RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part IV. Barytes

BY DR. R. S. KRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received May 6, 1946

1. INTRODUCTION

ALTHOUGH large transparent single crystals of barytes are easily available, comparatively little work has so far been done on its Raman spectrum. Nisi (1929) and Krishnamurti (1930) who were the early investigators on this subject recorded only a couple of Raman lines. Using the 2536·5 λ mercury radiation as exciter, Rasetti (1932) recorded a spectrum with a specimen of barytes which exhibited as many as eight low frequency lines and eight lines due to the SO_4 ion with frequency shifts 56·8, 62·2, 73·6, 88·3, 97·8, 127·3, 150·4, 189·8, 451·4, 462·2, 631·1, 647·5, 989·3, 1104·6, 1141·4 and 1167·2 cm.$^{-1}$ Using the same technique and giving longer exposures Roop Kishore (1942) repeated the experiment. Owing to the smaller dispersion of the spectrograph used by him, the number of Raman lines identified was less than that reported earlier by Rasetti. Roop Kishore, however, succeeded in recording an additional fainter line at 1088 cm.$^{-1}$ and a weak band extending from 1200 cm.$^{-1}$ to 1300 cm.$^{-1}$ He found that the orientation of the crystal with reference to the direction of illumination and observation had a marked influence on the relative intensities of the lines.

Using the 4046 and 4358 λ radiations of the mercury arc Balakrishnan (1941) investigated the effect of crystal orientation on the Raman lines due to the internal oscillations of the SO_4 ion in barytes. The specimen employed by him was in the form of a parallelepiped with its faces parallel to the cleavage planes (001), (110) and $(1\bar{1}0)$. He claimed to have observed 15 distinct Raman lines with frequency shifts 452, 458, 614, 620, 638, 650, 989, 1038, 1082, 1088, 1109, 1136, 1142, 1158 and 1170 cm.$^{-1}$, some of which did not appear for certain orientations of the crystal. According to him, none of the three settings of the crystal tried by him gave the complete spectrum. This result has neither been confirmed nor contradicted by Roop Kishore (1942). From an analysis of the polarisation data Balakrishnan concluded that the lines with frequency shifts 452, 458, 650, 989 and 1170 cm.$^{-1}$ belonged to the symmetric class.

It is clear that the results obtained by the earlier investigators on the Raman effect in barytes are neither complete nor in agreement. It is therefore thought desirable to study the problem afresh using the very powerful ultra-violet technique which has yielded much useful information in the case of diamond, calcite, quartz, etc. (Krishnan, 1945). The use of the 2536·5 λ resonance radiation as exciter would enable one not only to record the first order spectrum of barytes in all its detail but also to investigate the nature of its second order spectrum about which nothing is known at present. The present investigation was undertaken with this object in view and also to confirm or disprove Balakrishnan's findings regarding the effect of crystal orientation on the frequency shifts of the Raman lines.

2. DETAILS OF THE EXPERIMENT

From Sir C. V. Raman's personal collection of minerals two transparent specimens of barytes were chosen for the present study. The bigger crystal was in the form of a parallelepiped (10 × 8 × 5 cm.), with its faces parallel to the natural cleavage planes (001), (110) and $(1\bar{1}0)$. It was used as such. The smaller specimen which had a natural *c* (001) face was cut and polished with its faces perpendicular to the axes of the optical ellipsoid. This crystal measured nearly 1 × 1 × 2·5 cm.

The optical arrangement employed for recording the Raman spectrum using the mercury resonance radiation as exciter has been described in Part I of this series (Krishnan, 1945). Using the E 3 quartz spectrograph a preliminary investigation was carried out in order to find any variations in the frequency shifts of the Raman lines for different settings of the crystal. Using the cut crystal three different spectrograms of the Raman effect were taken with the crystal illuminated successively along the *a, b* and *c* axes, the traversely scattered light being taken along *b, c* and *a* axes respectively. A comparative study of the three spectra recorded in juxta-position on the same negative showed that the frequency shifts of the Raman lines remain invariant, whereas the relative intensities of the lines depend on the orientation of the crystal. The experiment was repeated with the bigger crystal which had the natural cleavage faces and the same result was obtained. Balakrishnan's claim that none of the orientations of the crystal of barytes gave a complete Raman spectrum is therefore not substantiated by the results obtained by the author.

In order to get accurate measurements of the frequency shifts of the principal Raman lines, a Hilger E 1 quartz spectrograph which has a dispersion of about 50 wavenumbers/mm. in the 2536 λ region was used.

Using a slit width of 0·03 mm. and the bigger crystal, exposures of the order of 4 days were given to photograph the Raman spectrum showing the first order lines with reasonable intensity. The frequency shifts of the lines were evaluated by comparison with the superposed iron arc spectrum.

In order to record the second order spectrum the high speed low dispersion E 3 quartz spectrograph was employed. With a slit width of 0·03 mm. exposures of the order of two to three days were given to get an intense spectrogram. The frequency shifts of the more intense and easily identifiable second order lines were evaluated from measurements made on the spectrogram. Those of the feebler ones were estimated from the microphotometric record.

3. RESULTS

A typical photograph of the Raman spectrum taken with the E 1 spectrograph together with its microphotometric record is reproduced in Fig. 1 in Plate I. The positions and the frequency shifts of the principal Raman lines are marked in Fig. 1 *b*. They are listed in Table I. The figures given in brackets represent visual estimates of the relative intensities of the lines. The direction of illuminaton was normal to the (001) face and the direction of observation was normal to the (110) face. Rasetti's values for the frequency shifts are shown in column 5. The author's results are in

TABLE I

Principal Raman lines of barytes

No.	Group	Frequency shifts in cm.$^{-1}$ author's value	Notations	Rasetti's value
1	Lattice	58·5 (6)	L_1	56·8
2	,,	64·0 (8)	L_2	62·2
3	,,	73·6 (10)	L_3	73·6
4	,,	88·3 (6)	L_4	88·3
5	,,	96·5 (4)	L_5	97·8
6	,,	127·4 (3)	L_6	127·3
7	,,	148·8 (3)	L_7	150·3
8	,,	151·4 (4)	L_8	
9	,,	189·7 (4)	L_9	189·8
10	Sulphate	452·9 (14)	ν_1	451·4
11	,,	462·2 (15)	ν_2	462·2
12	,,	617·1 (10)	ν_3	..
13	,,	630·3 (7)	ν_4	631·1
14	,,	648·3 (8)	ν_5	647·5
15	,,	988·6 (30)	ν_6	989·3
16	,,	1084·2 (6)	ν_7	1104·6
17	,,	1104·2 (5)		
18	,,	1139·1 (10)	ν_8	1141·4
19	,,	1144·8 (10)		
20	,,	1167·2 (8)	ν_9	1167·2

close agreement with those of Rasetti except for the three doublets with frequency shifts 148·8–151·4 cm.$^{-1}$, 1084·2–1104·2 cm.$^{-1}$ and 1139·1–1144·8 cm.$^{-1}$ Rasetti treated them as single lines. The principal Raman line with the frequency shift of 617·1 cm.$^{-1}$ has been recorded for the first time. The 20 Raman frequencies tabulated above have been classified into two groups, namely, lattice spectrum denoted by L_1, L_2, ... L_9 and the spectrum of the SO_4 ions in the crystal denoted by ν_1, ν_2, ... ν_9.

TABLE II

Second order Raman lines of barytes

No.	Frequency shifts in cm.$^{-1}$	Assignment	Calculated frequency shifts
1	170	$L_3 + L_5$	170
2	246	$L_5 + L_7$; $L_5 + L_8$	245; 248
3	273	$L_6 + L_7$	276
4	293	$2L_7$	298
5	341	$L_8 + L_9$	341
6	518	$\nu_1 + L_2$	517
7	542	$\nu_1 + L_4$	541
8	750–800	$\nu_3 + L_6$; $\nu_4 + L_6$ $\nu_3 + L_7$; $\nu_5 + L_6$ $\nu_5 + L_7$; $\nu_5 + L_8$	744 ; 757 ; 766 ; 775 ; 797 ; 799
9	900	$2\nu_1$	906
10	923	$2\nu_2$	924
11	967		
12	1216	$\nu_8 + L_3$	1215
13	1238	$2\nu_3$	1235
14	1267	$\nu_3 + \nu_5$	1266
15	1439	$\nu_6 + \nu_1$	1442
16	1450	$\nu_6 + \nu_2$	1451
17	1603	$\nu_6 + \nu_3$	1606
18	1970	$2\nu_6$	1978
19	2220	$\nu_7 + \nu_8$	2223

An intense photograph of the Raman spectrum of barytes taken with the E 3 spectrograph is reproduced in Fig. 2 together with a spectrum of the mercury arc for purposes of comparison. The corresponding microphotometric records are shown in Fig. 3. The second order Raman lines can be clearly seen on the microphotometric record. Most of them can also be identified on the reproduced photograph. In addition to the 20 Raman lines belonging to the first order spectrum, there are not less than 18 Raman lines and one Raman band constituting the spectrum of the second order. The frequency shifts of these are listed in Table II. They have all been recorded as such for the first time. Roop Kishore (1942) reported the existence of only a band extending from 1198 cm.$^{-1}$ to 1300 cm.$^{-1}$ consisting of unresolved lines.

Of the second order lines, the Raman line with the frequency shift 967 cm.$^{-1}$ is the most intense one as it appears even in the lightly exposed photograph taken with the E 1 spectrograph. See Fig. 1. The pair of lines with frequency shifts 1216 cm.$^{-1}$ and 1238 comes next in the order of intensity.

As in the case of other crystals like calcite, gypsum, etc., the intensity of the 2536·5 λ line relative to that of its companion at 2534·8 λ is greater in the spectrum of the scattered light than in that of the direct arc. The enhanced intensity of the unmodified line can be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour, compare the microphotometric records reproduced in Fig. 3.

4. DISCUSSION

Barytes is an ionic crystal belonging to the orthorhombic bipyramidal class. The unit cell contains four molecules of $BaSO_4$, the space group is V_h^{13}. James and Wood (1925) carried out a detailed X-ray analysis of the crystal structure of barytes. Their results go to show that the SO_4 ions preserve their tetrahedral symmetry in the crystal.

Spectrum of the SO_4 ion.—The SO_4 ion in the free state has only four distinct modes of oscillation with frequency shifts 454 (2), 622 (3), 983 (1) and 1106 (3) cm.$^{-1}$ The figures given in brackets are the respective degeneracies. From group theoretical analysis Bhagavantam (1938) showed that in the case of anhydrite which belongs to the orthorhombic class the four distinct modes of oscillation characteristic of the free SO_4 ions split up into nine components in the crystal. We may expect to get similar results with barytes also which has a structure similar to that of anhydrite. With the disappearance of the degeneracy, the spectrum of barytes should exhibit all the nine lines characteristic of the SO_4 ion. Actually 11 frequency shifts are recorded in the first order spectrum all of which are attributable to the oscillations of the SO_4 ion. By comparing the values of the frequency shifts of barytes with those of the free SO_4 ion it is possible to identify seven out of the expected nine modes. These are denoted by ν_1, ν_2, $\nu_3 \ldots \nu_6$ and ν_9 (see Table I). The remaining two fundamentals, namely ν_7 and ν_8 appear to have suffered a Fermi splitting due to accidental degeneracy giving rise to 4 Raman lines as indicated below. It is probably correct to take ν_7 as 1094 cm.$^{-1}$ which splits up into 1084 and 1104 cm.$^{-1}$ on account of the fact that the combination $\nu_2 (462 \cdot 2) + \nu_4 (630 \cdot 3)$ falls on the top of ν_7. In same way, ν_8 which has a frequency shift of 1142 cm.$^{-1}$ splits up into two lines with frequency shifts 1139 and 1145 cm.$^{-1}$ since the combination of ν_6 (988·6) and L_8 (151·4), one of the lattice lines falls in the region of this doublet.

TABLE III

Raman frequencies of the SO_4 ion

In the free state	454 Double		622 Triple			983 Single	1106 Triple		
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
In barytes ..	452·9	462·2	617·1	630·3	648·3	988·6	1094	1142	1167
In anhydrite	415	499	609	628	674	1018	1108	1128	1160
In gypsum ..	415	492	618	622	672	1006	1115	1136	1144

The values of the frequency shifts of the nine Raman lines due to the internal oscillations of the SO_4 ions in barytes, anhydrite and gypsum are listed in Table III. The corresponding Raman frequencies of the free SO_4 ion are also included for comparison. The values of the frequency shifts for anhydrite were those reported by other workers. The values for gypsum were taken from Part II of this series (Krishnan, 1945). A comparative study of the frequency shifts of the SO_4 ion in barytes and anhydrite shows that the influence of the cation on the splitting of the degenerate frequencies 454 cm.$^{-1}$ and 622 cm.$^{-1}$ and on the enhancement of the totally symmetric oscillation frequency 983 cm.$^{-1}$ of the free SO_4 ion is inversely proportional to its atomic weight. Polarisation studies made by Rousset and Lochet (1945) show that in the case of gypsum the frequencies ν_1, ν_2, ν_4, ν_8 and ν_9 come under the symmetric class, whereas in the case of barytes Balakrishnan's measurements indicate that ν_1, ν_2, ν_5, ν_6 and ν_9 come under the symmetric class. The fact that out of the nine SO_4 lines of barytes, five come under symmetric class and four antisymmetric shows that the vibrating SO_4 ion possesses only as elements of symmetry a binary axis parallel to the binary axis of the crystal, although the ion has the full tetrahedral symmetry when the atoms are at rest.

The lattice spectrum.—Bhagavantam (1938) has shown that in anhydrite which has a structure similar to that of barytes there should be eighteen Raman active lattice oscillations. The recorded spectrum of barytes, on the other hand, consists of 9 lattice lines, *i.e.*, exactly half the theoretical number. Comparing the lattice spectrum of gypsum with that of barytes one finds that there is no striking similarity between the two except for the fact that both the spectra consist of sharp, intense and closely spaced lattice lines.

Combinations of the principal frequencies.—In the second order spectrum the overtones and combinations of all the fundamental frequencies listed in Table I can appear. On this basis satisfactory assignments have been given to all the lines except one with frequency shift 967 cm.$^{-1}$ appearing in the second order Raman spectrum (see Table II). The calculated frequency shifts agree reasonably well with the observed values. Of the sulphate frequencies, the octaves of ν_1 (452·9), ν_2 (462·2), ν_3 (617·1) and ν_6 (988·6) are recorded as clearly resolved lines. There is indication of some unresolved lines in the neighbourhood of 1238 and 1267 cm.$^{-1}$ (see Fig. 3). These can be assigned as the octaves of ν_4 (630·3) and ν_5 (648·3). It is interesting to note that the octave of the most intense principal Raman line, namely, ν_6 (988·6 cm.$^{-1}$) is very weak compared to the octave of some of the other sulphate lines, *e.g.*, ν_1 (452·9 cm.$^{-1}$) or ν_2 (462·2 cm.$^{-1}$).

5. INFRA-RED SPECTRUM

Comparatively little work has so far been done on the infra-red absorption spectrum of barytes. Schæfer and Schubert (1916) reported the existence of two reflection maxima in barytes, one at 8·30 μ (1204 cm.$^{-1}$) and the other at 8·93 μ (1120 cm.$^{-1}$). Matossi and Kindler (1934) investigated the infra-red absorption spectrum of barytes in the range from 2 μ to 16 μ. They observed two strong absorption bands at 9 μ and at 15·65 μ corresponding frequencies being 1100 cm.$^{-1}$ and 640 cm.$^{-1}$ These absorption bands might correspond to the observed Raman lines 630·3 and 1094 cm.$^{-1}$ which come under the antisymmetric class and hence active in the infra-red. The above authors have also reported the existence of two weak absorption bands at 12·35 μ (810 cm.$^{-1}$) and 10·81 μ (925 cm.$^{-1}$) in the infra-red. There are no first order Raman lines corresponding to these. The second order spectrum, on the other hand, exhibits two Raman lines with corresponding frequency shifts.

The author is grateful to Sir C. V. Raman for the loan of the crystals of barytes and also for his interest in the work. The author is also indebted to the authorities of the Annamalai University for the loan of the Hilger E 3 quartz spectrograph.

SUMMARY

The previous work on the Raman effect in barytes has been briefly reviewed.

The Raman effect in natural crystals of barytes has been studied in detail using the 2536·5 λ mercury resonance radiation as exciter. The recorded spectrum consists of not less than 39 Raman lines nearly half of which have been recorded for the first time. Of these 20 lines belong to the first order Raman spectrum and are distributed as follows:—9 lattice lines and 11 lines

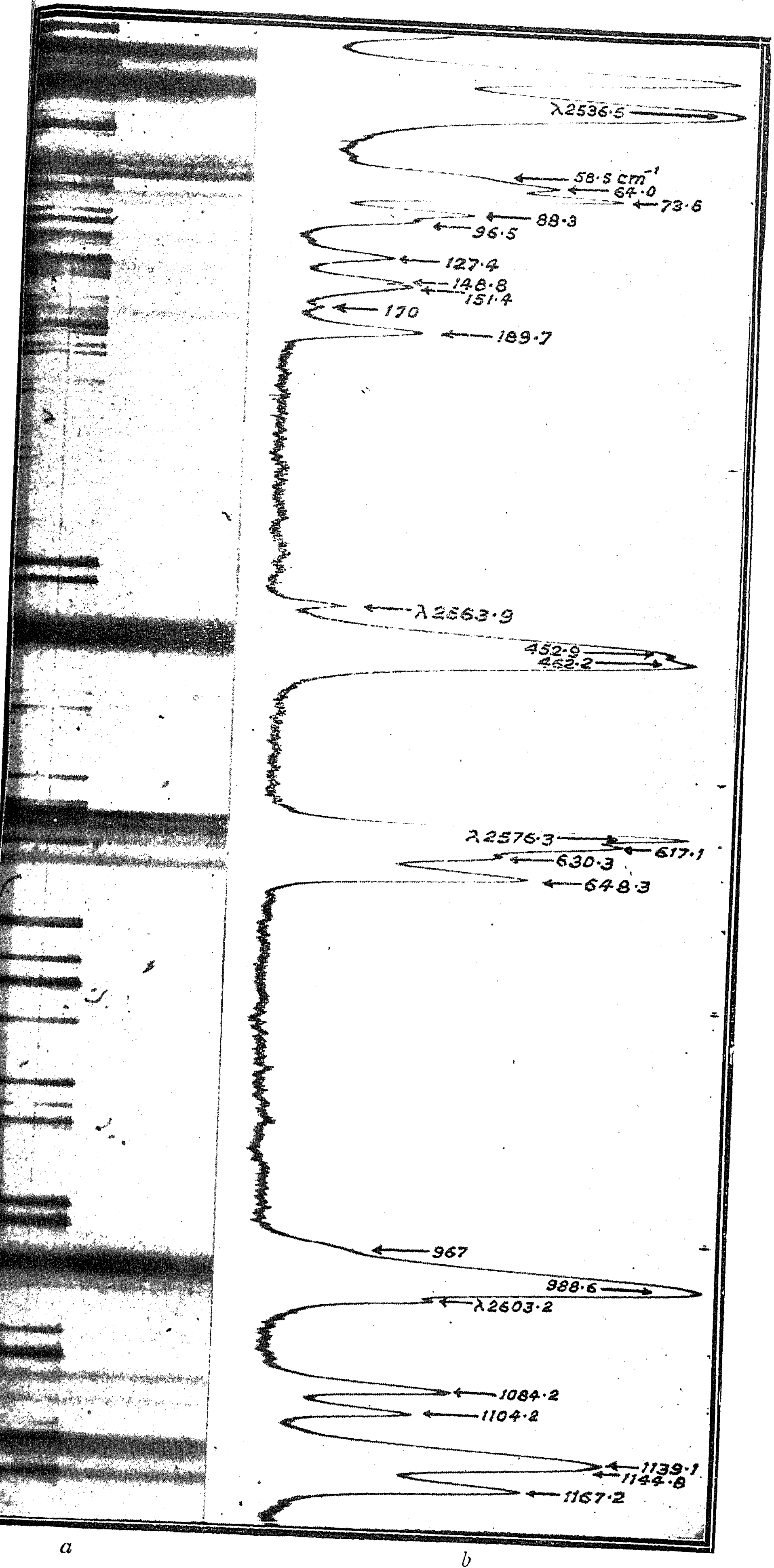

Fig. 1

(*a*) Raman spectrum of barytes taken with the E1 spectrograph;
(*b*) its microphotometric record.

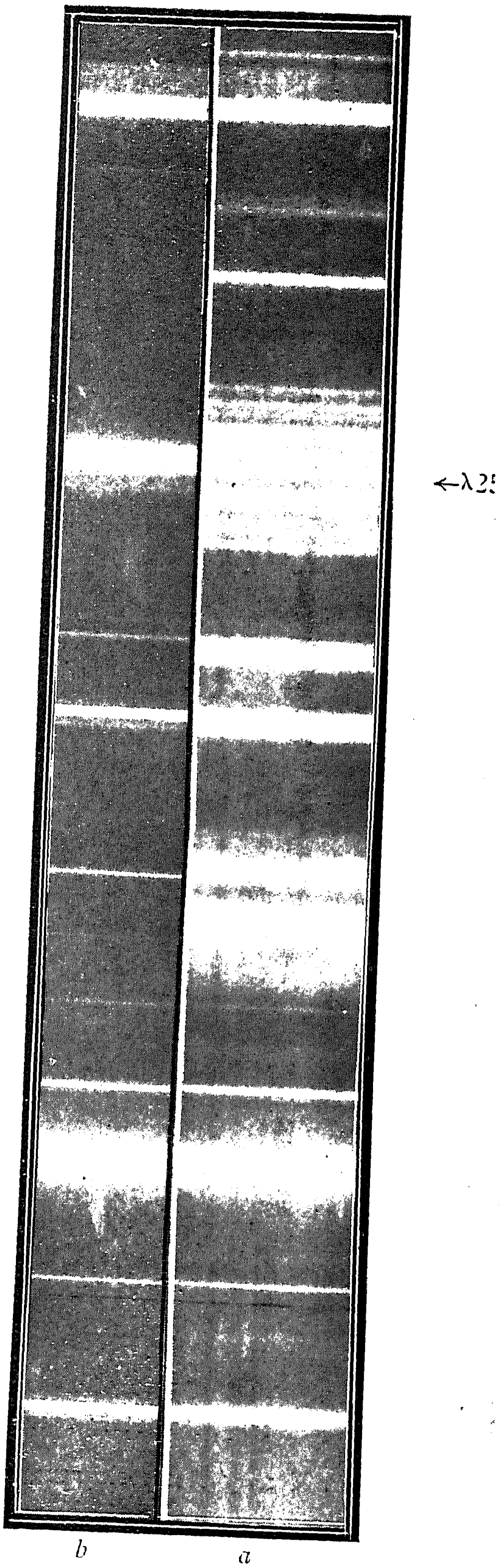

Fig. 2

(*a*) Raman spectrum of barytes taken with the E3 spectrograph.
(*b*) Comparison spectrum of the mercury arc.

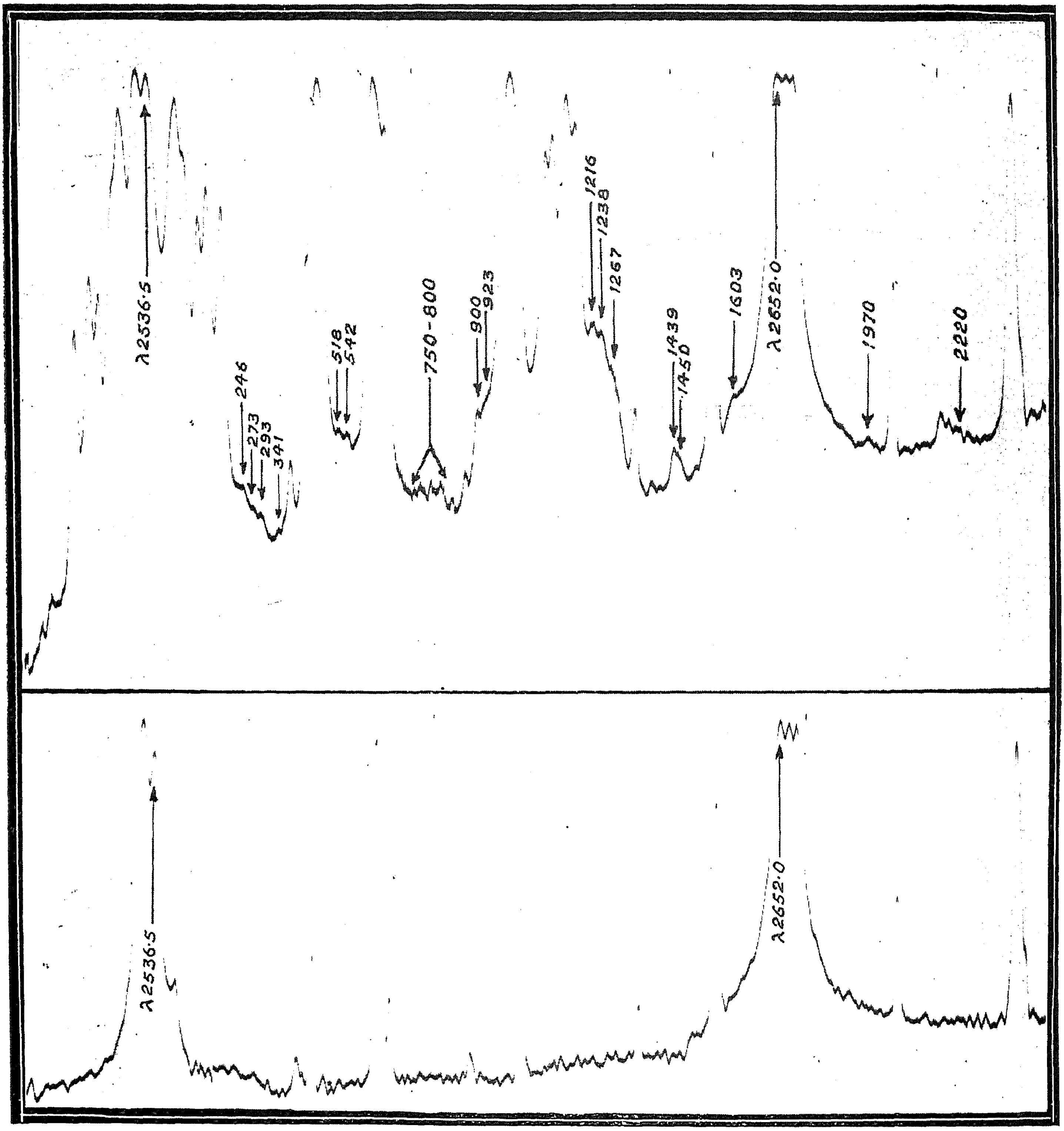

Fig. 3

(*a*) Microphotometric record of the Raman spectrum of barytes taken with the E3 spectrograph.

(*b*) Microphotometric record of the mercury spectrum.

due to the internal oscillations of the SO_4 ion. The frequency shifts of these lines have been accurately measured. The appearance of 11 Raman lines in the first order spectrum of the SO_4 ion has been satisfactorily explained on the basis of the lower order of symmetry of barytes crystal and also due to Fermi resonance splitting.

19 Raman lines of comparatively feeble intensity which constitute the second order spectrum have been assigned as octaves and combinations of some of the 20 principal Raman frequencies.

The frequencies corresponding to the maxima observed in the infra-red absorption spectrum of barytes have been compared with those observed in the Raman effect.

A complete bibliography on the Raman effect and infra-red studies in barytes is included.

REFERENCES

1. *Raman Effect*

1. Nisi .. *Proc. Imp. Acad. Japan*, 1929, **5**, 407.
2. Krishnamurti .. *Ind. Journ. Phys.*, 1930, **5**, 183.
3. Rasetti .. *Nuovo Cimento*, 1932, **9**, 72.
4. Balakrishnan .. *Proc. Ind. Acad. Sci.*, A, 1941, **14**, 257.
5. Roop Kishore *Ibid.*, 1942, **16**, 36.

2. *Crystal Structure*

6. James and Wood .. *Proc. Roy. Soc.*, A, 1925, **109**, 528.

3. *Infra-red*

7. Sehæfer and Schubert .. *Ann. der Phys.*, 1916, **50**, 283.
8. Matossi and Kindler .. *Zeit. für Phys.*, 1934, **92**, 303.

4. *General*

9. Bhagavantam .. *Proc. Ind. Acad. Sci.*, A, 1938, **8**, 345.
10. Krishnan, R. S. .. *Ibid.*, 1945, **22**, 182, 274 and 329.
11. Rousset and Lochet .. *Journ. de Physique*, 1945, **6**, 57.