

## Infra-red investigation of dicalcium phosphates

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(Received 4 January 1967)

**Abstract**—The infrared spectra of anhydrous dicalcium phosphate (DCPA),  $\text{CaHPO}_4$  and dicalcium phosphate dihydrate (DCPD),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and of their deuterated analogues have been studied between 4000 and  $300\text{ cm}^{-1}$ . The observed bands were assigned to modes which are, predominantly, P—O vibrations, to O—H vibrations of the  $\text{HPO}_4$  group and to motions of the water molecules (in DCPD only). Distribution of the acidic hydrogen is thought to take place in DCPA but not in DCPD. Two distinct types of water molecules were found in the unit cell of DCPD.

### INTRODUCTION

ANHYDROUS dicalcium phosphate (monetite),  $\text{CaHPO}_4$  and dicalcium phosphate dihydrate (brushite),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  have been studied rather extensively by X-ray techniques [1–4] by which the crystal structure of both compounds was established.

The infra-red and Raman spectra of orthophosphates (mainly alkaline) have also been studied by many authors, the most complete being the studies by RYSKIN and STAVITSKAYA [5] and by CHAPMAN and THIRLWELL [6]. In their extensive paper on the infra-red spectra of inorganic ions, MILLER *et al.* [7] have given the spectrum and reported the frequencies of the absorption bands of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in the region between 700 and  $300\text{ cm}^{-1}$ , but this spectrum, according to our results, does not belong to dicalcium phosphate dihydrate (DCPD), but rather to the anhydrous dicalcium phosphate (DCPA). LECOMTE, BOULLÉ and their co-workers have studied DCPD by combined dehydration, rehydration, infra-red and NMR techniques [8–10], but their infra-red spectra are limited to only certain spectral regions ( $3600$ – $2600\text{ cm}^{-1}$  and, approximately,  $700$ – $600\text{ cm}^{-1}$ ).

We therefore investigated the infra-red spectra of DCPA and DCPD in the entire region between  $4000$  and  $300\text{ cm}^{-1}$  and are, to the best of our knowledge, the first

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- [1] G. MACLENNAN and C. A. BEEVERS, *Acta Cryst.* **8**, 579 (1956).  
 [2] C. A. BEEVERS, *Acta Cryst.* **11**, 273 (1958).  
 [3] D. W. JONES and (in part) D. W. J. CRUICKSHANK, *Z. Krist.* **116**, 101 (1961).  
 [4] D. W. JONES and J. A. S. SMITH, *J. Chem. Soc.* 1414 (1962).  
 [5] YA. I. RYSKIN and G. P. STAVITSKAYA, *Opt. i Spektroskopiya* **8**, 606 (1960).  
 [6] A. C. CHAPMAN and L. E. THIRLWELL, *Spectrochim. Acta* **20**, 937 (1964).  
 [7] F. A. MILLER, G. L. CARLSON, F. F. BENTLEY and W. H. JONES, *Spectrochim. Acta* **16**, 135 (1960).  
 [8] J. LECOMTE, A. BOULLÉ and M. LANG-DUPONT, *Compt. Rend.* **241**, 1927 (1955).  
 [9] M. LANG-DUPONT, *Bull. Soc. Chim. France* 1897 (1959).  
 [10] J. FRAISSARD, A. DE SALIER DUPIN and A. BOULLE, *Compt. Rend.* **261**, 5040 (1965).

to report the spectra of the deuterated analogues of DCPA and DCPD,  $\text{CaDPO}_4$  and  $\text{CaDPO}_4 \cdot 2\text{D}_2\text{O}$  respectively.

#### EXPERIMENTAL

Well-developed crystals of dicalcium phosphate dihydrate and its deuterated analogue were prepared by gradually adding solution of ammonium hydroxide to an equimolar mixture of  $\text{CaCl}_2$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , as described in detail elsewhere [11].

Anhydrous dicalcium phosphate was prepared from  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  at pH 3 and  $83^\circ\text{C}$  by the method given by SMITH *et al.* [12] and also by dehydration *in vacuo* at  $180\text{--}200^\circ\text{C}$  of the hydrous salt. The same procedures were used to prepare the deuterated analogue. The infra-red spectra of the samples prepared by the two methods showed no difference.

The infra-red spectra were recorded on a Perkin-Elmer 521 and a Beckman IR 12 spectrophotometers, using KBr and/or CsI pressed discs. In order to eliminate the influence of water content in the matrix material, a duplicate pellet of KBr or CsI was placed in the reference beam. Spectra of mulls in Nujol and hexachlorobutadiene were also run of all the compounds under investigation and it was found that the spectra obtained by the two techniques were identical. A low-temperature cell, cooled with liquid nitrogen and with AgCl windows was used to record the low-temperature spectra.

#### RESULTS AND DISCUSSION

The spectra of DCPA and DCPA-*d* are shown in Fig. 1 and those of DCPD and DCPD-*d*<sub>3</sub> in Fig. 2. The frequencies of the infra-red bands, an estimation of their intensity and their assignments are given in Table 1 (for DCPA) and Table 2 (for DCPD).

##### 1. 4000–1600 $\text{cm}^{-1}$ region

Three bands in the region above  $1600\text{ cm}^{-1}$  in the spectrum of  $\text{CaHPO}_4$  shift considerably on deuteration (cf. Fig. 1 and Table 1). These are the broad band with a shoulder (this shoulder becomes a separate band in the low-temperature spectrum) around  $3200\text{ cm}^{-1}$  and a maximum around  $2820\text{ cm}^{-1}$  and the broad band centered around  $2400\text{ cm}^{-1}$ . Of these, the frequencies of  $2820$  and  $2400\text{ cm}^{-1}$  clearly correspond to the bands reported by JONES and CRUICKSHANK [3] at  $2784$  and  $2403\text{ cm}^{-1}$ , whereas the band around  $3200\text{ cm}^{-1}$  may not be identical with the shoulder these authors report to have found around  $3000\text{ cm}^{-1}$  and which we were unable to detect even when the DCPA concentration in the pellet was quite high. An additional band, found, in the spectrum of DCPA around  $1650\text{ cm}^{-1}$ , seems to be shifted slightly upwards in the spectrum of DCPA-*d*, thus demonstrating no clear relation to a motion in which hydrogen atoms would be involved. This band is probably a combination of P—O vibrations with possible influence of the OH groups. A similar band is found in the spectrum of DCPD (around  $1720\text{ cm}^{-1}$ ) as well as in the spectra of other phosphates, arsenates, periodates etc. [13]. In his extensive discussion of the origin of this and the bands in the OH stretching region, HADŽI [13] advocated

[11] I. PETROV and B. ŠOPTRAJANOV, *Annuaire Fac. Sci. Univ. Skopje* **16**, 123 (1965).

[12] J. P. SMITH, J. R. LEHR and W. E. BROWN, *Am. Mineralogist* **40**, 893 (1955).

[13] D. HADŽI, *Pure Appl. Chem.* **11**, 435 (1965).

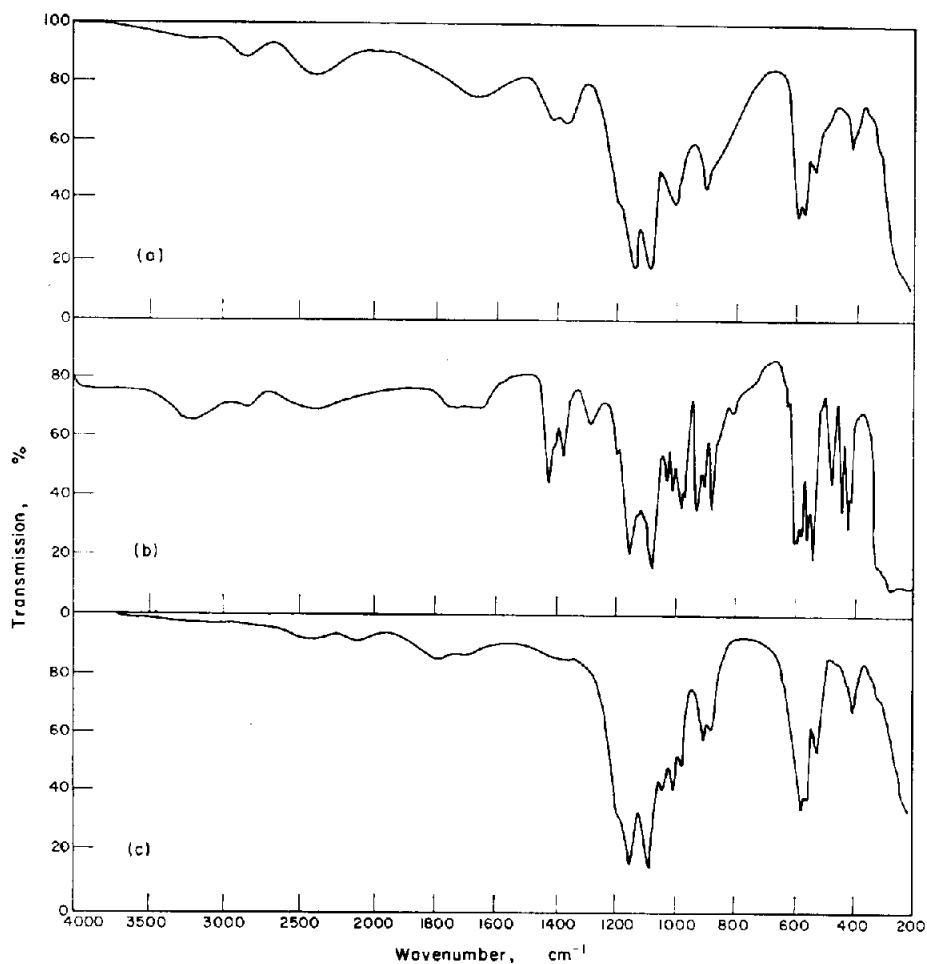


Fig. 1. Infra-red spectra of DCPA.

- (a)  $\text{CaHPO}_4$  (300°K);  
 (b)  $\text{CaHPO}_4$  (77°K);  
 (c)  $\text{CaDPO}_4$  (300°K).

an interpretation of this band as a combination of OH vibrations, but such does not seem to be the case here.

The appearance of multiple bands in the O—H stretching region (as mentioned, three such bands are found in the spectrum of DCPA) has been generally interpreted as a result of different types of hydrogen bonds, proton tunnelling or interaction with overtone or combination frequencies [13]. The NMR data of JONES *et al.* [3, 4], as well as some other evidence [13, 14], show that proton tunnelling is hardly possible in either  $\text{CaHPO}_4$  or  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . On the other hand, JONES and CRUICKSHANK [3] found in the crystal unit of DCPA three short O...O distances (2.44, 2.58 and

[14] D. HADŽI, personal communication.

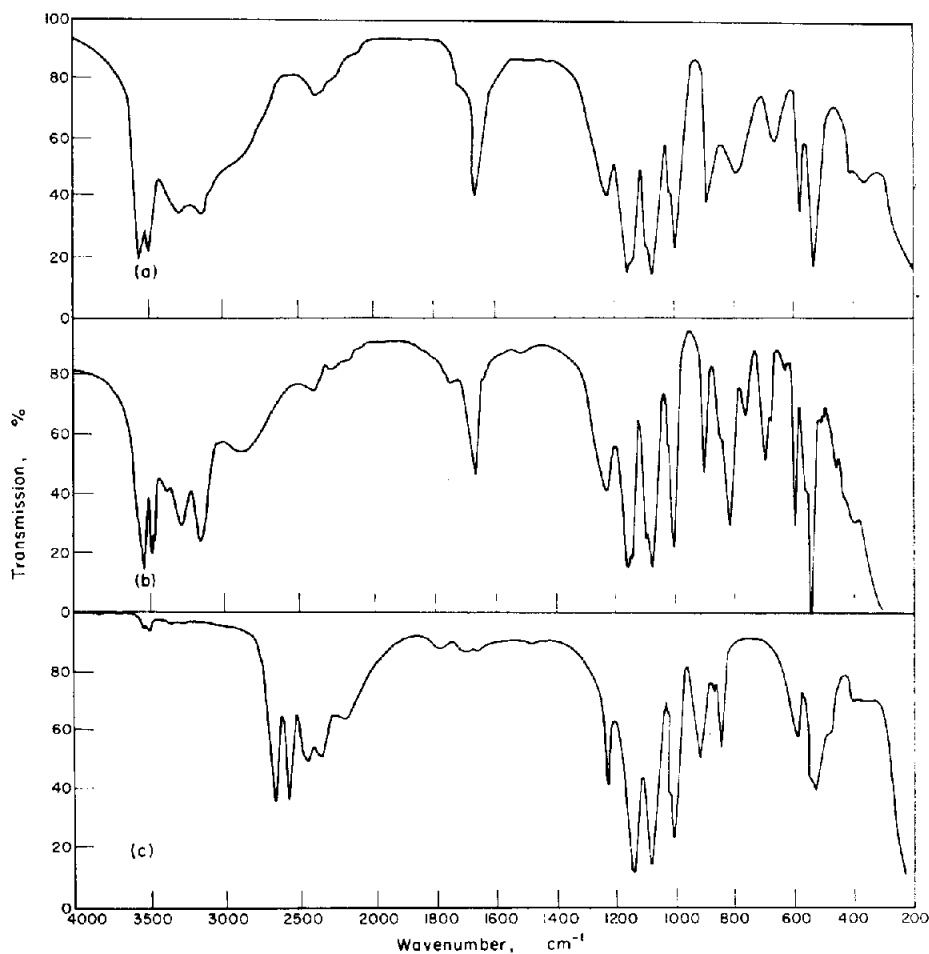


Fig. 2. Infra-red spectra of DCPD.

- (a)  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (300°K);  
 (b)  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (77°K);  
 (c)  $\text{CaDPO}_4 \cdot 2\text{D}_2\text{O}$  (300°K).

2.66 Å) suitable for hydrogen bond formation and suggested that the acidic hydrogen (the hydrogen of the  $\text{HPO}_4$  group) was distributed between more than one pair of oxygen atoms. Our infra-red spectra show that such a distribution is indeed present but it is hard to determine (especially on the basis of the analysis of the O—H stretching region only) whether all three bands between 2400 and 3200  $\text{cm}^{-1}$  are due to such a distribution (thus implying three types of hydrogen bonds) or one of them may be an overtone or combination band (in which OH vibrations take part) reinforced by Fermi resonance.

In the spectrum of DCPD in the same (4000–1600  $\text{cm}^{-1}$ ) region one can find (except for the band around 1720  $\text{cm}^{-1}$  mentioned before) two intense doublets: one with components around 3548 and 3490  $\text{cm}^{-1}$  and the other with components around 3281 and 3163  $\text{cm}^{-1}$ ; a shoulder around 2950  $\text{cm}^{-1}$ , a weak band around 2390  $\text{cm}^{-1}$  and a strong and sharp band around 1652  $\text{cm}^{-1}$ .

Table 1. Infra-red spectrum of  $\text{CaHPO}_4^*$

DCPA (300°K)		DCPA (77°K)		DCPA-d		Assignment	
$\nu$	I	$\nu$	I	$\nu$	I		
3200	vw	3220	w	2390	vw	OH stretching	
2820	w	2820	w	2100	w	OH stretching	
2400	m	2400	w	1800	m	OH stretching	
1650	w	1730	w	1700	m	combination	
1400	m	1660	w				
1356	m	1410	m	1030	m	OH in-plane bending	
		1390	sh				
		1356	m				
		1265	w	995	m	OH in-plane bending?	
1170	sh	1180	w	1180	sh	PO stretching ( $\nu_3'$ )	
1130	s	1135	s	1140	s		
1070	s	1060	s	1073	s	PO stretching ( $\nu_3''$ )	
1000	m	1013	m	969	m	585 + 428 = 1014	
		996	m			568 + 429 = 997	
		967	m			PO stretching ( $\nu_1$ )	
		950	m			523 + 429 = 957	
900	m	910	m	896	m	P—O(H) stretching ( $\nu_2''$ )	
		890	m				
		868	m				
		849	sh				
		790	vw	~580?		OH out-of-plane bending	
		760?	sh				
		700?	sh				
581	m	585	s	576	s	PO bending ( $\nu_4'$ )	
		578	s				
568	sh	568	s	562	s	PO bending ( $\nu_4''$ )	
		545	s				?
		540	sh				?
530	m	528	s	523	m	PO bending ( $\nu_4'''$ )	
480	sh	470	s			combination	
428	vw	429	s	420	w	PO bending ( $\nu_2'$ )	
405	m	405	s	403	m	PO bending ( $\nu_2''$ )	
398	sh	394	s	398	sh		

\*  $\nu$ : frequency in wave numbers; I: intensity; vw: very weak; w: weak; m: medium; s: strong; sh: shoulder.

The two doublets disappear on heating and are easy to assign to vibrations of the water molecules. The shape of the two doublets is quite different (Fig. 2): the high-frequency doublet is made up of sharp bands, whereas the components of the low-frequency doublet are much broader. The isotopic shift of the bands of the former doublet is bigger than that of the latter and the position of the components of the low-frequency doublet indicates participation in stonger hydrogen bonds. The appearance of two doublets has led to the idea that two different kinds of water molecules were present in the structure of brushite [8, 9] even before it was established [4] by X-ray analysis. The question still remains about the difference in nature between these two types of water molecules. LECOMTE and his co-workers [8, 9]

Table 2. Infra-red spectrum of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}^*$ 

$\nu$	DCPD (300°)		DCPD (77°K)		DCPD- $d_3$		Assignment
	$\nu$	I	$\nu$	I	$\nu$	I	
3548	s		3530	s	2637	s	OH stretching (of water)
3490	s		3480	s	2555	s	
			3460	s			
			3375	m	2458	s	OH stretching (of water)
3281	s		3290	s	2360	s	
3163	s		3150	s			
2950	sh		2900	m	2190	m	OH stretching
2390	w		2390	w	1785	w	$2 \times 1217 = 2434$
2270	vw		2270	vw			$1217 + 1060 = 2277$
2140	vw		2140	vw			$2 \times 1073 = 2146$
1720	w		1740	w	1740	w	combination
1652	s		1655	s	1217	s	$\text{H}_2\text{O}$ bending
			1498	vw			$990 + 527 = 1517$
1217	s		1216	s	907	s	OH in-plane bending
			1140	s			
1135	s		1128	s	1143	s	PO stretching ( $\nu_3'$ )
1075	s		1083	s	1083	s	PO stretching ( $\nu_3''$ )
1060	s		1061	s			
1005	sh		1008	m	1005	sh	PO stretching ( $\nu_1$ )
988	s		990	s	986	s	
875	s		885	s	837	s	P—O(H) stretching ( $\nu_3'''$ )
			825	sh			
790	s		798	s	~580?		$\text{H}_2\text{O}$ libration
			750	m			OH out-of-plane bending
			680	s			
660	m		665	m	480	sh	$\text{H}_2\text{O}$ libration
			615	vw			?
577	m		579	s	582	s	PO bending ( $\nu_4'$ )
			542	sh	535	s	PO bending ( $\nu_4''$ )
			527	s	515	s	PO bending ( $\nu_4'''$ )
							?
526	m		445	m			PO bending ( $\nu_2'$ )†
418	sh		420	sh			PO bending ( $\nu_2''$ )
400	m				400	m	PO bending ( $\nu_2'''$ )
370	m				370?	m	$\text{H}_2\text{O}$ translation

\*  $\nu$ : frequency in wavenumbers; I: intensity; vw: very weak; w: weak; m: medium; s: strong; sh: shoulder.

believed, on the basis of their dehydration–rehydration studies, that the high-frequency doublet belonged to “bound” and the low-frequency doublet to “free” water molecules. DEANE *et al.* [15] similarly assigned the sharp bands in the 3400–3600  $\text{cm}^{-1}$  region in the ATR spectrum of uranyl nitrate hexahydrate to vibrations of co-ordinated water. On the other hand, FRAISSARD *et al.* [10] attributed the high-frequency doublet in the spectrum of DCPD to water molecules bound more firmly than those giving rise to the low-frequency doublet.

Both the shape and the isotopic shift of the components of the 3548/3490  $\text{cm}^{-1}$  doublet show that the vibrations giving rise to this doublet are less perturbed than those responsible for the 3281/3163  $\text{cm}^{-1}$  doublet. Furthermore, the frequencies of the former doublet correspond very closely to those of the asymmetric and symmetric

[15] A. M. DEANE, E. W. T. RICHARDS and I. G. STEPHEN, *Spectrochim. Acta* **22**, 1253 (1966).

stretching of free water molecules calculated by FURLANI and his co-workers [16, 17] which are 3520 and 3445  $\text{cm}^{-1}$  respectively. We, therefore, favour the assignment of the high-frequency doublet to vibrations of water molecules only loosely bound and the low-frequency doublet to vibrations of those water molecules which, according to the crystallographic data of BEEVERS [2], form direct bonds to calcium atoms (the  $\text{Ca} \cdots \text{O}_w$  distance being 2.54 Å).

In the low-temperature spectrum the bands of the two doublets are split and two groups of three bands (with frequencies around 3530, 3480 and 3460  $\text{cm}^{-1}$  and around 3375, 3290 and 3150  $\text{cm}^{-1}$  respectively) are formed, apparently as a result of the correlation field splitting effects.

Whereas the shoulder in the room-temperature and band in the low-temperature spectrum around 2950  $\text{cm}^{-1}$  undoubtedly corresponds to the O—H stretching of the acidic hydrogen, the three weak bands (around 2390, 2270 and 2140  $\text{cm}^{-1}$ ) are probably overtones and combination bands. The 2390  $\text{cm}^{-1}$  in the spectrum of DCPD does not apparently correspond to the 2400  $\text{cm}^{-1}$  band in the spectrum of DCPA, since the analysis of the O—H in-plane bending region does not indicate a distribution of the acidic hydrogen in DCPD.

The sharp and strong band around 1652  $\text{cm}^{-1}$  is easily assigned to the in-plane bending of water and its frequency is for only a couple of wavenumbers different from the calculated [16, 17] frequency for free water molecules (1660  $\text{cm}^{-1}$ ). It is remarkable that only one such band is found, as compared with the two doublets in the O—H stretching region. It appears that this band is due to the deformation of the non-bonded water molecules, the band corresponding to the bending of the bonded water molecules being too broad and/or hidden under some more intense band (possibly the 1652  $\text{cm}^{-1}$  band itself).

## 2. 1600–300 $\text{cm}^{-1}$ region

In the region below 1600  $\text{cm}^{-1}$  the stretching and bending frequencies of the phosphate ion, the in-plane and out-of-plane O—H bending frequencies of the  $\text{HPO}_4$  group and the librational and translational modes of the water molecules are expected to appear. To distinguish between the modes that are predominantly P—O vibrations from those mainly involving motions in which hydrogen atoms take part, the isotopic shift of the infra-red bands is a reliable criterion.

2.1 P—O stretching and P—O bending vibrations. In the region 1200–900  $\text{cm}^{-1}$  where the P—O stretching frequencies are expected to fall, one can find, in the spectrum of DCPA, one doublet (around 1170 and 1130  $\text{cm}^{-1}$ ) and three bands (around 1070, 996 and 900  $\text{cm}^{-1}$ ) which do not shift appreciably on deuteration. In the spectrum of DCPA-*d* instead of the band around 900  $\text{cm}^{-1}$  a doublet (around 896/877  $\text{cm}^{-1}$ ) is found. Three more bands (around 581, 566 and 530  $\text{cm}^{-1}$ ) are found in the region where the  $\nu_4$  mode of the phosphate group is expected to appear and, at least, two bands are found around 400  $\text{cm}^{-1}$  which do not shift very much on deuteration either (cf. Table 1). Quite similar is the case with  $\text{CaPHO}_4 \cdot 2\text{H}_2\text{O}$  (cf. Table 2), except that more doublets are observed and that is hard to determine either the frequency or the number of bands in the 400  $\text{cm}^{-1}$  region. The slight isotopic shifts

[16] G. SARTORI, C. FURLANI and A. DAMIANI, *J. Inorg. Nucl. Chem.* **8**, 119 (1958).

[17] C. FURLANI, *Gazz. Chim. Ital.* **88**, 65 (1958).

and the changes in intensity of some of these bands are due to interaction with other modes: the P—O stretching vibrations probably interact with the O—H in-plane bending mode and some of the P—O bending modes (around  $500\text{ cm}^{-1}$ ) apparently [14] interact with the summation frequencies of the low-lying modes of the hydrogen bonds.

The appearance of many bands attributable to P—O vibrations shows that the  $T_d$  symmetry which the free  $\text{PO}_4^{3-}$  ion possesses [18] is lowered not to  $C_{3v}$ , as could be expected for  $\text{HPO}_4$ , but to a very low symmetry class ( $C_s$  or, more likely,  $C_1$ ) under which all the degeneracies should be removed and all the modes should become infra-red active.

Of the P—O stretching modes, we assign the band around  $996\text{ cm}^{-1}$  in the spectrum of DCPA and the band around  $988\text{ cm}^{-1}$  with a shoulder around  $1005\text{ cm}^{-1}$  in the spectrum of DCPD to the symmetric  $\nu_1$  stretching mode, mainly because of the close correspondence of the frequencies of these bands to the frequency of the  $\nu_1$  mode for the free phosphate ion ( $= 980\text{ cm}^{-1}$  [19]). The doubling of this mode in DCPD, as well as the doubling of some other P—O bands is undoubtedly a consequence of correlation field splitting effects.

It should be noted that one of the components of the  $\nu_3$  mode ( $\nu_3''$ ) is well removed from the other two in both the spectra of DCPA and of DCPD. The reason for such a difference in the frequencies lies probably in the lengthening of the P—O bond (with a corresponding decrease in the force constant) when a hydrogen atom is attached to the oxygen in question. In the spectrum of DCPA- $d$  a doublet of bands (around  $896$  and  $877\text{ cm}^{-1}$ ) correspond to this mode and the  $900\text{ cm}^{-1}$  band in the spectrum of DCPA is itself probably complex, as seen from the low-temperature spectrum (cf. Fig. 1) in which three bands are seen in this region (around  $910$ ,  $890$  and  $867\text{ cm}^{-1}$ ). The reason for such a splitting apparently lies in the distribution of the acidic hydrogen between at least two (and possibly three) oxygens of the phosphate group, thus producing unequally long P—O bonds. The corresponding band in the spectrum of DCPD is found around  $874\text{ cm}^{-1}$  whereas in the spectrum of DCPD- $d_3$  it lies around  $837\text{ cm}^{-1}$ . Such an appreciable isotopic shift is a further indication that this band is indeed due to stretching of the bond between phosphorus and oxygen to which hydrogen (deuterium) is attached. On the other hand, the fact that in the spectrum of DCPD a single band is found, contrary to the case with DCPA, shows that the distribution of the acidic proton is less pronounced in DCPD than in DCPA. The foregoing interpretation is in agreement with the X-ray data on DCPA [3], but not on DCPD [4].

The assignment of the three bands in the region  $580$ – $520\text{ cm}^{-1}$  to the three components of the  $\nu_4$  mode and the interpretation of the  $428\text{ cm}^{-1}$  band and the  $405/398\text{ cm}^{-1}$  doublet in the spectrum of DCPA as well as the  $418/400\text{ cm}^{-1}$  doublet in the spectrum of DCPD to the  $\nu_2$  mode seems to be quite straightforward.

**2.2 O—H bending vibrations.** The  $1217\text{ cm}^{-1}$  band in the spectrum of DCPD is readily assigned, on the basis of its isotopic shift, to the O—H in-plane bending of

[18] G. HERZBERG, *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules*. Van Nostrand (1964).

[19] K. W. F. KOHLRAUSCH, *Der Smekal-Raman-Effekt, Ergänzungsband 1931–1937*. Springer (1938).



the  $\text{HPO}_4$  group. In the spectrum of DCPA two bands are found at room temperature, whereas at the liquid nitrogen temperature a third band (around  $1265\text{ cm}^{-1}$ ) appears and the  $1410\text{ cm}^{-1}$  exhibits a shoulder. The appearance of two bands in the room-temperature spectrum of DCPA serves as a further proof that distribution of the acidic hydrogen takes place and at least two types of hydrogen bonds are formed. In fact, the number of such types may be different at room temperature and at  $77^\circ\text{K}$  (the analysis of the low-temperature spectrum indicates, namely, existence of three types of hydrogen bonds).

If the upward shift of the bending frequencies is a measure of the strength of the hydrogen bonds (as seems to be generally accepted) one could conclude that the hydrogen bonds built by the acidic hydrogen in DCPA should be classified as stronger than those in DCPD.

The identification of the O—H out-of-plane deformation modes is much more complicated. In the spectrum of DCPA this vibration should be located somewhere under the low-frequency side of the  $900\text{ cm}^{-1}$  band. This band is asymmetric and its low-frequency side is much broader than the high-frequency one. On deuteration, when a doublet appears in the place of this band, the feature is more symmetric and much narrower, as if a band causing the broadening of the low-frequency side of the  $900\text{ cm}^{-1}$  band has been isotopically shifted. On the other hand a weak band (at about  $790\text{ cm}^{-1}$ ) and two shoulders (at lower frequencies) appear in the low-temperature spectrum of DCPA. All this justifies the assignment of the  $790\text{ cm}^{-1}$  low-temperature band to this mode. The corresponding band in the spectrum of DCPD is again easier to locate in the low-temperature spectrum in which either the shoulder around  $825\text{ cm}^{-1}$  or the band around  $750\text{ cm}^{-1}$  should be assigned to this mode. At this time we favour the latter assignment.

A shoulder around  $480\text{ cm}^{-1}$  in the spectrum of DCPA is also sensitive on deuteration, but its origin is unclear; it may be due to some sort of combination in which the low-lying modes of the hydrogen bond take part [14].

*2.3 Librational and translational modes of water.* Three bands in the spectrum of DCPD do not have a counterpart in the spectrum of DCPA: the bands at about  $790$ ,  $660$  and  $370\text{ cm}^{-1}$ . All three bands disappear on dehydration and the former two are considerably isotopically shifted (the ratio of the protonated to deuterated frequency being 1.36 and 1.38 respectively). The isotopic shift of the  $370\text{ cm}^{-1}$  band could not be determined exactly, but it seems that in the spectrum of DCPD- $d_3$  this band is located again around  $370\text{ cm}^{-1}$ , somewhere in the broad feature between  $400$  and  $300\text{ cm}^{-1}$ . The  $790$  and  $660\text{ cm}^{-1}$  bands in the low-temperature spectrum are split each into two closely lying components.

The large isotopic shift of the  $790$  and  $660\text{ cm}^{-1}$  bands characterizes them as due to librations of the water molecules and we assign the  $790\text{ cm}^{-1}$  band to a rocking and the  $660\text{ cm}^{-1}$  band to a wagging librational motion. VAN DER ELSKEN and ROBINSON [20] suggested that each crystallographically different type of water molecule should give rise to two infra-red active librational modes. It should, however, be borne in mind that, in order to have a large enough dipole moment change, the water molecules should be bound with reasonably strong metal-oxygen bonds and strong or moderately strong hydrogen bonds with the neighbouring

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

atoms [21]. The splitting of the bands due to librations in the low-temperature spectrum could be caused either by librational motions of the two types of water molecules or it is another case of correlation field splitting. Since it is rather unlikely that the loosely bound water molecules (responsible for the 3548/3490  $\text{cm}^{-1}$  doublet) could form, with calcium and the neighbouring oxygens, a system rigid enough, so that the librational modes would change the dipole moment significantly, the latter interpretation is to be preferred.

Although the isotopic shift of the 370  $\text{cm}^{-1}$  band could not be accurately determined it does not seem to be more than a couple of wavenumbers. This would, then, characterize the 370  $\text{cm}^{-1}$  band as due to "translation" of the water molecules, i.e. to Ca—O<sub>w</sub> stretching. In some other instances bands due to "translations" of the co-ordinated water molecules have indeed been found in this region [22].

*Acknowledgements*—This work was supported in part by a grant from the National Institute of Dental Research, Washington, D.C. The authors wish to express their deepest gratitude to Professor D. HADŽI for reading the manuscript and for the many useful suggestions.

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