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## 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°K, 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,  $\text{HPO}_4^{2-}$ . However, in the solid state the site symmetry of the phosphate ions of the analysed compounds is appreciably 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,  $\text{PO}_4^{5-}$ , is known<sup>1</sup> to have tetrahedral symmetry. Its nine vibrational degrees of freedom give, under  $T_d$  symmetry, four vibrational modes: the non-degenerate  $\nu_1$  stretching mode, the doubly degenerate  $\nu_2$  bending mode and the two triply degenerate modes,  $\nu_3$  and  $\nu_4$ , 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  $\text{cm}^{-1}$  respectively<sup>2</sup>. Nakamoto<sup>3</sup>, quoting the Landolt-Börnstein Tables<sup>4</sup>, gives slightly different values, namely 970, 358, 1080 and 500  $\text{cm}^{-1}$  for the frequencies of the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes respectively.

For the  $\text{HPO}_4^{2-}$  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  $C_1$ .

Several possible factors may act towards the lowering of the symmetry in the solid state. Ross and his co-workers<sup>5-9</sup> 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<sup>5-9</sup>, 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<sup>10</sup>, Chapman and Thirlwell<sup>11</sup>, Stutman *et al.*<sup>12</sup>, Fowler *et al.*<sup>13</sup>, Baddiel and Berry<sup>14</sup> and Hezel and Ross<sup>9</sup>. In their calculation of the force constants of the phosphate ions, Chapman *et al.*<sup>15</sup>

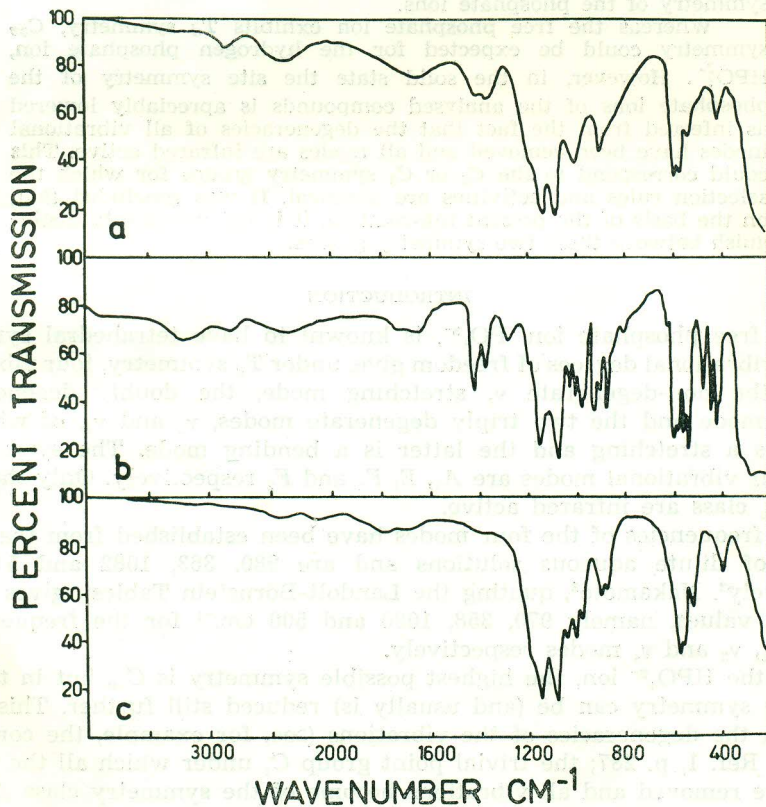


Fig. 1. Infrared spectra of DCPA:

- a. Room-temperature (300°K) spectrum of  $\text{CaHPO}_4$
- b. Low-temperature (77°K) spectrum of  $\text{CaHPO}_4$
- c. Room-temperature (300°K) spectrum of  $\text{CdDPO}_4$

assumed  $T_d$  symmetry for the  $\text{PO}_4^{3-}$  ion,  $C_{3v}$  symmetry for the P—O skeleton of the  $\text{HPO}_4^{2-}$  ion and  $C_s$  symmetry for the P—O skeleton of the  $\text{H}_2\text{PO}_4^-$  ion. In our investigation of some calcium phosphates<sup>16,17</sup> we also made some conclusions with respect to the symmetry of the  $\text{HPO}_4^{2-}$  ion in anhydrous dicalcium phosphate (DCPA),  $\text{CaHPO}_4$  and dicalcium phosphate dihydrate (DCPD),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  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),  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ , 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<sup>18,19</sup>. 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  $\text{cm}^{-1}$  because of the use of AgCl as window material.

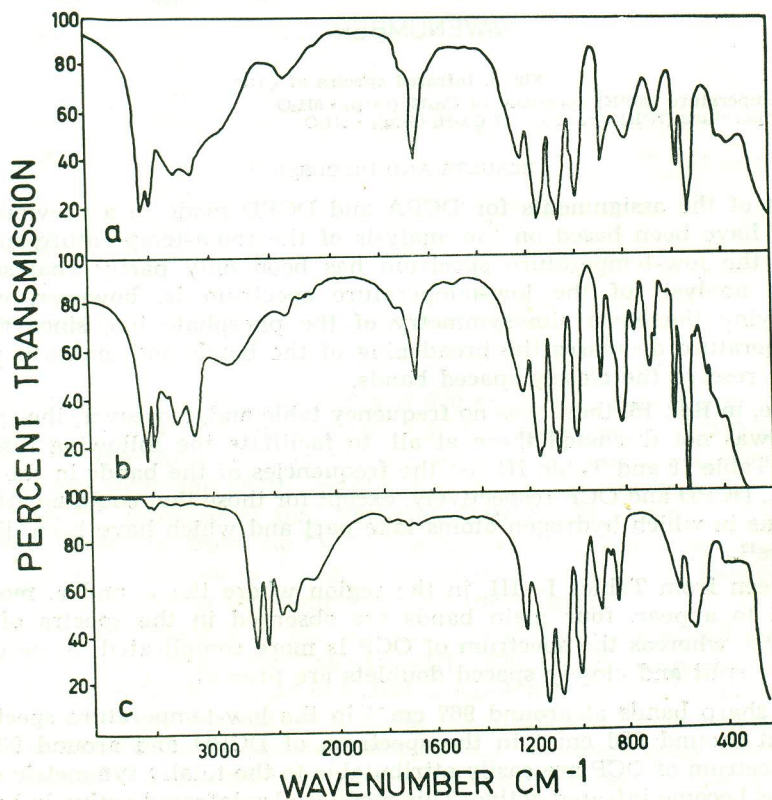


Fig. 2. Infrared spectra of DCPD

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

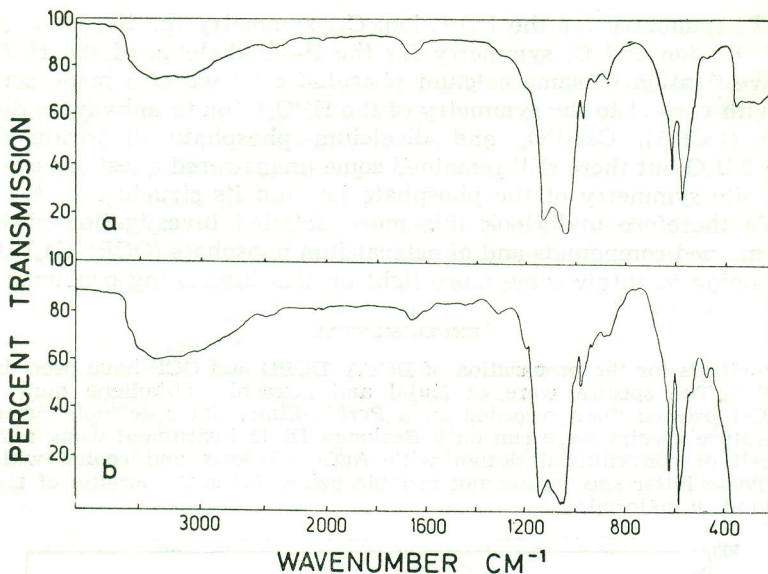


Fig. 3. Infrared spectra of OCP

- a. Room-temperature (300°K) spectrum of  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$   
 b. Low-temperature (77°K) spectrum of  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$

#### RESULTS AND DISCUSSION

Most of the assignments for DCPA and DCPD made in a previous paper of ours<sup>16</sup> 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<sup>17</sup>.

As seen from Tables I—III, in the region where the  $\nu_3$  and  $\nu_1$  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  $967\text{ cm}^{-1}$  in the low-temperature spectrum of DCPA, at around  $988\text{ cm}^{-1}$  in the spectrum of DCPD and around  $962\text{ cm}^{-1}$  in the spectrum of OCP are easily attributable to the totally symmetric  $\nu_1$  mode which has become infrared active. This mode is also infrared active in hydroxyapatite, fluoroapatite<sup>14</sup> and chlorapatite<sup>12</sup>, 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
$\nu$	I	$\nu$	I	$\nu$	I	
1170	sh	1180	w	1180	sh	$\nu_3'$
1130	s	1135	s	1140	s	
1070	s	1060	s	1073	s	$\nu_3''$
1000	m	1015	w	969	m	$\nu_2' + \nu_4'$
		996	w			$\nu_2' + \nu_4''$
		967	m			$\nu_1$
		950	w			$\nu_2' + \nu_4'''$
900	m	910	s	896	m	] $\nu_3'''$ : P—O(H) stretch
		890	m	877	m	
		868	s			
		849	sh			
581	m	585	s	576	s	$\nu_4'$
		578	s			
566	sh	566	s	562	sh	$\nu_4''$
		545	s			?
		540	sh			?
530	m	528	s	523	m	$\nu_4'''$
480	sh	470	s	?		combination?
428	vw	429	s	420	w	$\nu_2'$
405	m	405	s	403	m	$\nu_2''$
398	sh	394	s	398	sh	

\*  $\nu$  : frequency (cm.<sup>-1</sup>); I : intensity; vw : very weak; w : weak; m : medium; s : strong; sh : shoulder

The bands around 1170/1130, 1070 and 900 cm.<sup>-1</sup> in the spectrum of DCPA and around 1135, 1075/1060 and 875 cm.<sup>-1</sup> in the spectrum at DCPD undoubtedly belong to the three components ( $\nu_3'$ ,  $\nu_3''$  and  $\nu_3'''$ ) of the  $\nu_3$  mode. The situation is less clear for OCP, mainly due to the lack of the spectrum of deuterated OCP<sup>17</sup>. 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  $\nu_3$  mode.

Two of the components of the  $\nu_3$  mode are close together and the third is far removed from them (see Tables I—III). This third component (around 900 cm.<sup>-1</sup> in the spectrum of DCPA and around 875 cm.<sup>-1</sup> in the spectrum of DCPD) has been attributed<sup>11,15,16</sup> 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.<sup>-1</sup> 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<sup>16,17,23</sup>. 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 <sub>3</sub> (300° K)		Assignment
$\nu$	I	$\nu$	I	$\nu$	I	
1135	s	1140 1128	s s	1143	s	$\nu_3'$
1075	s	1083	s	1083	s	$\nu_3''$
1060	s	1061	s			
1005	sh	1008	m	1005	sh	$\nu_1$
988	s	990	s	986	s	
875	m	885	s	837	s	$\nu_3'''$ : P—O(H) stretch
577	m	579	s	582	s	$\nu_4'$
526	m	542	sh	535	s	$\nu_4''$
		527	s	515	s	$\nu_4'''$
		445	m			?
418	sh	420	sh			$\nu_2' ?$
400	m			400	m	$\nu_2''$

\*  $\nu$  : frequency (cm.<sup>-1</sup>); 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  $\nu_4$  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<sub>3</sub> show that such a splitting (into three components) of the  $\nu_4$  mode also takes place in the hydrated dicalcium phosphate.

The detection of the components of the  $\nu_2$  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<sub>w</sub> 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<sup>17</sup>). It should be mentioned that the components of the  $\nu_2$  mode in hydroxyapatite and fluoroapatite were assigned<sup>14</sup> 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<sup>24</sup>. The non-equivalence of all phosphate groups in the unit cell (indicated by the crystallographic data<sup>21-23,25</sup>) 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	
$\nu$	I	$\nu$	I		
1175	sh	1180	w	?	
1120	s	1128	s		
		1113	sh		
1080	sh	1080	s		$\nu_3$
1045	s	1043	s		
1018	s	1025	s		
		990	sh		
962	m	970	m		$\nu_1$
		955	sh		
910	w	922	w		$\nu_3$ : P—O(H) stretch and/or H <sub>2</sub> O libration
		900	sh		
868	sh	870	w		
855	w	850	w		
600	s	603	s	$\nu_4'$	
		580	sh	$\nu_4''$	
561	s	564	s	$\nu_4'''$	
		465	w	?	
465	vw	468	w	$\nu_2$ and Ca—O <sub>w</sub> stretch (H <sub>2</sub> O »translation«)	
		420	sh		
		400	sh		
355	sh				
340	m				
305	m				
285	m				

\*  $\nu$  : frequency (cm.<sup>-1</sup>); 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 CaHPO<sub>4</sub> could be found in the literature (the related, isostructural, SrHPO<sub>4</sub>, however, has a high-temperature and a low-temperature modification<sup>26</sup>).

It should be noted that the general appearance 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  $\nu_3$  mode on deuteration. It can be seen (cf. Table I and Table II) that the  $\nu_3'$  and  $\nu_3''$  bands have higher and the  $\nu_3'''$  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  $1400\text{ cm.}^{-1}$  (two bands are actually found: at  $1400$  and  $1356\text{ cm.}^{-1}$ ) in DCPA and about  $1217\text{ cm.}^{-1}$  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  $1000\text{ cm.}^{-1}$  in DCPA and to about  $900\text{ cm.}^{-1}$  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<sup>25</sup> 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<sup>21</sup>, whereas  $C_s$  symmetry is possible for DCPD, if the P—O distances given by Jones and Smith<sup>22</sup> are taken or on their face values. Our calculation of the interatomic distance in OCP<sup>23</sup>, based on the atomic parameters by Brown<sup>25</sup>, 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 appearance of the  $\nu_1$  mode, the splitting of the triply degenerate  $\nu_2$  and  $\nu_4$  modes each into three components and the likely splitting of the  $\nu_2$  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° 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,  $\text{HPO}_4^{2-}$  би можела да се очекува  $C_{3v}$  симетрија. Меѓутоа, 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

Примено 7. февруари, 1967.