RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part II. Gypsum

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1. PREVIOUS WORK ON GYPSUM

THE Raman spectrum of gypsum has been studied in some detail by numerous investigators. As usual, most of the earlier work was confined to the cataloguing the frequency shifts of the Raman lines in gypsum and estimating their relative intensities, *viz.*, Krishnan (1929), Hollænder and Williams (1929, 1931), Dickinson and Dillon (1929), Nisi (1929), Schæfer, Matossi and Aderhold (1929, 1930*a*), Krishnamurti (1930) and Rasetti (1931, 1932).

The effect of crystal orientation on the intensity and/or polarisation of the Raman lines of single crystals of gypsum was investigated by Schæfer, Matossi and Aderhold (1930*b*, *c*), Nisi (1931), Cabannes (1932, 1938), Aynard (1940), Roop Kishore (1942) and Cabannes and Aynard (1942) using incident unpolarised light, and by Saksena (1941), Rao (1941) and Rousset and Lochet (1945) using incident polarised light. Among them Nisi (1931) and Roop Kishore (1942) confined themselves to the study of the variations of the intensities of the Raman lines for different orientations of the crystal. Schæfer, Matossi and Aderhold, Saksena and Rao investigated in particular the intensities and depolarisations of the Raman lines corresponding to the internal oscillations of the SO_4 ions and to the oscillations of the water molecules.

Cabannes (1932) and Rousset and Lochet (1945) made a special study of the frequencies characteristic of the SO_4 ions in gypsum. Rousset and Lochet recorded nine Raman lines due to the SO_4 ion, the frequency shifts being 413, 492, 621, 623·5, 669, 1006, 1117, 1138 and 1144 wave numbers. Thus the results of Rousset and Lochet are the most complete as regards the fundamental frequencies of the SO_4 ions are concerned. From an analysis of the polarisation data, they have concluded that the lines 413, 492, 621, 1006 and 1144 cm.$^{-1}$ come under the symmetric class, while the rest come under the antisymmetric class.

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Cabannes (1938) and Aynard (1940) made a detailed study of the Raman water bands in gypsum. Aynard gave the frequency shifts of the water bands due to the stretching vibrations of the water molecules as 3404 (symmetric) and 3493 cm.$^{-1}$ (antisymmetric) and that of the deformation vibration as 1660 cm.$^{-1}$ Later, these two authors (1942) jointly worked out the Raman activity and depolarisation of the various co-operative vibrations of the water molecules in the unit cell of gypsum and compared the results obtained thereby with the experimental data.

The results obtained by the numerous investigators quoted above show wide discrepancies especially with regard to the number and frequency shifts of the low frequency or lattice lines. Rasetti (1932) using the 2536·5 mercury resonance radiation as exciter recorded as many as nine lattice lines, while those who employed the 4046 and 4358 radiations recorded only a couple of lines instead. Roop Kishore (1942) using the Rasetti technique and giving long exposures reported for the first time the existence of a weak line at 1622 cm.$^{-1}$, a weak band at about 2249 cm.$^{-1}$ and three more weak water bands with mean frequency shifts 3244, 3309 and 3584 cm.$^{-1}$ in the neighbourhood of the two principal water bands.

In continuation of the work on calcite (Krishnan, 1945), the author has now undertaken a detailed study of the Raman effect in gypsum using the mercury resonance radiation λ 2536·5 as exciter in order to record the first order spectrum in all its detail, and also to get some data regarding the second order spectrum in gypsum. The results are presented in this paper.

2. DETAILS OF THE EXPERIMENT

The technique of using the mercury resonance radiation λ 2536.5 for exciting the Raman spectrum of a crystal has already been described in some of the earlier papers of the author. A transparent crystal of gypsum in the form of a triangular disc ($4\frac{1}{2}''$ side and $\frac{3}{4}''$ thick) was selected for the present investigation from Sir C. V. Raman's personal collection. The flat faces were parallel to the cleavage plane. In all the experiments the specimen was illuminated with unpolarised light through one of its flat faces and the scattered light was photographed through one of its edges.

As in the case of calcite, two different instruments were used for recording the Raman spectra: (1) A Hilger E1 quartz spectrograph and (2) a Hilger E3 quartz spectrograph. The high dispersion instrument was used in order to record the lattice and SO_4 spectra in all their detail and also to measure the frequency shifts and widths of the lattice and SO_4 lines very accurately. For this purpose an iron arc comparison spectrum was taken on the same

negative partially overlapping the Raman spectrum. Using a slit width of 0·04 mm. exposures of the order of three days were given in order to get a spectrogram showing the lines with reasonable intensity.

The E3 quartz spectrograph was used to get intense photographs of the complete Raman spectrum of gypsum. With a slit width of 0·03 mm. exposures of the order of two days were given to record intense spectrograms, a sample of which is reproduced in Fig. 1 (a).

3. RESULTS

The spectrograms and the microphotometric records of some of them are reproduced in Figs. 1 to 5. Descriptions of the figures are given at the end of this paper. The positions and the frequency shifts of the Raman lines are marked in the figures. Most of the Raman lines have also been recorded on the anti-Stokes side.

In Table I are listed the frequency shifts of the Raman lines observed in the various spectrograms obtained in the present investigation. The shifts of the first 23 Raman lines and the widths of the most prominent of them have been measured from the spectrogram taken with the higher dispersion instrument and should therefore be considered as accurate. The temperature of the crystal was in the neighbourhood of 35°. The frequency shifts of the remaining Raman lines except the feeble ones at 1500, 2143 and 2268 cm.$^{-1}$ were evaluated from measurements made on the spectrogram taken with the E3 spectrograph. The frequency shifts of the three feebler lines have been estimated from the microphotometric record of this region of the spectrum. The values of the frequency shifts of the Raman lines of gypsum recorded earlier by Rasetti (1932), Saksena (1941), Roop Kishore (1942) and by Rousset and Lochet (1945) are included in Table I for purposes of comparison. The Raman spectrum recorded by the present author is more complete in respect of the lattice lines, the lines due to the sulphate ions and the water bands than any obtained by the earlier investigators. The lines with frequency shifts 565, 990, 1500, 2143, 2268 and 3680 cm.$^{-1}$ have been recorded for the first time.

The 34 Raman frequencies tabulated above have been classified into three groups namely, lattice spectrum denoted by l, the spectrum of the SO$_4$ ions in the crystal denoted by s and the spectrum of the water molecules denoted by w. The assignment of the lines into the group w was based particularly on considerations of their widths.

In addition to the Raman lines the positions of which have been marked in the figures there are indications of the existence of other feebler lines and

TABLE I

No.	Author			Rasetti (1932)	Saksena (1941)	Roop Kishore (1942)	Rousset and Lochet (1945)
	Frequency shift in cm.$^{-1}$	Width in cm.$^{-1}$	Group				
1	32 (2)	..	l	37	..	..	..
2	50 (2)	..	l	60	..	56	..
3	93 (1)	..	l	..	80	..	..
4	110 (4)	3	l	110	..	101	..
5	121 (5)	3	l	122	125	..	..
6	132 (4)	2	l	134	..	..	..
7	145 (4)	3	l	146	..	145	..
8	162 (3)	2	l	164	..	..	..
9	180 (5)	3	l	182	175	180	..
10	211 (3)	4	l	211	..	210	..
11	315 (2)	12	w	..	315	318	..
12	415 (9)	3	s	415	415	416	413
13	492 (10)	4	s	495	492	492	492
14	565 (2)	20	w	..	..	..	..
15	588 (2)	20	w	..	585	588	..
16	618 (5)	3	s	..	618	620	621
17	622 (5)	3	s	..	..	..	623·5
18	672 (6)	3	s	672	672	672	669
19	990 (3)	3	s	..	..	..	..
20	1006 (30)	5	s	1009	1006	1004	1006
21	1115 (4)	4	s	..	1115	1115	1117
22	1136 (20)	4	s	1137	1136	1135	1138
23	1143 (4)	4	s	..	..	..	1144
24	1500 (1)	..	s	..	..	..	..
25	1631 (2)	..	s	..	..	1622	..
26	2143 (1)	..	s	..	..	..	..
27	2215 (2)	40	w	..	..	2249	..
28	2268 (1)	..	s	..	..	..	..
29	3258 (3)	15	w	..	..	3244	..
30	3334 (3)	15	w	..	..	3309	..
31	3406 (30)	15	w	3399	3406	3410	..
32	3495 (30)	15	w	3476*	3493	3480	..
33	3606 (3)	15	w	..	..	3584	..
34	3680 (2)	..	w	..	..	..	..

l—Means lattice oscillation. *s*—Oscillation of the SO$_4$ group. *w*—Oscillation of the water molecules.

The figures given within brackets represent visual estimates of the relative intensities of the lines.

* This is obtained from measurements made on the photographs reproduced in Rasetti's paper. The value given by Rasetti (1932) for this band is 3426 which should evidently be wrong.

In addition to those listed in the above table, there are a few more fainter lines and bands (*cf.* text).

bands. One such line falls in between the Raman lines at 162 and 180 cm.$^{-1}$ The existence of a broad band superposed on the four lattice lines at 110, 121, 132 and 145 cm.$^{-1}$ is discernible from an examination of Figs. 4 and 5. The lattice line with a frequency shift of 211 cm.$^{-1}$ has a feeble companion on the longer wavelength side (see Fig. 5).

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The spectrograms of the mercury arc and of the Raman effect in gypsum which are reproduced in Figs. *2a* and *2b,* were taken under identical conditions. In the mercury arc photograph the $\lambda\, 2536 \cdot 5$ line is much less intense than its companion, $\lambda\, 2534 \cdot 8$, whereas in the scattered picture they are of comparable intensity although the same column of mercury vapour was used in both cases. The enhanced intensity of the unmodified line should be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour. Similar observations have already been reported by the author in the case of calcite.

4. Discussion

Gypsum is an ionic crystal and the unit cell which belongs to the monoclinic class contains four molecules of $CaSO_4.2H_2O$. There is a perfect cleavage plane parallel to the (010) face. The crystal possesses only one symmetry axis called the *b*-axis, which is perpendicular to the cleavage plane. The space group is C^3_{2h}. Wooster (1936) made a detailed X-ray analysis of the crystal structure of gypsum. The relevant details are quoted from his paper. " It is a layer lattice, layers being parallel to the face (010). Two sheets of SO_4 groups are intimately bound together by Ca ions so as to form a strong double sheet; successive double sheets are separated by sheets of water molecules. Each Ca atom is surrounded by six oxygen atoms belonging to the SO_4 groups and by two water molecules. Each water molecule links a Ca atom both to an oxygen in the same double sheet and to one in a neighbouring sheet. The latter bonds are comparatively weak and explain the easy cleavage parallel to the (010) face. The concentration of the water of crystallisation in sheets parallel to (010) is a very interesting feature ". Wooster's analysis shows that the four oxygen atoms belonging to the same sulphate group are situated at the corners of a regular tetrahedron. On the basis of the above structure let us proceed to discuss the results obtained from Raman effect studies.

Spectrum of the SO_4 ion.—It is well known that the SO_4 ion in the free state, *viz.,* in solutions of sulphates, has only four distinct modes of oscillation of which one is single, one doubly degenerate and the remaining two triply degenerate. The corresponding Raman frequencies are 983, 454, 622 and 1106 cm.$^{-1}$ In gypsum the degeneracies of the frequencies belonging to the tetrahedral SO_4 ion are split up and the spectrum shows nine Raman lines, the frequency shifts of which are given below:

Raman Frequencies of SO_4 Ion

In the free state	..	454			622			983	1106	
In gypsum	..	415	492 ;		618	622	672 ;	1006 ;	1115,	1136 1144

There are two possible explanations for the appearance of nine distinct modes as fundamentals in the Raman spectrum of the SO_4 ion in gypsum. The structure of the ion may be permanently distorted in the crystalline state so that it does not possess the full symmetry of the point group Td. In order to account for the depolarisation of the Raman lines observed by Rousset and Lochet (1945), the distorted ion should have only the symmetry of the point group C_2. This explanation was originally suggested by Cabannes (1932). On the basis of this picture when gypsum is dissolved in water, there should be an abrupt and violent change in the structure of SO_4 ion. *Prima facie* this view appears to be unreasonable. Moreover, the X-ray evidence is also inconsistent with the above point of view.

The alternative is to assume that the SO_4 ion retains its tetrahedral structure in the crystalline state also. During the internal oscillations of the ion, in addition to the valency forces between the constituent atoms in the ion, subsidiary forces due to the potential field of the neighbouring ions have to be taken into account in the crystal. It is these forces operating against the freedom of movement of the constituent atoms of the ion that cause the splitting of the degenerate frequencies and also the enhancement of the non-degenerate ones. The above explanation has been favoured by Bhagavantam (1938) and it appears to be a reasonable one. He pointed out from a simple group theoretical analysis that the four distinct modes of oscillation appropriate to the free SO_4 ion split up into nine components on account of the lower symmetry of the crystal, the selection rules for the various components being entirely different among themselves and from those of the ion. This offers a satisfactory explanation for the observed polarisation characters of the SO_4 lines in gypsum, although the ion has the full tetrahedral symmetry when the atoms are at rest. Analogous quantitative explanation has already been offered with success in order to account for some of the features observed in the Raman spectra of crystalline nitrates.

The feeble lines with frequency shifts 990, 1500, 1631, 2143 and 2268 cm.$^{-1}$ evidently belong to the second order Raman spectrum of the SO_4 ion in gypsum. These are assigned as octaves and combinations of the some of the nine fundamental frequencies of the SO_4 ion as indicated below:—

990	Octave	492 + 492
1500	Combination	1006 + 492
1631	Combination	1006 + 622
2143	Combination	1006 + 1136
2268	Octave	1136 + 1136

The lattice spectrum.—The mutual oscillations of the ions in the unit cell in which the SO_4 group and $2H_2O$ group act as entities constitute the

lattice spectrum of gypsum. Neglecting the influence of the H_2O molecules on the mutual oscillations of the Ca and SO_4 ions, Bhagavantam (1938) has shown that there should be eighteen Raman active lattice oscillations in gypsum. On the other hand, the recorded spectrum consists of seven sharp, intense and closely spaced lattice lines and three relatively feebler lines with low frequency shifts. Further experimental work on the effect of crystal orientation on the intensity and polarisation of the lattice lines is called for in order to give satisfactory assignments to the observed lattice lines.

The spectrum of water of crystallisation.—On comparing the Raman bands of water in gypsum as observed in the present investigation with those of ordinary water and of ice (summarised in Hibben's book), we find that the number and distribution of the bands are common to all the three.

TABLE II

Frequency Shifts of Raman Bands

Gypsum	Ordinary water	Ice at 0° C.
318	170	205
565 ⎫ 588 ⎭	500	600
1631	1650	1650
2215	2170	2225
3258 ⎫ 3334 ⎭ (m)	3231 (st.)	3193
3406 ⎫ 3495 ⎭ (v. st.)	3436 (v. st.)	3391
3606 ⎫ 3680 ⎭ (m)	3605	3549

The correspondence follows as a natural consequence of the fact that in gypsum the water molecules are concentrated in separate sheets which are only loosely bound with other sheets of ions and as such the oscillations of the water molecules are not appreciably modified in the crystalline state. The bands in gypsum are very much sharper than those observed with ordinary water and consequently their maxima could be measured with a high degree of accuracy. The spectrum of gypsum shows another interesting feature. The three principal water bands are split into six fairly narrow bands. They form three pairs as shown in Table II. The difference in the frequency shifts of the two components of each pair is approximately constant for the three pairs, the average value being 80 wave numbers. The splitting of the principal water bands can be attributed to the low symmetry of gypsum crystal compared to that of ice. Results obtained by Cabannes (1938), Saksena (1941)

and Rao (1941) from polarisation studies indicate that the band at 3406 belongs to the symmetric class, while the one at 3495 belongs to antisymmetric class. Similar behaviour should be exhibited by the other two pairs of bands also. Because of the antisymmetric nature of the band at 3495 cm.$^{-1}$ Cabannes (1938) had suggested that this band should correspond to the Raman inactive valence vibration of the H_2O molecule, which was rendered active in the crystalline environment.

The Raman bands of water in several crystalline hydrates have been the subject of study by numerous investigators notably by Nisi (1931), Ananthakrishnan (1937), Hibben (1937), Canals and Peyrot (1938), Nayar (1938) and Lakshman Rao (1941). The results reported up to the end of 1938 have been summarised in Hibben's book (1939). The spectrum of water of crystallisation in gypsum as recorded by Roop Kishore and the present author shows far greater detail than any recorded by others not only in gypsum but in other crystalline hydrates as well. The success is due to the use of the intense mercury resonance radiation for exciting the Raman spectrum. A similar study with other crystalline hydrates would furnish us with valuable data which could be correlated with the physical properties of the molecules involved.

5. Infra-Red Spectrum

Investigations on the infra-red spectrum of gypsum are very scanty. Kock (1908) who studied the nature of residual rays of gypsum reported the existence of a narrow intense band at $8 \cdot 69 \, \mu$ due to the SO_4 ion and a fairly broad one at about $24 \, \mu$. Coblentz (1910, 1911) made a detailed analysis of the high frequency infra-red absorption bands of the water of crystallisation in gypsum. On the whole seven absorption maxima were observed by him. They are at $1 \cdot 5 \, \mu$, $2 \cdot 05 \, \mu$, $2 \cdot 95 \, \mu$, $4 \cdot 54 \, \mu$, $5 \cdot 95 \, \mu$, $6 \cdot 5 \, \mu$ and $6 \cdot 68 \, \mu$. The corresponding frequencies in wave numbers are 6666, 4880, 3390, 2200, 1680, 1540 and 1495. Bands corresponding to 3390 and 2200 appear in the Raman spectrum of gypsum. Schæfer and Schubert (1916) investigated the infra-red absorption spectrum of gypsum in the region of the specific frequencies of the sulphate ion. They observed two strong absorption maxima at $8 \cdot 74 \, \mu$ (1144 cm.$^{-1}$) and at $14 \cdot 84 \, \mu$ (674 cm.$^{-1}$) and a secondary maxima at $8 \cdot 62 \, \mu$ (1160 cm.$^{-1}$). The Raman lines corresponding to $8 \cdot 74 \, \mu$ and $14 \cdot 84 \, \mu$ infra-red bands have been observed with frequency shifts 1136 and 672 cm.$^{-1}$ As is to be expected, the depolarisation data given by Rousset and Lochet indicate that these two Raman lines come under the antisymmetric class.

In conclusion, the author wishes to express his grateful thanks to Professor Sir C. V. Raman for the loan of the crystal of gypsum and for his kind interest in the work.

6. SUMMARY

The earlier work on the Raman effect in gypsum has been briefly reviewed.

The results obtained from a detailed study of the Raman effect in gypsum using the mercury resonance radiation as exciter are described. The recorded spectrum consists of 34 Raman lines and bands distributed as follows: 10 lines belong to the lattice spectrum, 14 Raman lines constitute the spectrum of the SO_4 ion and ten Raman bands make up the spectrum due to the water of crystallisation. The frequency shifts and widths of most of them have been accurately determined. In addition to these, a few other fainter lines and bands have been recorded.

Of the 14 Raman lines belonging to the internal oscillations of the SO_4 ion, nine are comparatively more intense and they constitute the first order spectrum. On the basis of the known crystal structure of gypsum, the appearance of the nine lines as fundamentals has been satisfactorily explained. The five feebler lines have been assigned as octaves and combinations of the fundamental frequencies. They constitute the second order spectrum of the SO_4 ion. The Raman bands of water of crystallisation in gypsum exhibit some of the important features characteristic of the Raman bands of ordinary water and of ice. The similarity in the behaviour of the water bands has been attributed to the fact that the water molecules in gypsum are concentrated in separate sheets parallel to the cleavage face and are only loosely linked up with other ions.

The frequencies corresponding to the various maxima observed in the infra-red absorption spectrum of gypsum have been compared with those observed by the author in the Raman spectrum.

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

REFERENCES

1. *Raman Effect*

Krishnan, K. S.   .. *Ind. Journ. Phys.*, 1929, **4**, 131.

Hollaender and Williams   .. *Phys. Rev.*, 1929, **34**, 994 ; 1931, **38**, 1739.

Dickinson and Dillon   .. *Proc. Nat. Acad. Sci.*, *U.S.A.*, 1929, **15**, 695.

Nisi   .. *Proc. Imp. Acad. Tokyo*, 1929, **5**, 407.

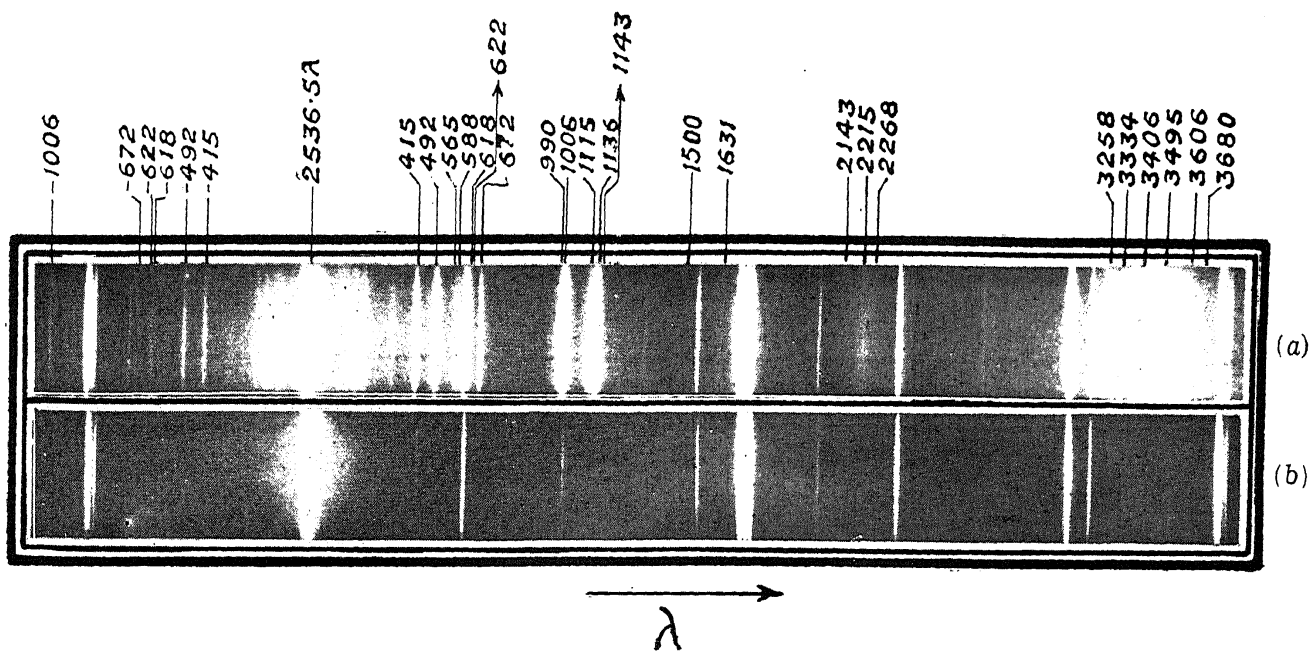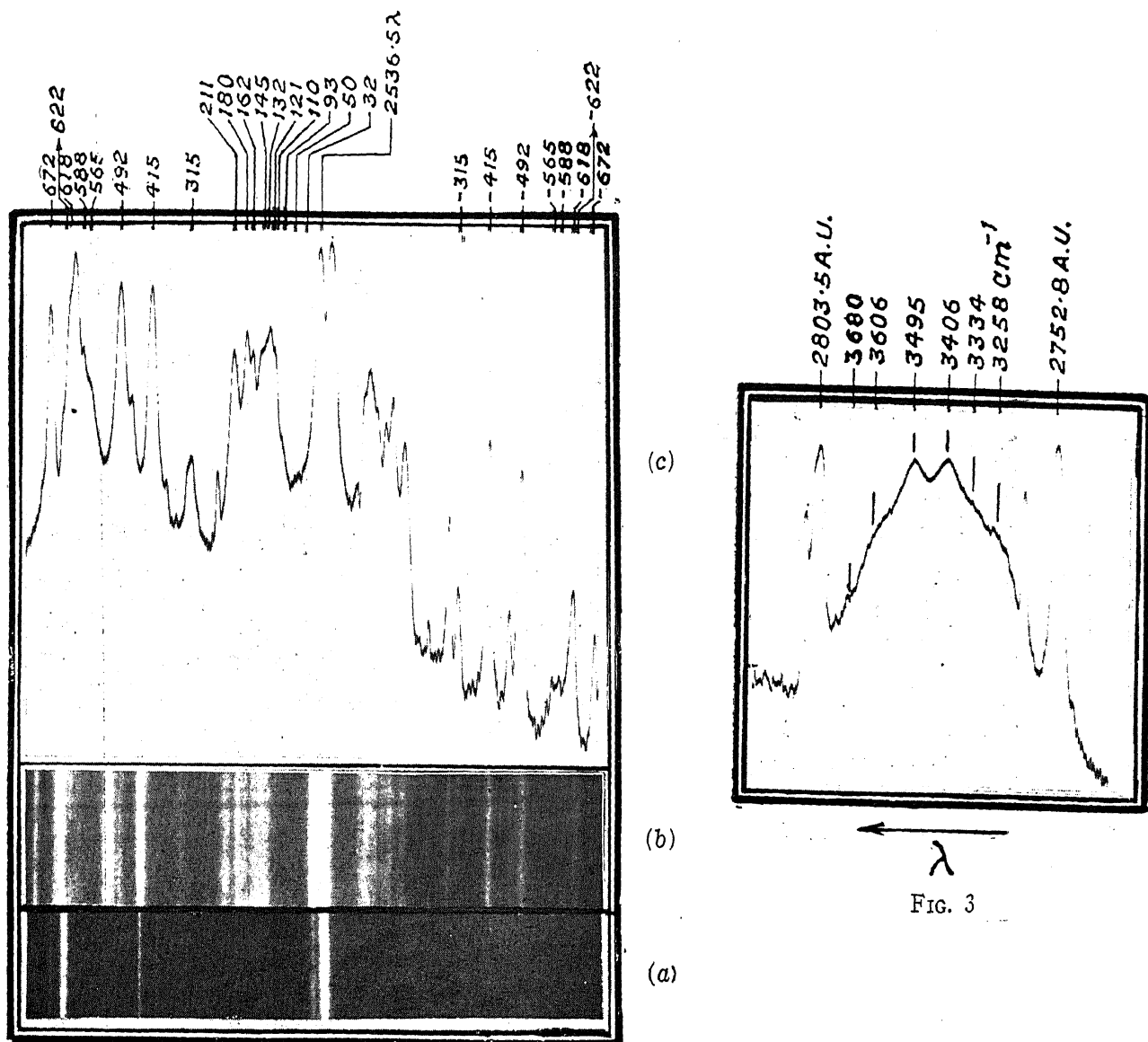Schæfer, Matossi and Aderhold   *Phys. Zeits.*, 1929, **30**, 581 ; *Zeits. f. Phys.*, 1930a, **65**, 289.
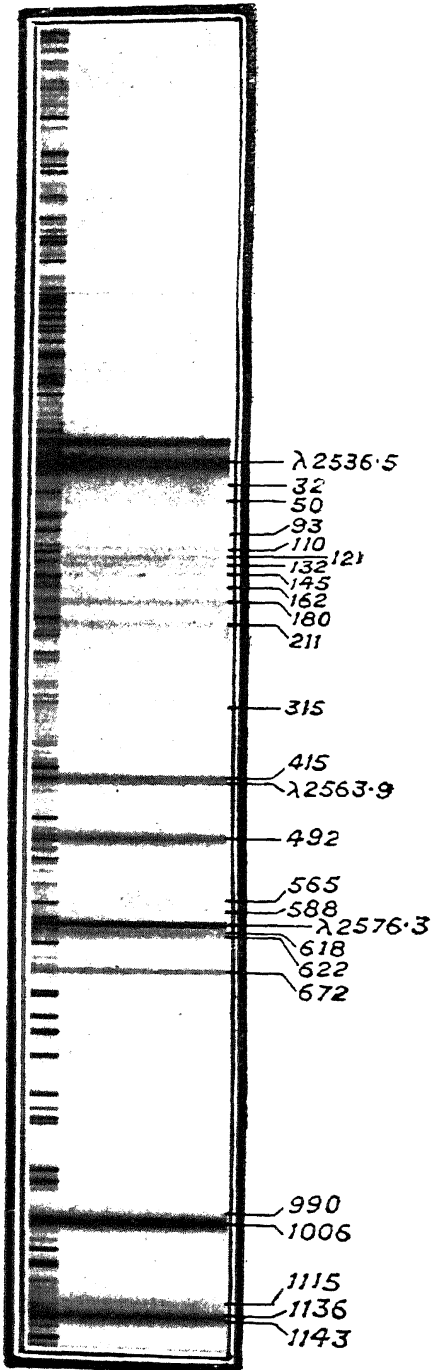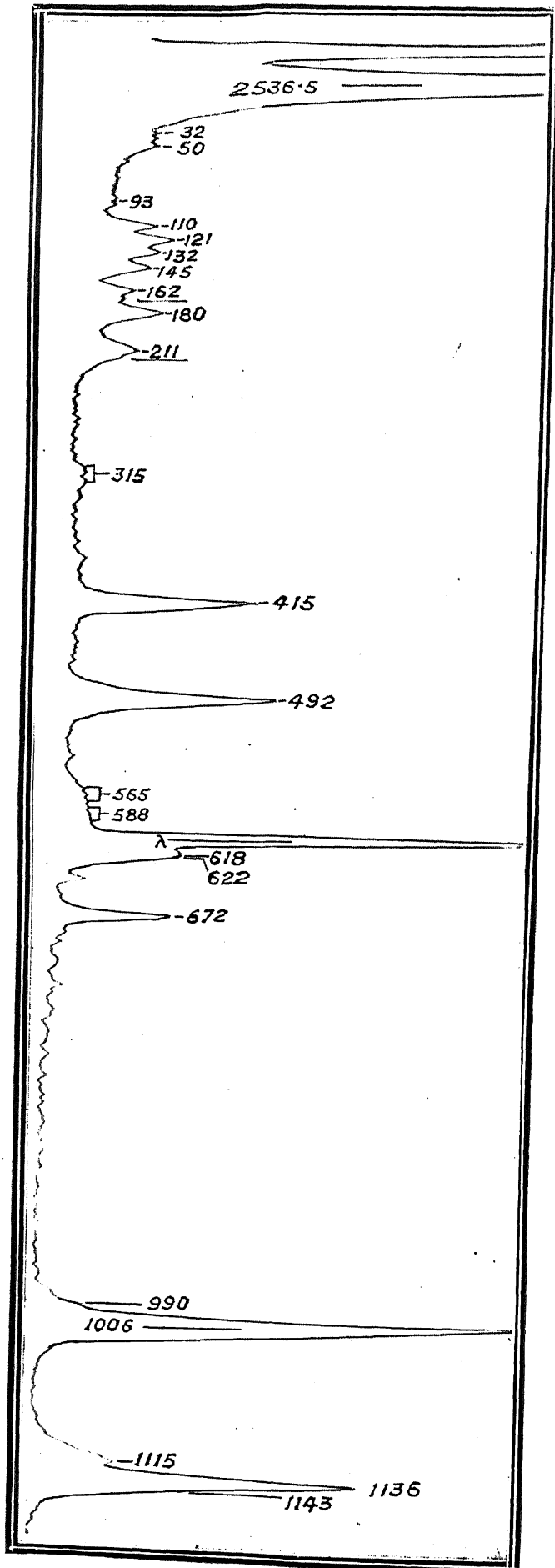
Fig. 1

Fig. 3

Fig. 4

Fig. 5

Krishnamurti	.. *Ind. Journ. Phys.*, 1930, **5**, 183.
Rasetti	.. *Nuovo Cimento, Rivista*, 1931, **8**, 89 ; 1932, **9**, 72.
Schæfer, Matossi and Aderhold	*Phys. Zeits.*, 1930*b*, **31**, 801 ; *Zeits. f. Phys.*, 1930*c*, **65**, 319.
Nisi	.. *Japanese Journ. Phys.*, 1931, **7**, 1.
Cabannes	.. *Compt. rend.*, 1932, **195**, 1353 ; 1938, **207**, 700.
*Aynard	.. *Ibid.*, 1940, **211**, 647.
Roop Kishore	.. *Proc. Ind. Acad. Sci.*, A, 1942, **16**, 36.
*Cabannes and Aynard	.. *Journ. de Physique*, 1942, **3**, 137.
Saksena	.. *Proc. Ind. Acad. Sci.*, A, 1941, **13**, 25.
Rao, D. A. A. S. N.	.. *Ibid.*, 1941, **13**, 137.
Rousset and Lochet	.. *Journ. de Physique*, 1945, **6**, 57.

2. *General*

Krishnan, R. S.	.. *Proc. Ind. Acad. Sci.*, A, 1945, **22**, 182.
Wooster, W. A.	.. *Zeits. f. Kristallographie*, 1936, **94**, 375.
Bhagavantam, S.	.. *Proc. Ind. Acad. Sci.*, A, 1938, **8**, 345.
Hibben	.. *The Raman Effect and its Chemical Applications*, 1939.

3. *Water of Crystallisation*

Nisi	.. *Japanese Journ. Phys.*, 1931, **7**, 1.
Ananthakrishnan	.. *Proc. Ind. Acad. Sci.*, A, 1937, **5**, 447.
Hibben	.. *Journ. Chem. Phys.*, 1937, **5**, 166.
Canals and Peyrot	.. *Compt. rend.*, 1938, **207**, 224.
Nayar	.. *Proc. Ind. Acad. Sci.*, A, 1938, **8**, 419.
Lakshman Rao	.. *Ibid.*, 1941, **14**, 48.

4. *Infra-red*

Kock, J.	.. *Ann. der Phys.*, 1908, **26**, 974.
Coblentz	.. *Phys. Rev.*, 1910, **30**, 322 ; *Bull. Bur. Stds.*, 1911, **7**, 619.
Schæfer and Schubert	.. *Ann. der Phys.*, 1916, **50**, 283.

* The author could not refer to the original papers as the relevant journals have not been received in India. The results were taken from the American *Chemical Abstracts*.

DESCRIPTION OF PLATES

FIG. 1. (*a*) The complete Raman spectrum of gypsum taken with E3 spectrograph. (*b*) Comparison spectrum of the mercury arc.

FIG. 2. (*a*) Spectrum of the mercury arc. (*b*) The lattice spectrum of gypsum taken with the same instrument but using a finer slit and an efficient mercury vapour filter. (*c*) Its microphotometric record.

FIG. 3. The microphotometric record of the high frequency water bands.

FIG. 4. The spectrum of gypsum showing the lattice lines and the lines due to the SO_4 ion, taken with the E1 spectrograph.

FIG. 5. Its microphotometric record.