

THE INFRA-RED ABSORPTION SPECTRUM OF BARYTES

BY A. K. RAMDAS

(Memoir No. 47 of the Raman Research Institute, Bangalore)

Received February 4, 1954

(Communicated by Sir C. V. Raman)

1. INTRODUCTION

THOUGH the Raman spectrum of barytes has been studied in detail by many workers, in particular by R. S. Krishnan¹ and L. Couture,² the infra-red absorption studies have remained inadequate. The earlier works have been those of Coblenz,³ Schæfer and Schubert,⁴ and Matossi and Kindler⁵ in the short wavelengths from 2μ to 16μ by absorption and reflexion methods; and of Liebisch and Rubens⁶ in the far infra-red upto 300μ by reflexion method. The present author has reinvestigated the infra-red spectra of barytes by transmission in the range 1μ to 25.5μ . In this paper it is proposed to present the experimental results obtained by the author and discuss them in the light of selection rules and the Raman effect data.

2. EXPERIMENTAL RESULTS

The crystals of barytes were examined in the 001 and 110 cleavage sections. A Beckman infra-red spectrophotometer provided with KBr-optics was used to measure the percentage transmission at 0.05μ intervals and at still closer intervals near absorption maxima. Ten specimens of different thicknesses were examined. We reproduce in Figs. 1, 2 and 3, the infra-red spectra (% cut-off vs. $\lambda\mu$) of three specimens showing all the features in the clearest manner. (Fig. 1: Specimen VI, 001 section, thickness 1.7 mm. ; Fig. 2: Specimen VII, 001 section, thickness 3.0 mm. ; Fig. 3: Specimen VIII, 110 section, thickness 0.25 mm.) The following features are noticed.

I. Numerous very weak absorption maxima are exhibited between 1μ and 4μ , viz., at 2.5μ , 3μ , 3.3μ and 3.5μ for specimen VI; at 2.5μ , 3μ , 3.3μ and 3.7μ for specimen VII; at 2.5μ , 3μ , 3.3μ , 3.5μ and at 3.7μ for specimen VIII. Of these the 3.3μ absorption maximum is the strongest and is brought out best in Fig. 2. Matossi and Kindler found additional bands at 2.35μ , 2.41μ , 2.66μ , 3.19μ , 3.8μ and 3.9μ . Coblenz reported the one at 3.0μ .

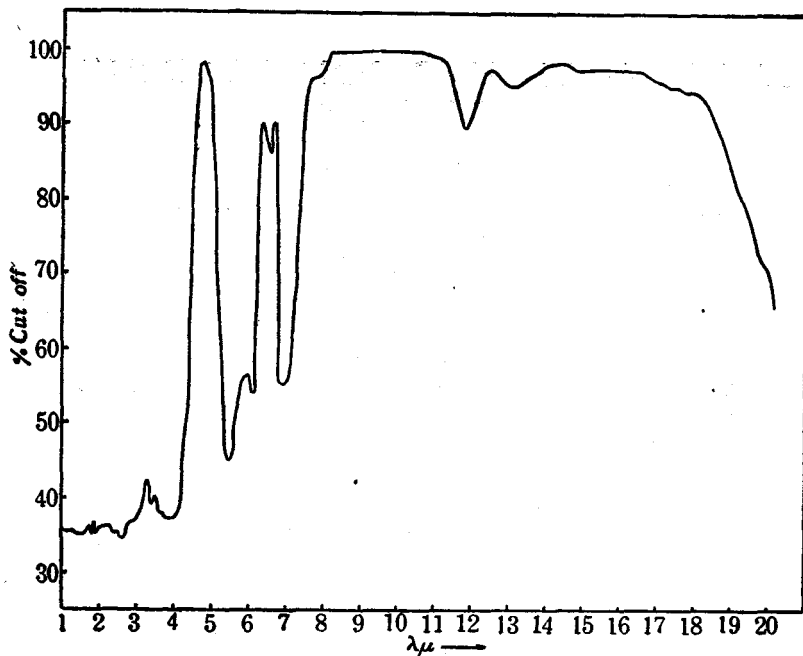


FIG. 1. Infra-red absorption spectrum of barytes (Specimen VI)

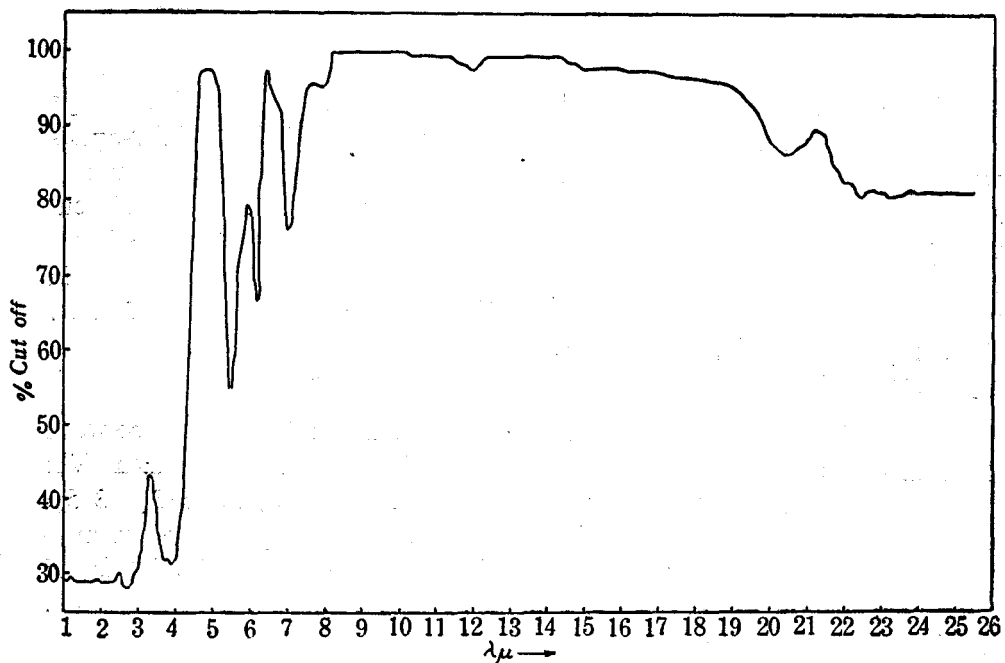


FIG. 2. Infra-red absorption spectrum of barytes (Specimen VII)

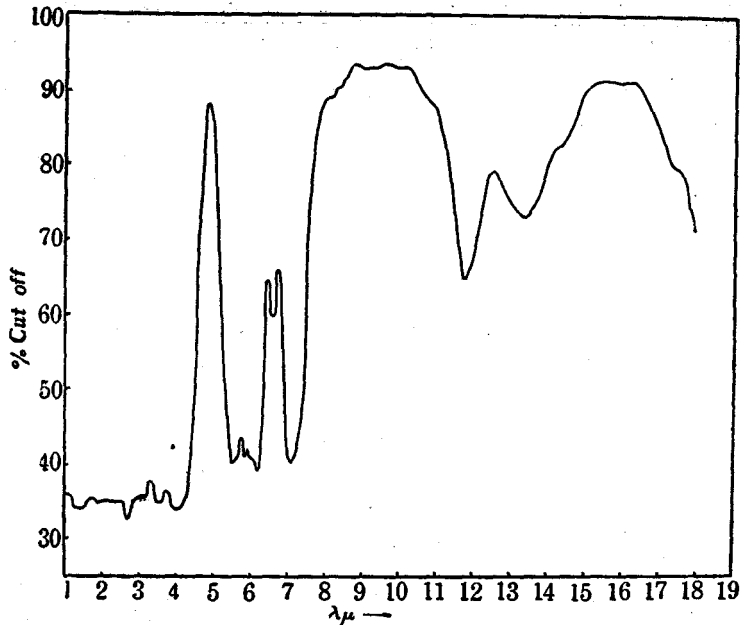


FIG. 3. Infra-red absorption spectrum of barytes (Specimen VIII)

II. The region between 4μ and 7μ shows intense and well defined absorption maxima. Fig. 1 shows a sharply defined band at 4.8μ with a companion at 4.9μ , a weak one at 5.9μ , an intense doublet at 6.4μ and 6.7μ . Fig. 2 shows a slightly broad band between 4.7μ to 4.9μ ; the 5.9μ band is rather strong and well brought out, while instead of a well resolved doublet 6.4μ and 6.7μ , a maximum at 6.4μ and an inflexion at 6.7μ are observed. This is due to the greater thickness of specimen VII. In Fig. 3, bands at 4.9μ (intense), 5.75μ , 5.85μ (very weak), and a well resolved doublet 6.4μ and 6.7μ , the latter being the stronger band. These differences observed between specimens VI and VII on the one hand and specimen VIII on the other are evidently connected with the fact that the former are 001 sections and the latter is a 110 section. In this range Matossi and Kindler reported the following maxima: 4.32μ , 4.61μ , 4.82μ , 5.12μ , 5.87μ , 6.27μ , 6.51μ and 6.99μ ; Coblenz observed bands at 4.6μ , 6.2μ and 6.5μ .

III. The region from 7μ to 12μ is one of intense cut-off. Reflexion studies of Coblenz and of Schaefer and Schubert reveal reststrahlen maxima at 8.3μ , 8.93μ and 9.1μ indicating the presence of fundamentals. Observations with polarised light and orientational studies show that these reflexion maxima are polarised along the a , b and c axes of the crystal. Figs. 1 and 2 exhibit strong cut-off between 8μ and 11μ . In Fig. 3 there are indications

of resolution of this strong band into several maxima such as those at $8.3\ \mu$, $8.8\ \mu$, $9.6\ \mu$ and $10.2\ \mu$, with an inflexion at $10.8\ \mu$.

IV. We notice a rather broad absorption from $12.3\ \mu$ to $14.4\ \mu$ in Fig. 2, while a well defined maximum at $12.55\ \mu$ replaces it in both Figs. 1 and 3. In Fig. 1, beyond this, a maximum at $14.4\ \mu$ is seen followed by constant and strong absorption region right upto $16.6\ \mu$. Thereafter it shows a rapid fall upto $20.2\ \mu$. No observations could be made with this specimen beyond $20.2\ \mu$ as its area was too small for accurate measurements. In Fig. 2, there is almost total cut-off from $15\ \mu$ to $19\ \mu$. From $19\ \mu$ onwards a slow falling off is seen, and at $21.3\ \mu$ a well defined maximum has been obtained, with hints of maxima at $22.2\ \mu$, $22.8\ \mu$ and $23.8\ \mu$. The very large area of specimen VII has enabled observations to be made right upto $25.5\ \mu$, the limit of the instrument employed in the present work. It appears that the above maxima beyond $20\ \mu$ have been observed for the first time. In Fig. 3, an inflexion at $14.4\ \mu$ is noticed and, instead of the strong cut-off seen in the other figures, a comparatively narrower band between $15\ \mu$ to $16.4\ \mu$ is seen, with definite indications of maxima at $15.6\ \mu$, $15.8\ \mu$ and $16.3\ \mu$. Matossi and Kindler obtained maxima at $12.35\ \mu$ and $15.65\ \mu$. Schæfer and Schubert report a reflexion maximum at $15.8\ \mu$.

3. THEORETICAL CONSIDERATIONS

Barytes belongs to the space group V_h^{16} (Pnma) with four molecules of BaSO_4 per unit cell. The vibrations of barytes can be divided into two classes: (1) low frequency lattice oscillations in which SO_4 molecules move as units against Ba atoms, and (2) high frequency oscillations which constitute internal movements of the atoms comprising the SO_4 molecule. In the range studied in this investigation, we may expect (as we shall see presently) only the high frequency oscillations, internal to SO_4 molecules to appear as fundamentals.

The free SO_4 molecule belongs to the T_d symmetry. Accordingly it possesses four fundamental vibrations: totally symmetric ν_1 (A_1); doubly degenerate ν_2 (E); and triply degenerate ν_3 (F_2) and ν_4 (F_2). All of these are Raman active, but only the F_2 -type vibrations are infra-red active.

Corresponding to each of the vibration of the free SO_4 molecule, one expects to find a number of vibrations in the crystalline state. The number and their respective symmetry properties can be found out according to the procedure outlined by Couture and Mathieu.⁷ The effect of the crystalline state on the free SO_4 oscillations is two-fold. The symmetry of a single SO_4 molecule is changed from the tetrahedral group T_d to the monoclinic

local symmetry C_s , lifting the degeneracies of the doubly and triply degenerate oscillations; in this manner the *four* fundamentals of the free SO_4 molecule give *nine* fundamentals. A further increase in the modes of vibrations is brought about by the coupled oscillations of the four SO_4 molecules in the unit cell; in this way the above nine fundamentals multiply to yield a total of *thirty-six* internal vibrations of the barytes crystal. The transformation of the vibrations of the free SO_4 molecule into the internal modes of barytes can be pictured as given in Table I.

TABLE I

Free SO_4 molecule \rightarrow (T_d)	Local symmetry \rightarrow (C_s)	Unit cell symmetry (V_h)
$\nu_1(A_1) \longrightarrow$	$\nu_1^1 (A')$	$\nu_1^1 (A_{1g}), \nu_1^2 (B_{2g}), \omega_1^1 (B_{1u}), \omega_1^2 (B_{3u})$
$\nu_2(E) \longrightarrow$	$\left\{ \begin{array}{l} \nu_2^1 (A') \\ \nu_2^2 (A'') \end{array} \right.$	$\left\{ \begin{array}{l} \nu_2^1 (A_{1g}), \nu_2^2 (B_{2g}), \omega_2^3 (B_{1u}), \omega_2^4 (B_{3u}) \\ \nu_2^3 (B_{1g}), \nu_2^4 (B_{3g}), \omega_2^1 (A_{1u}), \omega_2^2 (B_{2u}) \end{array} \right.$
$\nu_3(F_2) \longrightarrow$	$\left\{ \begin{array}{l} \nu_3^1 (A') \\ \nu_3^2 (A') \\ \nu_3^3 (A'') \end{array} \right.$	$\left\{ \begin{array}{l} \nu_3^1 (A_{1g}), \nu_3^3 (B_{2g}), \omega_3^1 (B_{1u}), \omega_3^2 (B_{3u}) \\ \nu_3^2 (A_{1g}), \nu_3^4 (B_{2g}), \omega_3^3 (B_{1u}), \omega_3^4 (B_{3u}) \\ \nu_3^5 (B_{1g}), \nu_3^6 (B_{3g}), \omega_3^5 (A_{1u}), \omega_3^6 (B_{2u}) \end{array} \right.$
$\nu_4(F_2) \longrightarrow$	$\left\{ \begin{array}{l} \nu_4^1 (A') \\ \nu_4^2 (A') \\ \nu_4^3 (A'') \end{array} \right.$	$\left\{ \begin{array}{l} \nu_4^1 (A_{1g}), \nu_4^3 (B_{2g}), \omega_4^1 (B_{1u}), \omega_4^2 (B_{3u}) \\ \nu_4^2 (A_{1g}), \nu_4^4 (B_{2g}), \omega_4^3 (B_{1u}), \omega_4^4 (B_{3u}) \\ \nu_4^5 (B_{1g}), \nu_4^6 (B_{3g}), \omega_4^5 (A_{1u}), \omega_4^6 (B_{2u}) \end{array} \right.$

Selection rules show that: for T_d , all are Raman active but only F_2 's are infra-red active; for C_s , all are Raman and infra-red active; for V_h , all g 's are Raman active, infra-red inactive, all u 's are infra-red active, Raman inactive, with the exception of A_{1u} 's which are inactive in both. The ν 's are Raman active, and the ω 's infra-red active, the two sets being mutually exclusive because of the presence of centre of inversion. Further, the infra-red vibrations are polarised along a (B_{3u}), b (B_{2u}) or c (B_{1u}) axes of the crystal.

Hence under favourable conditions one should be able to observe eighteen Raman lines and fifteen infra-red lines corresponding to the internal modes of SO_4 in barytes.

4. DISCUSSION OF RESULTS

The four fundamentals of the free SO_4 molecule from studies of Raman effect in the liquid state are found to be: 980 cm.^{-1} [$\nu_1 (A_1)$], 450 cm.^{-1} [$\nu_2 (E)$], 620 cm.^{-1} [$\nu_3 (F_2)$] and 1100 cm.^{-1} [$\nu_4 (F_2)$]. According to the analysis given above eighteen Raman lines and fifteen infra-red lines of the

internal type should be observed in the proximity of these frequencies, falling into four groups as indicated. The two sets are mutually exclusive.

Couture² has been able to discover thirteen internal fundamental Raman lines and give them proper assignments, by a detailed investigation of their depolarisation values with directional excitation.

The infra-red active fundamentals corresponding to $\nu_4(F_2)$, expected in the neighbourhood of 1100 cm.^{-1} lie in a region of intense cut-off. The reflexion studies, however, give three maxima at $8.3\ \mu$, $8.93\ \mu$ and $9.1\ \mu$, and according to their polarisations one can ascribe to them B_{3u} , B_{2u} and B_{1u} types respectively. In the present studies we get maxima at $8.3\ \mu$, $8.8\ \mu$ and $9.6\ \mu$ with 110 section. The former two are presumably the same as $8.3\ \mu$ and $8.93\ \mu$ reflexion maxima while $9.6\ \mu$ appears to be a weak B_{3u} type of vibration. We have entered them as the infra-red active fundamentals in Table II.

The infra-red fundamental corresponding to $\nu_1(A_1)$ is taken as the one at $10.2\ \mu$ observed in the present study. The $\nu_1(A_1)$ is a totally symmetric infra-red inactive, Raman-active vibration. The infra-red activity which the corresponding vibrations in the crystalline state acquire will be as a result of the distortion caused by the crystalline state. Barytes is weakly birefringent ($N_g - N_p = 0.012$) and thus, though qualitatively allowed to appear on symmetry considerations alone, quantitatively the vibrations may appear only weakly. However, these can be expected to appear with great intensity in Raman effect, especially the totally symmetric one. The most intense Raman line observed by Krishnan is the one at 988.6 cm.^{-1} (A_{1g}). Another Raman line at 967 cm.^{-1} has been observed by Krishnan which he describes as 'the most intense one (of the 2nd order lines) as it appears even in the lightly exposed photograph'. It has not been possible to identify it as an overtone or a combination. This is highly suggestive of its being the $\nu_1^2(B_{2g})$ vibration.

Similar remarks as to the activity of the infra-red vibrations corresponding to $\nu_2(E)$ can be made. We have observed in the present work fairly strong and sharp maximum at $21.3\ \mu$ (469.5 cm.^{-1}) and a rather weak one at $22.8\ \mu$ (439 cm.^{-1}) using a very thick crystal. These have been observed with 001 section and hence must belong to B_{2u} or B_{1u} symmetry. Polarisation studies must be made to decide to which of them they actually belong. The Raman lines at 453 cm.^{-1} and 462 cm.^{-1} are among the most intense Raman lines observed by Krishnan.

The knowledge of the infra-red active fundamentals representing $\nu_3(F_2)$ in the crystal is perhaps the least. Theoretically, five vibrations are expected,

three in the 001 section and all the five in the 110 section. Reflexion studies have yielded but one at 15.8μ with 001 section and the present work three at 15.6μ , 15.8μ and 16.3μ with 110 section. Nothing is known about their polarisation properties.

The Raman active and the infra-red active internal oscillations of barytes which can be derived from the data available can be summarised as in Table II.

TABLE II

Raman active	Infra-red active	Raman active	Infra-red active
$\nu_1^1(A_{1g}) = 988 \text{ cm.}^{-1}$	$\omega_1^1(B_{1u})$ } 980 cm.^{-1}	$\nu_3^1(A_{1g}) = 622 \text{ cm.}^{-1}$	$\omega_3^1(B_{1u})$ } 641 cm.^{-1}
$\nu_1^2(B_{2g}) = 967$	$\omega_1^2(B_{3u})$ }	$\nu_3^2(A_{1g}) = 630$	$\omega_3^2(B_{3u})$ }
	..	$\nu_3^3(B_{2g}) = ?$	$\omega_3^3(B_{1u})$ } 633 ..
$\nu_2^1(A_{1g}) = 453$		$\nu_3^4(B_{2g}) = 647$	$\omega_3^4(B_{3u})$ } 614 ..
$\nu_2^2(B_{2g}) = 453$	$\omega_2^2(B_{2u} \text{ or } B_{1u}) = 439$	$\nu_3^5(B_{1g}) = \text{---?}$..
$\nu_2^3(B_{1g}) = 462$	$\omega_2^3(B_{1u} \text{ or } B_{2u}) = 470$	$\nu_3^6(B_{3g}) = 622$	$\omega_3^6(B_{2u})$ }
$\nu_2^4(B_{3g}) = \text{---?}$	$\omega_2^4(B_{3u}) = \text{---?}$	$\nu_4^1(A_{1g}) = 1105$	$\omega_4^1(B_{1u}) = 1136$
		$\nu_4^2(A_{1g}) = 1145$	$\omega_4^2(B_{3u}) = 1042$
		$\nu_4^3(B_{2g}) = 1138$	$\omega_4^3(B_{1u}) = \text{---}$
		$\nu_4^4(B_{2g}) = 1167$	$\omega_4^4(B_{3u}) = 1205$
		$\nu_4^5(B_{1g}) = \text{---?}$..
		$\nu_4^6(B_{3g}) = 1084$	$\omega_4^6(B_{2u}) = 1100$

As described in the experimental part of the paper, there are several absorption maxima in the wavelengths below 8μ . These will naturally find explanation only as harmonics of the fundamentals. Selection rules show that they too will be polarised along the axes *a*, *b* or *c*. Hence to give them proper assignments, their polarisations should be considered. Matossi and Kindler have given assignments to these higher order absorption maxima on the basis of the four fundamentals of the free SO_4 molecule. As the theory predicts and the experiments confirm, one has to explain the infra-red and Raman spectra on the basis of vibrations of the four SO_4 molecules contained in the unit cell of the crystal. Even with the incomplete knowledge of the fundamentals, it is possible to give satisfactory assignments to the entire body of data (Table III). When the remaining unknown fundamentals

TABLE III

$\lambda\mu$	Observed		Assignment	Calculated cm. ⁻¹
	cm. ⁻¹	Section		
2.35	4255	001	..	4142
2.41	4149	"	$2\nu_4^2 + \nu_3^4 + \omega_4^4$	4003
2.5	4000	„,+110	$\left\{ \begin{array}{l} 2\nu_4^6 + \omega_4^4 + \nu_3^2 \\ 2\nu_4^4 + \omega_4^2 + \nu_3^1(\nu_3^6) \\ 2\nu_4^8 + \omega_4^6 + \nu_3^1(\nu_3^6) \end{array} \right.$	3998 3998
2.66	3759	"	$3\omega_4^6 + \nu_2^1(\nu_2^2)$	3753
3.0	3333	„,+110	$2\nu_4^2 + \omega_4^2$	3332
3.2	3125	"	$3\omega_4^2$	3126
3.3	3030	„,+110	$2\nu_1^1 + \omega_4^2$	3018
3.5	2857	„,+110	$\nu_4^1 + \nu_3^4 + \omega_4^6$	2852
3.7	2703	„,+110	$\nu_4^2 + \omega_4^6 + \nu_2^1(\nu_2^2)$	2698
3.8	2632	"	$\nu_4^6 + \omega_4^6 + \nu_2^1(\nu_2^2)$	2637
3.9	2564	"	$\nu_4^3 + \omega_1^1 + \nu_2^1(\nu_2^2)$	2571
4.32	2315	"	$2\nu_3^2 + \omega_4^2$	2302
4.61	2169	"	$\nu_1^2 + \omega_4^4$	2172
4.7	2128	"	$\nu_4^6 + \omega_4^2, \nu_4^1 + \omega_1^1, \nu_1^1 + \omega_4^6,$ $\nu_4^6 + \omega_1^1, \nu_4^8 + \omega_1^1$	2126, 2085, 2088, 2064, 2118
↓	↓			
4.9	2041	"	$\omega_1^1 + \nu_4^1, \nu_1^1 + \omega_4^6$	2085, 2088
4.8	2083	"	$\nu_1^1 + \omega_4^2$	2030
4.9	2041	110	$\nu_1^2 + \omega_1^1$	1947
5.12	1953	001	$\nu_3^2 + \omega_4^6$	1730
5.75	1739	110	..	
5.85	1709	"	..	
5.9	1695	001	..	
6.27	1595	"	$\nu_3^1 + \omega_1^1, \nu_3^6 + \omega_1^1$	1602
6.4	1562	"	$\nu_2^3 + \omega_4^6$	1562
6.51	1536	"	$\nu_4^1 + \omega_2^2$	1544
6.7	1493	"	$\nu_2^1 + \omega_4^2, \nu_2^2 + \omega_4^2$	1495
6.99	1431	"	$\nu_2^1 + \omega_1^1, \nu_2^2 + \omega_1^1$	1433
7.8	1282	"	$\nu_3^4 + \omega_3 (=633)$	1280
8.3	1203	"	ω_4^4	
8.8	1136	"	ω_4^1	
9.1	1100	"	ω_4^3	
9.6	1042	"	ω_4^2	
10.2	980	110	ω_1^1	
10.8	926	"	$\nu_2^1 + \omega_2^3$	923
12.35	810	001	$\nu_3^4 + 164$	811
12.55	796	„,+110	$\nu_3^2 + 164$	794
14.4	694.4	"	$\nu_3^1 + 77$	699
15.6	641	"	..	
15.8	633	110	ω_3^1 s	
16.3	614			
21.3	470	001	ω_2^3	
22.2	451	"	..	
22.8	439	"	ω_2^2	
23.8	420	"	..	

are also discovered, and accurate polarisation studies are made the assignments given in Table III, may have to be revised.

The extreme infra-red studies of Liebisch and Rubens already referred to, revealed the existence of low frequency infra-red fundamentals at 103 cm.⁻¹, 161 cm.⁻¹ (B_{1u}); at 83 cm.⁻¹, 164 cm.⁻¹ (B_{2u}); at 77 cm.⁻¹, ~ 140 cm.⁻¹

and 196 cm.^{-1} (B_{3u}). The Raman spectra have given lines at 67 cm.^{-1} (A_{1g}), 77 cm.^{-1} (A_{1g}), 92 cm.^{-1} (B_{2g}), 131 cm.^{-1} (A_{1g} ?), 149 cm.^{-1} (B_{3g}) and 193 cm.^{-1} (B_{2g} , A_{1g} ?) according to Couture and in addition at 58.5 cm.^{-1} , 88.3 cm.^{-1} and 151.4 cm.^{-1} according to Krishnan. All these are low frequency lattice oscillations. According to group theoretical analysis, eighteen Raman active—infra-red inactive, eleven infra-red active—Raman inactive, and four inactive in both—thus in all thirty-three lattice oscillations are expected. These naturally lie beyond the range studied in this investigation, but combinations between internal and lattice vibrations may appear when allowed to do so by selection rules. An interpretation on this basis has been given in Table III in a few cases, where no other assignment is possible.

In conclusion, I wish to express my best thanks to Professor Sir C. V. Raman for the encouragement and guidance he gave me during this investigation.

5. SUMMARY

The infra-red absorption spectrum of barytes has been studied in the range 1μ to 25μ using ten different specimens, belonging to 001 and 110 sections. The extension of the range of study beyond 16μ has revealed the presence of fundamentals at 21.3μ (470 cm.^{-1}) and 22.8μ (439 cm.^{-1}) besides other absorption maxima. The review of the available data shows that of the eighteen Raman active internal oscillations of barytes, fourteen can be identified including the one at 967 cm.^{-1} not previously recognised as such. The infra-red studies give ten of the fifteen theoretically possible infra-red active internal oscillations. The numerous absorption bands observed in the range studied find satisfactory explanation in terms of the infra-red active fundamentals in conjunction with the Raman active ones, applying selection rules appropriate to the unit cell of the crystal.

REFERENCES

- | | |
|------------------------|---|
| 1. Krishnan | .. <i>Proc. Ind. Acad. Sci.</i> , 1946, 23A , 288. |
| 2. Couture | .. <i>Annales de Physique</i> , 1947, 2 , 5. |
| 3. Coblentz | .. <i>Investigations of Infra-red Spectra</i> , Carnegie Institution of Washington, 1906, 53, 78. |
| Schæfer and Schubert | .. <i>Ann. der. Phys.</i> , 1916, 50 , 283. |
| Matossi and Kindler | .. <i>Zeit. für. Phys.</i> , 1934, 92 , 303. |
| 6. Liebisch and Rubens | .. <i>Sitz. Preuss. Akad. Wiss.</i> , 1919, 12 , 198. |
| 7. Couture and Mathieu | .. <i>J. Phy. Rad.</i> , 1949, 10 , 145. |