

RAMAN SPECTRUM OF AMMONIUM DI-HYDROGEN PHOSPHATE

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1. INTRODUCTION

AMMONIUM di-hydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) has in recent years been subjected to many investigations to elucidate the origin and cause of the Seignette electric anomaly that exists in the case of crystals isomorphic with Rochelle salt and the phosphates and arsenates of the tetragonal class. The elastic, piezo-electric and dielectric constants show analogous variations within the range of stress and temperature in which measurements have so far been carried out (Mason, 1946). Stephenson and Zettlemyer (1944) noticed a transition point in the specific heat curve at 147.9°K , while Klug and Johnson (1937) and later Jean Jaffray (1944) claim to have observed a second order transformation of the ammonia type at about 19°C . In view of the importance of the subject and as a study of the Raman spectrum of ammonium di-hydrogen phosphate in the form of single crystals can yield valuable information concerning the structure as well as the interatomic forces, an investigation of its Raman spectrum using $\lambda 2536.5$ radiation of mercury as exciter, has been undertaken.

The earlier investigations on the Raman spectra of the acids of phosphorus and their salts are not very numerous and the results obtained are very meagre. The solutions of the primary phosphates have been studied by C. S. Venkateswaran (1936) and in the case of $\text{NH}_4\text{H}_2\text{PO}_4$ 30% solution, only 4 lines with frequency shifts 360, 515, 885 and 1090 cm.^{-1} , corresponding to the internal oscillations of the PO_4 group, have been reported. The chief difficulty experienced by the earlier workers in recording the Raman spectra of the phosphates is the strong continuous spectrum which appears on every plate obliterating all the faint lines. C. S. Venkateswaran attributed this to the mercury arc itself and by a proper design of the arc and by the use of fan cooling directed towards the cathode, he reduced this to a minimum. However, as C. S. Venkateswaran himself has remarked in his paper, with crystals of the primary phosphates of sodium, potassium and ammonium, he was unable to get any satisfactory picture even after prolonged exposures. Apart from this, no work on $\text{NH}_4\text{H}_2\text{PO}_4$ has so far been reported. The use of the ultraviolet technique removes this difficulty at

once as the intense unmodified light is quenched completely from the scattered light before its entry into the spectrograph by a cool mercury vapour filter. This combined with the enormously increased scattering power owing to the use of ultraviolet radiation, made it possible to study the Raman spectrum of ammonium di-hydrogen phosphate.

2. EXPERIMENTAL DETAILS AND RESULTS

Two fine transparent specimens of $\text{NH}_4\text{H}_2\text{PO}_4$ with fully developed faces, one of size $1\frac{1}{2}$ cm. \times 1 cm. \times $\frac{3}{8}$ cm. and the other $7'' \times 2\frac{1}{2}'' \times 2\frac{1}{2}''$ made in the Bell Telephone Company's laboratories at Murray Hill and presented to Sir C. V. Raman were used in the present investigation, the smaller one being cut suitably to enable a study of the effect of orientation on the Raman spectrum. The spectra were excited by the resonance radiation of mercury from a water-cooled magnet-controlled quartz arc and the scattered light was focussed on to the slit of a Hilger medium quartz spectrograph, all precautions being taken to eliminate parasitic light from fogging the plate.

Fig. 1 (a) is a reproduction of the picture obtained with the big crystal and with a slit width of 5 div. (0.025 mm). For this slit width exposures

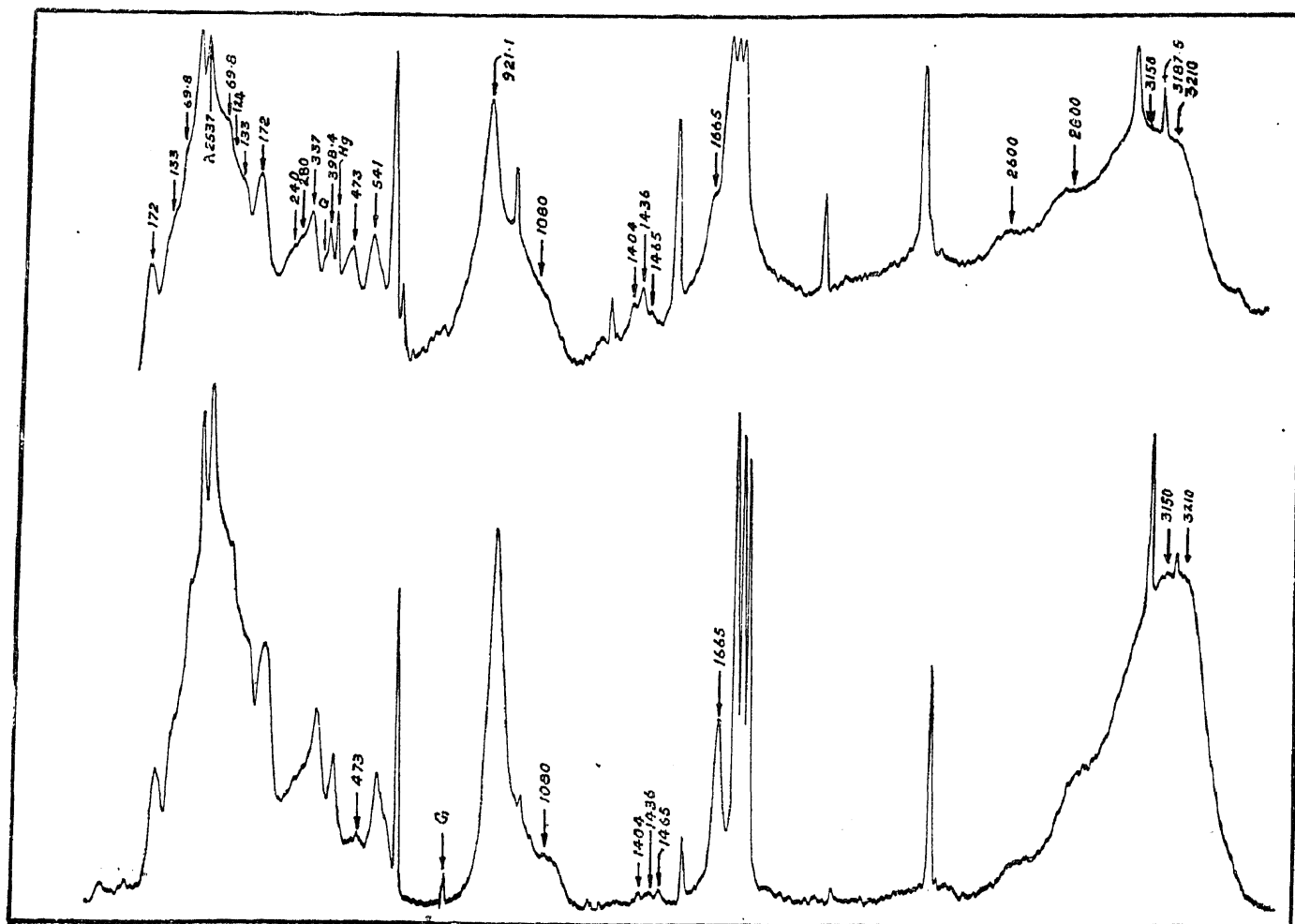


FIG. 2

of the order of 12 hours were found to be necessary to bring out the salient features of the spectrum, while 24 hours were sufficient to get a fairly intense picture. This is a really surprising and noteworthy point, for in the case of the ammonium halides, the exposure times were of the order of 4 hours (R. S. Krishnan, 1947). The characteristic feature of the Raman spectrum of ammonium di-hydrogen phosphate is that all the lines including those due to the internal oscillations of the PO_4 group as well as the NH_4 group are broad though fairly intense.

For a comparative study of the effect of orientation on the Raman spectrum, a picture with the scattered light taken along the tetragonal axis has also been reproduced in Fig. 1 (c). Fig 1 (b) is the mercury spectrum enlarged to the same extent as the other two. The first spectrogram was recorded with the direction of the scattered light normal to the fourfold axis of symmetry. As is to be expected, the pictures taken with the incident light being respectively along *a* and *b* axes, the direction of the scattered light being along the tetragonal axis, were found to be identical.

The frequency shifts of the Raman lines were evaluated by a comparison with the superposed iron arc spectrum and also by a direct measurement under a Hilger comparator. The Raman shifts of the feeble lines and bands, however, were computed from the microphotometer curves. The frequency shifts and the intensities of the principal Raman lines are listed in Table I.

TABLE I
Principal Raman lines of ammonium di-hydrogen phosphate

Serial No.	Group	Frequency shift in cm.^{-1}	Nature of the lines
1	lattice	69.8 (4)	very broad
2	do	124 (2)	broad
3	do	133 (2)	..
4	do	172 (4)	broad
5	phosphate	240 (1)	do
6	do	280 (1)	..
7	do	337 (3)	broad and diffuse
8	do	398.4 (2)	sharp
9	do	473 (2)	diffuse
10	do	541 (3)	do
11	do	921.1 (10)	sharp
12	do	1080 (1)	very broad
13	NH_4	1404 (1)	..
14	do	1436 (1)	..
15	do	1465 (1)	..
16	do	1665 (3)	sharp
17	do	2600 (1)	Extremely broad
18	do	2800 (1)	do
19	do	3150 (5)	diffuse
20	do	3210 (5)	..

The Raman lines with frequency shifts 1404, 1435, 1465 and 473 cm^{-1} were found to be influenced enormously by the direction of scattering and the intensity is considerably greater when the scattered light is taken along the fourfold axis of symmetry.

In the low frequency region the spectrum exhibits two broad bands and one line. The bands extend from 0 to 69.8 cm^{-1} and from 70 to 133 cm^{-1} with a sharp cut off at the upper limit. Of these the former is the more intense one. The line at 172 cm^{-1} is also intense and has a width of about 10 cm^{-1} .

3. DISCUSSION

Ammonium di-hydrogen phosphate is isomorphous with KH_2PO_4 , KH_2AsO_4 and $\text{NH}_4\text{H}_2\text{AsO}_4$ and crystallises in the tetragonal scalenohedral class. The space group is V_d^{12} . The X-Ray analysis has been carried out by O. Hassel (192C) and he found that the phosphate groups consist of a phosphorus atom tetrahedrally surrounded by four oxygens and that each group is surrounded tetrahedrally by four other groups. Neighbouring PO_4 groups are connected by hydrogen bonds. Like the PO_4 group, the NH_4 group retains its tetrahedral structure. The number of molecules in the unit cell is 4.

From a comparative study of the spectra of the aqueous solutions of the phosphates and the ammonium salts with the frequency shifts observed in the spectrum of $\text{NH}_4\text{H}_2\text{PO}_4$, we may broadly classify the observed lines into three groups, viz., (1) the lattice spectrum, (2) the spectrum of the PO_4 ion and (3) the spectrum of the NH_4 ion. The classification is indicated in Table I.

Lattice spectrum.—The appearance of the two broad bands in the lattice spectrum with continuous distribution of intensity from the exciting line suggests that the ions PO_4 and NH_4 are capable of hindered rotation more or less as in a liquid, the lower frequency band corresponding to the heavier ion. It is quite probable that the bands split up into lines at lower temperatures.

Spectrum of the PO_4 ion.—The PO_4 ion in the free state possesses full cubic symmetry and has only four distinct modes of oscillation with frequency shifts 361 (2), 515 (3), 980 (1) and 1080 (3) cm^{-1} , the figures within brackets giving the degeneracies. In the crystal the PO_4 ion has only the symmetry of the crystal which is lower than that of the free ion. One might therefore expect some of the degeneracies of the characteristic frequencies of the free ion to be removed in the crystal, as indicated in Table II.

TABLE II
Raman frequencies of the PO₄ ion

Nature	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
Free state ..	980	363	1082	515
NH ₄ H ₂ PO ₄ ..	921.1	337 ; 368.4	1080	473 ; 541

The splitting of ν_2 and ν_4 into two lines with widely different frequency shifts indicates the strong influence of the hydrogen bond on the PO₄ group. Further investigation has to be carried out before any satisfactory explanation can be given for the presence of the two lines with frequency shifts 240 and 280 cm.⁻¹ respectively.

Spectrum of the NH₄ ion.—Because of its tetrahedral symmetry, NH₄ ion in the free state should have only four distinct modes of oscillation of which ν_1 is single, ν_2 is doubly degenerate and ν_3 and ν_4 are triply degenerate. The corresponding Raman shifts are 3033, 1685, 3134 and 1397 cm.⁻¹ In the spectra of the ammonium compounds, the most intense line usually corresponds to the totally symmetric oscillation ν_1 . Contrary to this, there is no line in the Raman spectrum of NH₄H₂PO₄ at room temperature, with a frequency shift 3030 cm.⁻¹ It is quite likely that it has shifted to higher frequency and is lost in the intense background due to the Raman lines at 3150 cm.⁻¹

TABLE III
Raman frequencies of the NH₄ ion

State	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
Free ion ..	3033	1685	3134	1397
NH ₄ Br Crystal ..	3037	1686	3121	1398 ; 1429
NH ₄ Cl Crystal ..	3041	1710 ; 1765	3146	1400 ; 1418 ; 1440
NH ₄ H ₂ PO ₄	1665	3150 ; 3210	1404 ; 1437 ; 1465

The partial removal of the degeneracies of the characteristic frequencies of the penta-atomic group in the spectrum of ammonium di-hydrogen phosphate suggests that in the crystal lattice the vibrating NH₄ ion possesses lower symmetry evidently due to the presence of potential fields of the neighbouring ions, although the NH₄ ion has full tetrahedral symmetry when the atoms are at rest.

As in the spectra of the ammonium halides, there are two extra bands, one at 2600 cm.^{-1} and the other at 2800 cm.^{-1} . In the case of $\text{NH}_4\text{H}_2\text{PO}_4$ the band with a shift 2600 cm.^{-1} might be due to P-H oscillation. The origin of the other band is at present not clear.

In conclusion, the author wishes to express his grateful thanks to Prof. R. S. Krishnan for his kind interest and valuable suggestions in the course of the work.

SUMMARY

Using the $\lambda 2536.5$ mercury resonance radiation as exciter, the Raman spectrum of ammonium di-hydrogen phosphate has been investigated. The spectrum consists of 20 lines of which (1) 4 are lattice lines, (2) 8 are due to internal oscillations of the PO_4 group and (3) 8 due to NH_4 groups. The continuous distribution of intensity in the lattice spectrum indicates the possibility of the existence of hindered rotation of the NH_4 and PO_4 groups. The splitting up of some of the degenerate lines of both PO_4 and NH_4 groups might be due to the strong influence of the hydrogen bonds.

REFERENCES

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| Hassel, O. | .. | <i>Zeits. fur. Electrochemie</i> , 1920, 31, 523. |
| Hibben | .. | <i>The Raman Effect and its Chemical Applications</i> , 1939, 381-84. |
| Jean Jaffray | .. | <i>Comp. rendus</i> , 1944, 218, 798. |
| Klug and Johnson | .. | <i>Journ. Amer. Chem. Soc.</i> , 1937, 59, 2061. |
| Krishnan, R. S. | .. | <i>Proc. Ind. Acad. Sci., A</i> , 1947, 26, 432. |
| ————— | .. | <i>Ibid.</i> , 1948, 27, 321. |
| Mason, W. P. | .. | <i>Phys. Rev.</i> , 1946, 69, 173-94. |
| Schaefer, Matossi and
Aderhold | .. | <i>Z. Physik</i> , 1930, 65, 289. |
| Stephenson and Zettlemyer | .. | <i>Journ. Amer. Chem. Soc.</i> , 1944, 66, 1405-8. |
| Venkateswaran, C. S. | .. | <i>Proc. Ind. Acad. Sci., A</i> , 1936, 3, 25. |

