-of-plane bending (and listed as such in Table 1) can be sorted out⁹⁾. In the spectrum of DCPA-d a doublet is found corresponding to the P—O(D) stretching, whereas the exact position of the O—D out-of-plane bending modes could not be determined with certainty, although they apparently lie around 580 cm^{-1} .

All this seems to corroborate the idea that more than one (possibly two at room temperature and three at 77 °K) types of hydrogen bonds are present in the crystal unit of DCPA. The reason for this may be the distribution of the acidic hydrogen between more than one pair of oxygen atoms, as suggested first by JONES and his co-workers⁸⁾¹⁰⁾¹¹⁾ or the non-equivalence of all formula units in the crystal structure.

2. Dicalcium Phosphate Dihydrate

The existence, in the spectrum of DCPD (cf. Table 2 and Fig. 2), of two doublets in the region where the O—H stretching vibrations of water should

¹¹⁾ D. W. JONES and J. A. S. SMITH, J. chem. Soc. [London] 1962, 1414.

be expected to fall, clearly indicates presence of two types of water molecules in the unit cell. The molecules giving rise to the high-frequency ($3548/3490\text{ cm}^{-1}$) doublet are apparently essentially free, whereas those

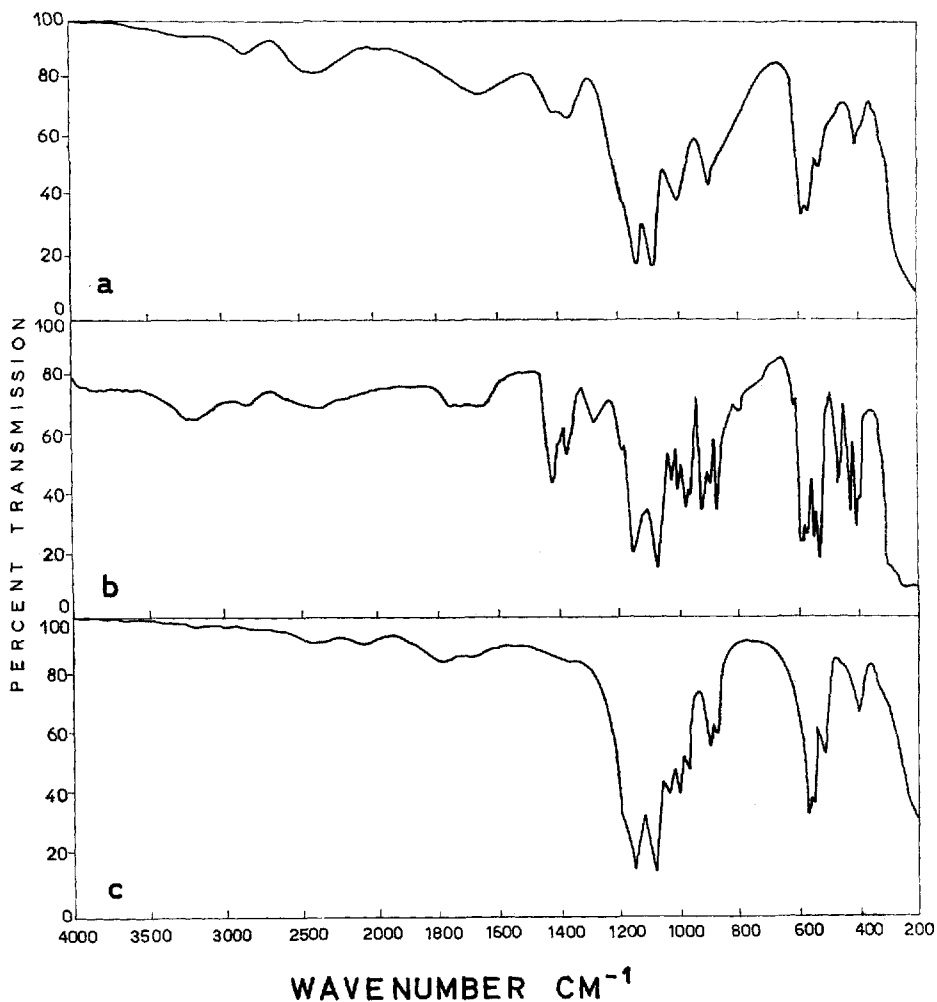


Fig. 1. Infrared spectra of CaHPO_4 in KBr pellet. a) Room-temperature spectrum of DCPA; b) Low-temperature (77°K) spectrum of DCPA; c) Room-temperature spectrum of DCPA-d

to which the low-frequency ($3281/3163\text{ cm}^{-1}$) doublet can be assigned are coordinated to Ca^9). On the other hand, the appearance of bands attributable to librations and $\text{Ca}-\text{O}_w$ stretching (originating from rotational and translational degrees of freedom of the free water molecules) show that the

Table 2
Infrared frequencies
[cm^{-1}] of the bands affected
by deuteration in the
spectrum of DCPD^{a)}

DCPD	DCPD-d ₂	R ^{a)}
3548	2637	1.35
3490	2555	1.37
3281	2458	1.34
3163	2360	1.34
2950	2190	1.35
2390	1785	1.34
1652	1217	1.36
1217	907	1.34
790	≈580	1.36?
750 ^{b)}		
660	480	1.37
370	370?	1.00?

^{a)} Ratio of the protonated to deuterated frequency.

^{b)} Seen in the low-temperature spectrum (77°K) only.

coordinated water molecules are bound, besides to calcium, to the neighbouring oxygen atoms via strong hydrogen bonds. A rather rigid frame is thus formed in which the rotation of water is transformed into libration. The frequency difference between the two doublets also shows that the coordinated water molecules participate in strong hydrogen bonds, whereas those that are not coordinated are only weakly hydrogen bonded or not bonded at all.

The acidic hydrogen of DCPD is also involved in hydrogen bonding, but the bonds in which it participates seem to be weaker than those in DCPA, as inferred from the lower values of the frequencies of both the in-plane (1217 cm^{-1}) and the out-of-plane (750 cm^{-1}) bending modes, as compared with the corresponding modes in DCPA.

It should be noted that in both the room-temperature and the low-temperature spectra of DCPD the bands assigned to the bending O—H motions of the HPO_4 group are single, whilst multiple bands are encountered in the spectrum of DCPA. It would, therefore, seem that the acidic proton is, more or less, located to only one oxygen atom and only one type of hydrogen bond is possible.

One of the two weak bands in the O—H stretching region (around 2950 and around 2390 cm^{-1}) should then be assigned to an overtone (or combination), interacting with the fundamental O—H frequency. The 2390 cm^{-1} band has just about right frequency for being an overtone of the 1217 cm^{-1} band, leaving the 2950 cm^{-1} band to be assigned to an

essentially fundamental O—H stretching vibration (HADŽI¹²) has discussed this and other possibilities for the appearance of multiple bands in the O—H stretching region). If this assignment is correct, it would be a further proof for the relatively lesser strength of the hydrogen bonds built by the acidic hydrogen of DCPD, as compared with DCPA.

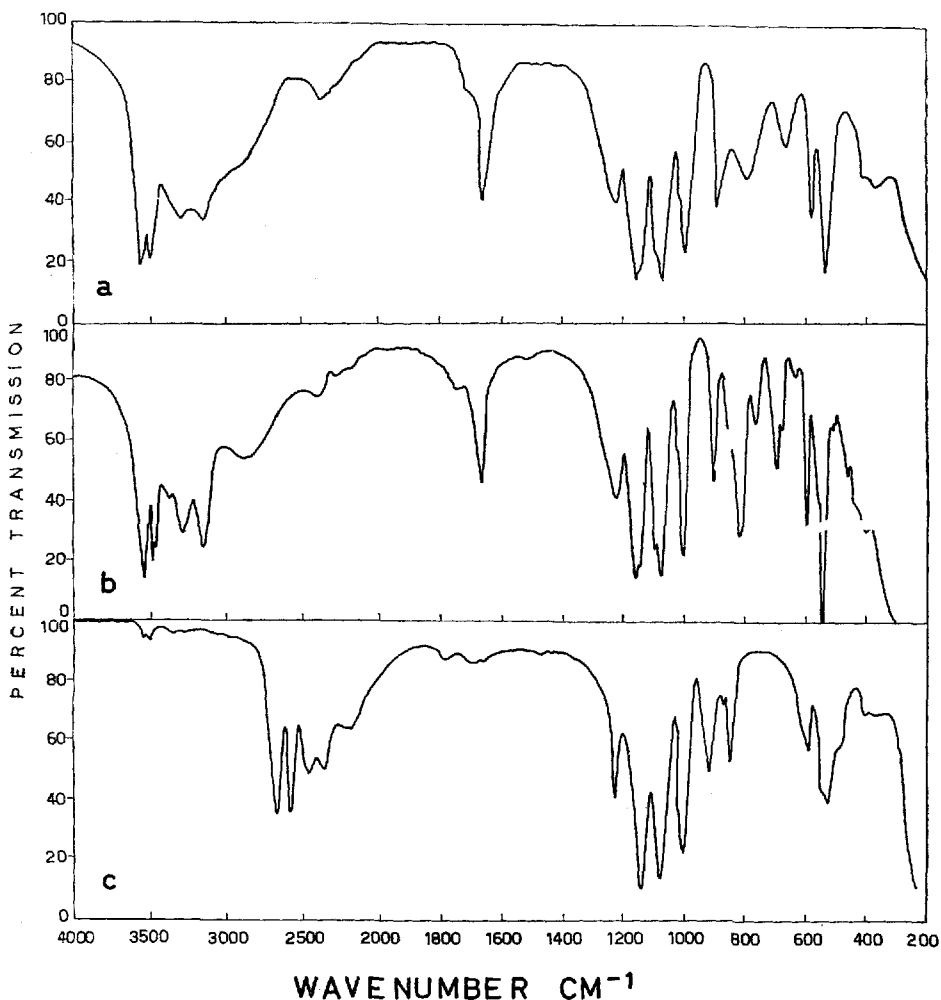


Fig. 2. Infrared spectra of $\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$ in KBr pellet. a) Room-temperature spectrum of DCPD; b) Low-temperature (77 °K) spectrum of DCPD; c) Room-temperature spectrum of DCPD- d_3

¹²) D. HADŽI, *Pure appl. Chem.* **11**, 435 (1965).

3. Octacalcium Phosphate

The interpretation of the spectrum of octacalcium phosphate (previously investigated by WINAND and DUYSKAERTS¹³) and FOWLER et al.¹⁴) was complicated by the fact that the deuterated analogue of OCP could not be prepared and, hence, the isotopic shift could not be used as a criterion in the assignment. On the other hand, the extremely low yield of the deuteration procedures seems to corroborate the crystal structure of OCP proposed by BROWN¹⁵), the channels in the water layer permitting an easy exchange of deuterium for hydrogen. Without having the spectrum of the deuterated compound, some useful guidance for the possibility of hydrogen bonding in OCP is furnished by the crystallographic data, but the inferences thus made should not be considered absolutely conclusive.

A calculation of the interatomic distances in OCP¹⁶), based on the published atomic parameters of BROWN¹⁵) shows that eight out of the ten existing molecules (there are two formula units of OCP per unit cell) have $\text{Ca}\cdots\text{O}_w$ distances of about 2.5 Å (similar to the $\text{Ca}\cdots\text{O}_w$ distance in DCPD which is again about 2.5 Å¹⁷) and several $\text{O}\cdots\text{O}$ separations between 2.7 and 3.0 Å. The two remaining water molecules do not have close $\text{Ca}\cdots\text{O}_w$ separations, but, on the other hand, have each two close $\text{O}\cdots\text{O}$ distances (of about 2.5 Å): one between themselves and the other with the neighbouring phosphate groups. It is thus conceivable that eight water molecules are coordinated to calcium atoms and form a variety of hydrogen bonds (which should not be strong) and the two remaining water molecules are bound by strong hydrogen bonds, but are not coordinated.

Returning now to the spectra (Fig. 3), the broad band ranging from 3700 to 2600 cm^{-1} can be attributed to the O—H stretching of all these molecules. The variety of hydrogen-bond types is obviously responsible for the breadth of the band and for the numerous, not well resolved, peaks on it¹⁸).

The weak band around 2400 cm^{-1} (becoming a doublet in the low-temperature spectrum) is apparently due to O—H stretching and the shoulder around 1280 cm^{-1} to O—H in-plane bending vibrations in which the acidic hydrogens take part. From the position of these two bands, the strength of the hydrogen bonds built by the acidic hydrogens of OCP can be estimated to be between that in DCPA and in DCPD. The location of the O—H out-of-plane bending mode is practically impossible in OCP. There is only a chance that the 800 cm^{-1} shoulder in the low-temperature spectrum may be due to such a motion¹⁹). The origin of the

¹³) L. WINAND and G. DUYSKAERTS, *Bull. Soc. chim. Belgique* **71**, 142 (1962).

¹⁴) B. O. FOWLER, E. C. MORENO and W. E. BROWN, *Arch. oral Biol.* **11**, 477 (1966).

¹⁵) W. E. BROWN, *Nature [London]* **196**, 1048 (1962).

¹⁶) B. ŠOPTRAJANOV and I. PETROV, *Annu. Fac. Sci. Univ. Skopje* **17** (1966) (in press).

¹⁷) C. A. BEEVERS, *Acta crystallogr. [Copenhagen]* **11**, 273 (1958).

¹⁸) After this work was completed, BERRY¹⁹) published a low-temperature spectrum of OCP mull in fluorolube in which some ten clearly resolved bands are visible.

¹⁹) E. E. BERRY, *J. inorg. nuclear Chem.* **29**, 317 (1967).

1180 cm^{-1} band is not possible to determine without having the spectrum of the deuterated compound. It can be a P—O stretching, an O—H-bending mode or a combination.

The coordinated water molecules, if hydrogen bonded, are expected to have librational and "translational" modes (as in DCPD), each kind giving rise to two librations²⁰). In the low-temperature spectrum there are

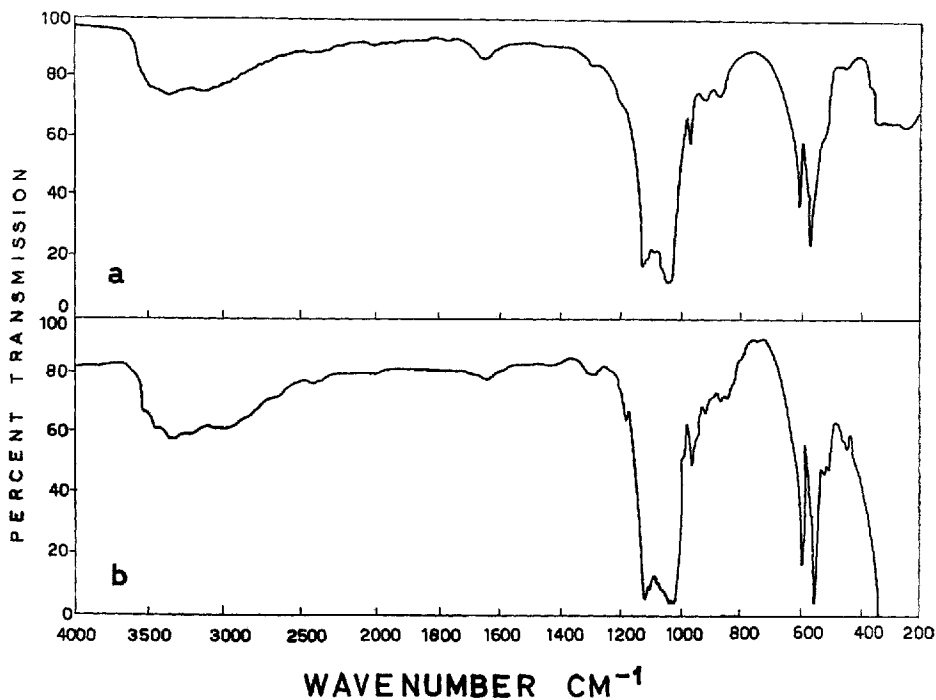


Fig. 3. Infrared spectra of $\text{Ca}_3\text{H}_2(\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O}$ in KBr pellet. a) Room-temperature spectrum of OCP; b) Low-temperature (77°K) spectrum of OCP

indeed three weak bands and a shoulder (around 920, 900, 870 and 850 cm^{-1}) in the region where the rocking librations of water could fall. Some of these bands, however, may be due to P—O(H) vibrations, as proposed by FOWLER et al.¹⁴). The two weak bands, observed around 530 and 520 cm^{-1} in the low-temperature spectrum may correspond to the wagging librational motion. More such bands may actually be hidden under the complex feature between 600 and 500 cm^{-1} , the latter becoming appreciably narrower

²⁰ J. VAN DER ELSKEN and D. W. ROBINSON, *Spectrochim. Acta* [London] **17**, 1249 (1961).

on both sides when the sample is heated. The fact that different librational bands could be located in the spectrum of OCP is a further indication that the water molecules are differently hydrogen-bonded.

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