RAMAN SPECTRUM OF POTASSIUM DI-HYDROGEN PHOSPHATE

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1. Introduction

The Raman spectra of ammonium and potassium di-hydrogen phosphates have been investigated by Jean Chapelle (1949) and Landsberg and Baryshanskaya (1949). In the case of KH_2PO_4, Chapelle, using the visible rediations of the mercury arc, identified 7 frequency shifts of which the two low frequency ones have been attributed to the rotational oscillations of the H_2PO_4 group around the two-fold axis. Comparing his results with those obtained by the author (Narayanan, 1948) in the case of $NH_4H_2PO_4$, it became clear that the lattice spectrum of KH_2PO_4 as recorded by Chapelle was incomplete. The author had occasion to study the Raman spectrum of KH_2PO_4 after that of $NH_4H_2PO_4$ using the resonance radiation of mercury as exciter. However, before the author could publish his results, Chapelle's paper on the subject appeared. Nevertheless, the author's investigation has brought to light the existence of some detail not observed by Chapelle. It was therefore considered worth while to put the same on record.

2. Experimental Results

A fine transparent specimen of KH_2PO_4 (2 cm. × 2 cm. × 1 cm.) with the faces 100, 010, 101 and 011 fully developed was used to record the Raman spectrum excited by λ 2537. Fig. 1 (*a*) is a reproduction of the microphotometer record of the spectrogram obtained when the incident light was along *a* and the scattered light was along the optic or *c* axis, while Fig. 1 (*b*) corresponds to the case in which the scattered light was taken along the *a* axis with the incident light along *b* axis. The spectrum consists of 15 lines some of which are broad and diffuse; the frequency shifts of these are 50, 98, 114, 153, 185, 358, 370, 393, 467, 528, 570, 913, 1080, 2500 and 2700 cm.$^{-1}$ of which those at 98, 114, 358, 393, 459, 531 and 911 cm.$^{-1}$ above have been reported by Chapelle in his published paper. In a private communication, he informed the author about his having recorded the bands at 2500 and 2700 cm.$^{-1}$ also. The lines at 114, 153, 370, 467, 2500 and 2700 are of different

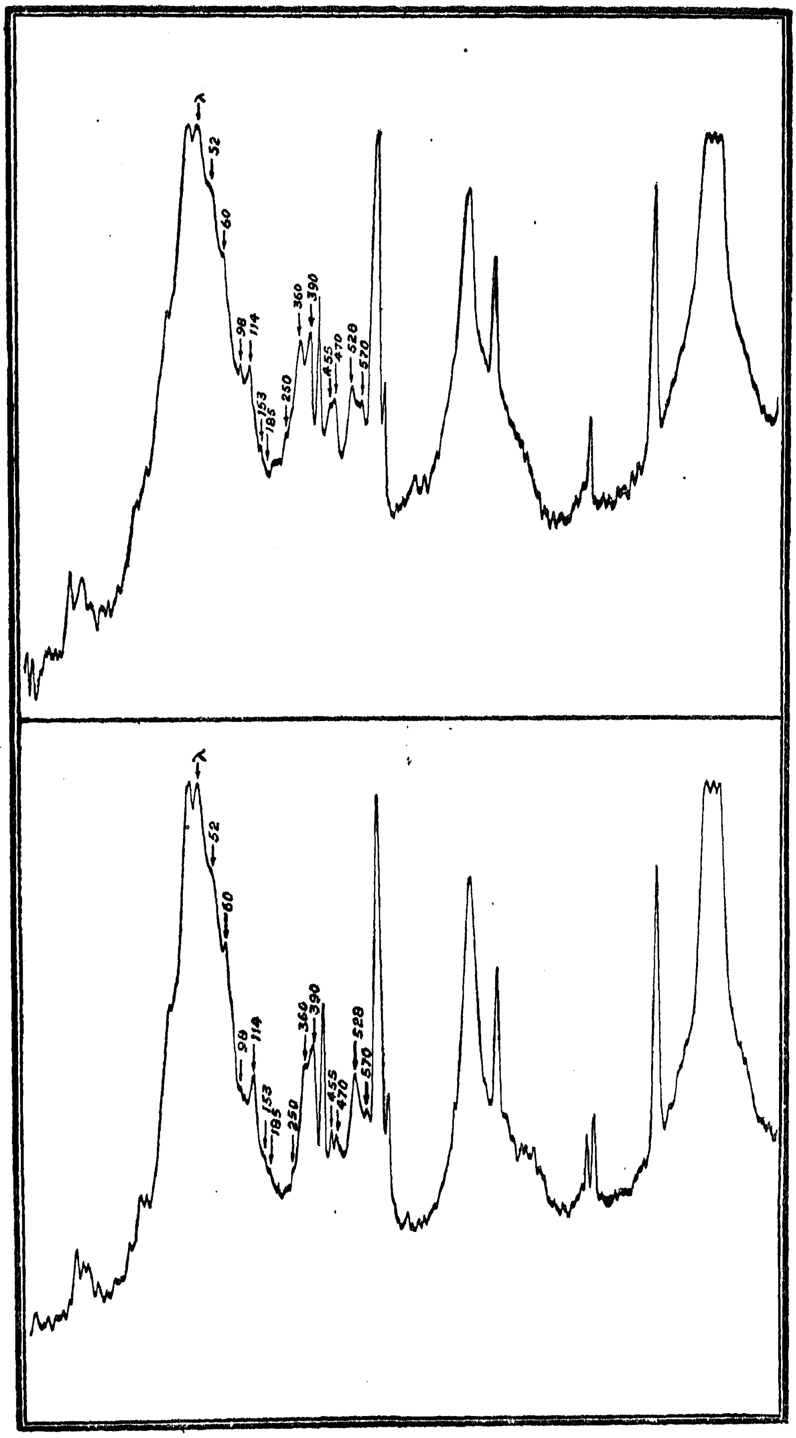

FIG. 1 (*a*)

FIG. 1 (*b*)

FIG. 1. Microphotometer curve of the Raman Spectrum of $KH_2\,PO_4$

intensity in the two orientations studied, all of them except 114 and 153 being absent when the optic axis is perpendicular to the directions of the incidence and scattering. The line 114 cm.$^{-1}$ is, however, nearly absent when the optic axis is along the direction of scattering.

3. DISCUSSION

Potassium di-hydrogen phosphate is isomorphous with $NH_4H_2PO_4$ and belongs to the space group $V_d{}^{12}$. The structure is based on two interpenetrating body centred tetragonal lattices. The interatomic distances suggest that the H_2PO_4 ion which is so stable in solution (C. S. Venkateswaran, 1938) is still present as a unit in the solid state (J. C. Slater, 1940). In order to write down the character table for the unit cell, the co-ordinates of the hydrogen atoms are taken as $\frac{1}{4}\,u\,\frac{1}{8}$; $u\,\frac{3}{4}\,\frac{7}{8}$; $\frac{3}{4}\,\bar{u}\,\frac{1}{8}$; $\bar{u}\,\frac{1}{4}\,\frac{7}{8}$; etc.

TABLE I

V_d	E	$2S_4^z$	C_2''	$2C_2$	$2\sigma_d$	n_i	T	T′	R	n_i'	Infra-red	Raman effect
A_1 ..	1	1	1	1	1	4	0	0	1	3	..	P
A_2 ..	1	1	1	−1	−1	5	0	0	1	4	..	..
B_1 ..	1	−1	1	1	−1	6	0	2	0	4	..	D
B_2 ..	1	−1	1	−1	1	7	1	1	0	5	M	D
E ..	2	0	−2	0	0	13	1	3	2	7	M	D
U_R ..	16	4	4	2	0							
$U_R(S)$ ..	4	4	4	0	0							
$U_R(s-v)$ ..	2	2	2	0	0							

If we neglect the coupling around the two-fold axis, the point group symmetry at the positions of the H_2PO_4 ions is only S_4 and consequently we should expect only 15 internal frequencies to appear in Raman effect. However, we find experimentally only 10 lines, some of which are broad and show some structure. A study of the Raman spectra of these two phosphates at low temperatures shows no radical change in width. In view of this fact it appears probable that the breadth of some of the lines is not so much of thermal origin, as due to an overlapping of faint and diffuse lines.

TABLE II

Vibration Type	Frequency shift in $cm.^{-1}$
A	358, 370, 913
B	393, 467, 2500, 2700
E	528, 570, 1080

If the fairly large birefringence of the crystal is taken as a measure of the optical anisotropy of the H_2PO_4 groups, then the lattice oscillations of the rotatory type will appear with considerable intensity. The frequency shifts 98 and 114 cm.$^{-1}$ have therefore to be attributed to the rotational oscillations of the H_2PO_4 groups, though the observed variation of intensity of the 114 cm.$^{-1}$ line with orientation is in disagreement with what should be expected for the degenerate class (Chapelle, 1949).

The frequencies of the translatory type of oscillations may be evaluated to a first approximation by taking into consideration the forces between the closest neighbours, as has been done in detail for $NH_4H_2PO_4$ by Jean Chapelle. The force constants used are given below along with the co-ordinates of the groups between which they act. $k_1 - (000) - (\frac{1}{2}0\frac{1}{4})$, $k_2 - (000) - (\frac{1}{2}\frac{1}{2}0)$, $k_3 - (000) - (00\frac{1}{2})$, $k_4 - (000) - (0\frac{1}{2}\frac{1}{4})$, $k_5 - (00\frac{1}{2}) - (0\frac{1}{2}\frac{1}{4})$.

The constants k_2 and k_3 may be evaluated utilising the relations given by Chapelle and the values of the elastic constants reported by Mason (1947).

$C_{66} = 6 \cdot 1 \times 10^{10}$ dynes per cm.^{2} $C_{44} = 12 \cdot 8 \times 10^{-10}$ dynes per sq. cm.

$S_{33} = 2 \cdot 1 \times 10^{-12}$ cm.^{2}/dyne. $S_{11} = 1 \cdot 7 \times 10^{-12}$ cm.^{2}/dyne.

$S_{12} = - \cdot 4 \times 10^{-12}$ cm.^{2}/dyne.

Identifying the line 185 cm.$^{-1}$ as belonging to the class E, we evaluate all the other frequencies and force constants (C.G.S.) $k_2 = \cdot 21 \times 10^4$, $k_3 = 1 \cdot 89 \times 10^4$, $k_4 = 3 \cdot 31 \times 10^4$, $k_1 = 2 \cdot 78 \times 10^4$, $k_5 = -1 \cdot 38 \times 10^4$, while the corresponding values for $NH_4H_2PO_4$ are $k_5 = (\cdot 22 \pm \cdot 02) \times 10^4$, $k_3 = \cdot 82 \times 10^4$, $k_4 = 1 \cdot 52 \times 10^4$, $k_1 = 2 \cdot 3 \times 10^4$, $k_4 = \cdot 24 \times 10^4$.

Comparing the two we find that one may legitimately expect a close correspondence between the oscillations in the two crystals which are antisymmetric with respect to the four-fold axis and some difference in the case of symmetric oscillations. However, as there are no symmetric oscillations in both these cases, the spectra show a striking similarity in accordance with our expectation.

TABLE III

External oscillations in KH_2PO_4

Type	Calculated in cm.$^{-1}$	Observed in cm.^{1}
B_1	72 189	50–60 185
B_2	189	185
E	150 185 230	153 185 ..

In conclusion, the author wishes to express his gratitude to Professor R. S. Krishnan for his constant encouragement.

SUMMARY

The Raman spectrum of potassium di-hydrogen phosphate has been studied using the λ2537 radiation of a quartz mercury arc. It consists of 15 lines of which 10 are due to internal osciallations of the H_2PO_4 group, 2 rotatory oscillations of the H_2PO_4 groups and 3 translatory type of external oscillations. Following Jean Chapelle, an approximate calculation of the frequencies of translatory type of oscillations has been made and compared with those observed.

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