

DESCRIPTION OF MOLECULAR DISTORTIONS. VI. SPECTRA-STRUCTURE CORRELATIONS IN  
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Second rank tensors were used to describe the distortions in a number of orthophosphate compounds, by a method introduced previously [1]. The results are compared with results obtained by other methods. A significant correlation was found between the principal values of the tensor of distortion and the frequencies of the components of the antisymmetric PO<sub>4</sub> stretching vibrations.

## INTRODUCTION

In the first paper of this series [1], tensors were used to describe the distortions of tetrahedral molecules. A rather good correlation was found between the principal values of the tensor of distortion and the frequencies of the components of the antisymmetric stretching vibration in a number of sulfate compounds. Later [2] it was proved that this method gives good results for trigonally planar molecules also (nitrate compounds were studied for that matter).

In the present paper, some spectra-structure correlations for orthophosphates are revealed. In addition, the distortions of the phosphate ions are calculated and compared with the distortions calculated by other methods [3-7].

## MATHEMATICAL METHOD AND CALCULATION

The method was explained in detail in our previous papers [1,2], hence a very brief summary is given here. Let us consider a single PO<sub>4</sub> ion; starting with the notation

$$\begin{aligned} P-01 &= \mathbf{p} = \{p_1, p_2, p_3\} \\ P-02 &= \mathbf{q} = \{q_1, q_2, q_3\} \\ P-03 &= \mathbf{r} = \{r_1, r_2, r_3\} \\ P-04 &= \mathbf{s} = \{s_1, s_2, s_3\} \end{aligned}$$

the following equation was introduced :

$$T_{ij} = p_1 \cdot p_j / |p|^\delta + q_1 \cdot q_j / |q|^\delta + r_1 \cdot r_j / |r|^\delta + s_1 \cdot s_j / |s|^\delta \quad i, j \in \{1, 2, 3\}$$

The right-hand side of this equation is a tensorial quantity, related to the PO<sub>4</sub> ion in question and describing its distortion. A value of 12 was assigned to the constant  $\delta$ . After diagonalization, the principal values may be chosen in such a way, that  $T_{11} \leq T_{22} \leq T_{33}$ . A correlation between this sequence of principal values and the sequence of the frequencies of the three components of  $\nu_3(\text{PO}_4)$  vibration (taken in ascending order) was searched for.

Once identified the principal values  $T_{11}$ ,  $T_{22}$ ,  $T_{33}$  define an ellipsoid with semi-major axes as follows :

$$\begin{aligned} a^2 &= 1/T_{11} \\ b^2 &= 1/T_{22} \\ c^2 &= 1/T_{33} \end{aligned}$$

The total distortion [1] of the PO<sub>4</sub> "tetrahedron" is :

$$D_t = [(1 - b/a)^2 + (1 - c/a)^2 + (1 - c/b)^2]/3$$

All calculations were performed on an IBM-PC compatible microcomputer. The programs for calculation of the distortions were written in BASIC. The statistical calculations were performed using STATGRAPH statistical package.

## RESULTS AND DISCUSSION

Sixteen phosphate compounds for which both crystallographic and spectroscopic data were available, were included in the regression analyses. The values for a "free"  $\text{PO}_4$  ion were also included. That makes a total of 50 points (the assignment of one of  $\nu_3$  the components in  $\text{NbOPO}_4$  is uncertain). The results of the regression analysis are presented in Fig. 1, the input data being summarized in Table I. The correlation coefficient ( $r^2 = 0.85$ ) is high, but significantly lower when compared with the value for

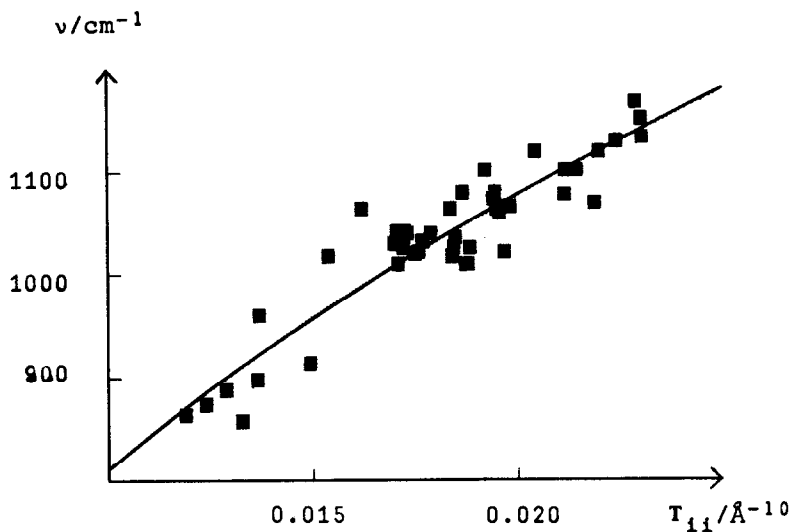


Figure 1. Regression of  $\nu_3$  on  $T_{11}$  - best curve fit.

TABLE I. Pairs of  $T_{11}$  -  $\nu_3$  data, included in the regression analysis.

Compound	$T_{11}/\text{\AA}^{-10}$	Ref.	$\nu_3/\text{cm}^{-1}$	Ref.
$\text{PO}_4$ - "free"	0.01840		1017	
	0.01840	[6]	1017	[9]
	0.01840		1017	
$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$	0.01750		1020	
	0.01846	[10]	1025	[11]
	0.01848		1036	
$\text{NbOPO}_4$	0.01837		?	
	0.01968	[12]	1023	[13]
	0.01968		1023	

TABLE I (continued)

	0.01712		1032	
$\text{Li}_3\text{PO}_4$	0.01768	[14]	1032	[13]
	0.01867		1080	
	0.01709		1010	
$\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$	0.01873	[15]	1010	[11]
	0.01882		1010	
	0.01732		1040	
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	0.01789	[16]	1040	[13]
	0.01942		1074	
	0.01722		1026	
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	0.01885	[17]	1064	[13]
	0.01948		1064	
	0.01707		1043	
$\text{Mg}_3(\text{PO}_4)_2$	0.01947	[18]	1080	[13]
	0.02202		1120	
	0.01700		1030	
$\text{LuPO}_4$	0.01700	[19]	1030	[13]
	0.02190		1070	
	0.01539		1018	
$\text{Zn}_3(\text{PO}_4)_2$	0.01962	[20]	1102	[13]
	0.02119		1102	
	0.01494		915	
$\text{SnHPO}_4$	0.01760	[21]	1022	[13]
	0.02148		1101	
	0.01369		960	
$\text{KMgPO}_4 \cdot \text{H}_2\text{O}$	0.01725	[22]	1041	[23]
	0.02045		1120	
	0.01364		897	
$(\text{NH}_4)_2\text{HPO}_4$	0.01956	[24]	1060	[13]
	0.02117		1079	
	0.01326		859	
$\text{Na}_2\text{HPO}_4$	0.01621	[25]	1064	[13]
	0.02305		1152	
	0.01288		888	
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	0.01836	[26]	1064	[13]
	0.02290		1168	
	0.01239		874	
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	0.01962	[27]	1066	[13]
	0.02306		1134	
	0.01189		864	
$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	0.01984	[28]	1065	[13]
	0.02243		1130	

nitrates and, especially, with the one for sulfates. Since the accuracy of the crystal structure determination was, on the average, about the same in

all three classes of compounds, the reasons for the scatter of the data points are not clearly evident. Perhaps it should be mentioned that according to McDonald and Cruickshank [29] the oxygen "framework" seems to be more rigid in the case of sulfates than in the case of phosphates. That is, the distortions in sulfates may be fairly well described as "...a central atom, moving in a rigid framework of oxygens...", this being only a crude approximation in the case of phosphates.

The distortions of the phosphate ions, calculated by various methods, are comparatively presented in Table II. The total distortion  $D_t$  correlates fairly well with the distortion indices and displacement vectors but, rather unexpectedly, not with the relative distortion,  $E_{rel}$ , introduced by Dollase [4]. It might be interesting to learn, whether the same appears to be the case for other molecules/ions.

TABLE II. Distortions of the  $PO_4$  groups - results obtained by various methods :  $D_t$  - total distortion [1];  $E_{rel}$  - relative distortion [4];  $DI(PO)$ ,  $DI(OPO)$   $DI(OO)$  - distortion indices [3];  $D_2$ ,  $D_3$ ,  $D_4$  - displacement vectors [5].

Compound	$D_t$	$E_{rel}/\%$	$DI(PO)$	$DI(OPO)$	$DI(OO)$	$D_2/^\circ$	$D_3/\text{\AA}$	$D_4/^\circ$
$PO_4$ "free"	0.0000	0.00	0.0000	0.0000	0.0000	0.00	0.000	0.00
$NH_4MgPO_4 \cdot 6H_2O$	0.0003	0.66	0.0008	0.0047	0.0029	1.14	0.003	1.23
$NbOPO_4$	0.0008	1.51	0.0000	0.0118	0.0079	3.34	0.000	0.00
$Li_3PO_4$	0.0009	0.34	0.0036	0.0020	0.0023	0.03	0.013	0.56
$KMgPO_4 \cdot 6H_2O$	0.0014	0.63	0.0038	0.0056	0.0025	1.06	0.014	1.22
$AlPO_4 \cdot 2H_2O$	0.0017	1.67	0.0026	0.0121	0.0082	3.66	0.009	0.92
$AlPO_4 \cdot 2H_2O$	0.0019	1.42	0.0038	0.0097	0.0066	2.37	0.012	2.70
$Mg_3(PO_4)_2$	0.0073	2.86	0.0061	0.0202	0.0139	5.74	0.022	3.83
$LuPO_4$	0.0094	5.45	0.0000	0.0428	0.0296	12.19	0.000	0.00
$Zn_3P_2O_8 \cdot 4H_2O$	0.0117	1.92	0.0104	0.0149	0.0078	2.94	0.038	4.48
$SnHPO_4$	0.0142	2.90	0.0113	0.0189	0.0119	5.09	0.039	5.54
$KMgPO_4 \cdot H_2O$	0.0172	2.40	0.0140	0.0168	0.0106	4.31	0.047	4.62
$(NH_4)_2HPO_4$	0.0225	2.65	0.0154	0.0220	0.0094	3.86	0.055	6.32
$Na_2HPO_4$	0.0312	2.68	0.0207	0.0228	0.0077	3.28	0.065	7.93
$MgHPO_4 \cdot 3H_2O$	0.0333	2.58	0.0175	0.0271	0.0078	3.01	0.069	7.46
$CaHPO_4 \cdot 2H_2O$	0.0398	2.94	0.0219	0.0265	0.0110	4.72	0.080	7.00
$Na_2HPO_4 \cdot 2H_2O$	0.0429	2.64	0.0154	0.0220	0.0094	3.86	0.055	6.32

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