RAMAN SPECTRUM OF ANHYDRITE

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1. Introduction

The Raman spectrum of anhydrite ($CaSO_4$) was first investigated by Rasetti (1932) using the λ 2536·5 mercury resonance radiation as exciter. He recorded ten Raman lines including four low frequency or lattice lines. A year later, Nisi (1933) photographed the Raman spectrum of anhydrite using the λ 4358 excitation and identified eleven frequency shifts of which nine were due to the internal oscillations of the sulphate ion. The only other experimental work on the Raman effect in anhydrite is that of Lucienne Couture (1948). She investigated the effect of crystal orientation on the intensities of eight of the nine Raman lines due to the sulphate ion. She did not study the lattice spectrum. Thus, it is clear that though the spectrum of the internal oscillations of anhydrite has been recorded in full, the lattice spectrum of anhydrite is far from being properly studied. It should contain many more Raman lines than have been recorded hitherto. This would be obvious when one examines the group theoretical analysis of the vibration spectrum of anhydrite lattice given later in the paper. A re-investigation of the Raman spectrum of anhydrite was therefore called for. This has been carried out by the authors using the well known ultra-violet excitation and the results are presented here.

2. Experimental Details and Results

The specimen of anhydrite used in the present investigation was obtained from the Geological Survey of India. The authors are indebted to Dr. W. D. West, Director of the Geological Survey of India, for the loan of the specimen. It had the following dimensions: 1[illegible] × 9 × [illegible] mm, the edges being parallel to *a*, *b* and *c* axes respectively.

An enlarged photograph of the Raman spectrum of anhydrite taken with the large E 1 quartz spectrograph using a slit width of 0·04 mm and an exposure of 6 days is reproduced in Fig. 1. The corresponding microphotometer record is reproduced in Fig. 2. The recorded spectrum exhibits seventeen Raman lines, the frequency shifts of which are tabulated below along with those reported by the earlier investigators. Four new Raman lines have been recorded in the low frequency shift region.

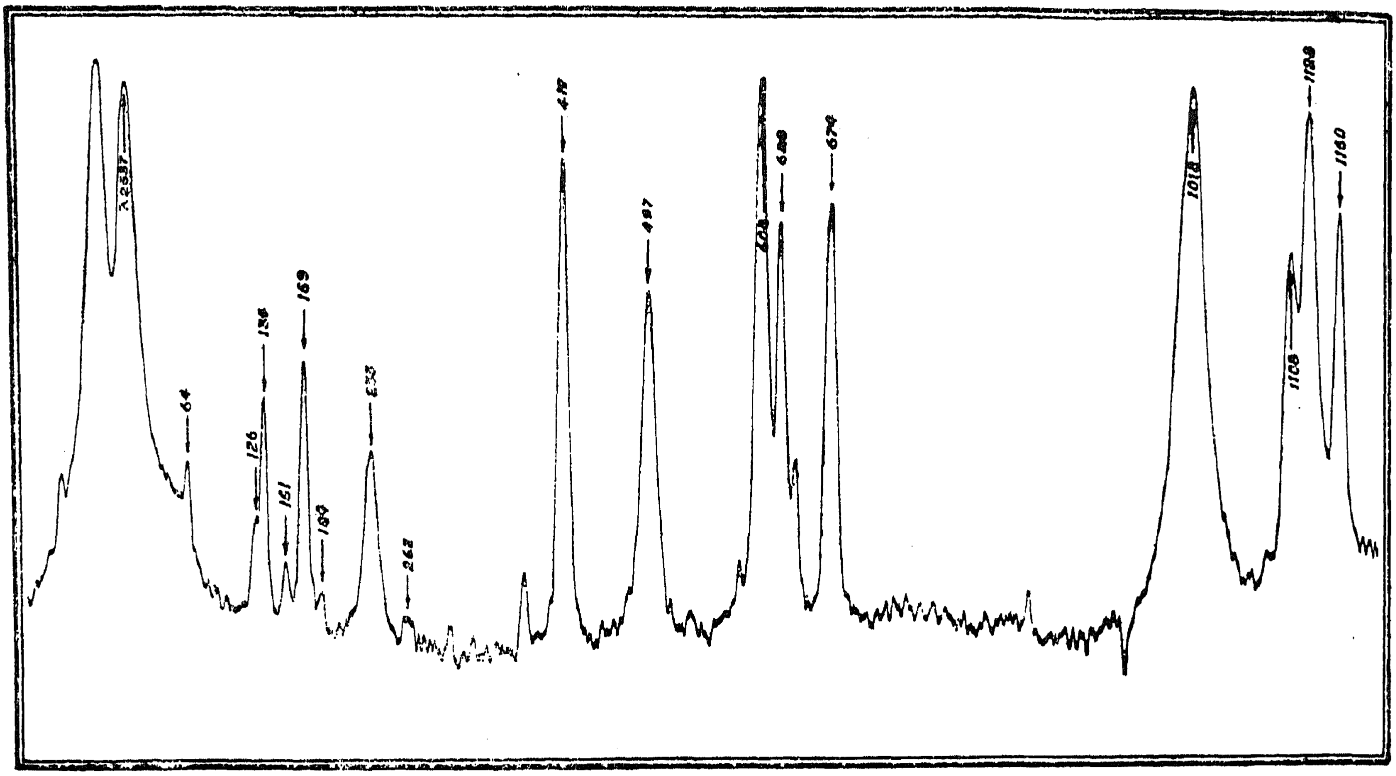

FIG. 2. Microphotometer record of the Raman spectrum of anhydrite taken with E_1 quartz spectrograph.

TABLE I

Sl. No.	Authors	Couture	Rasetti	Nisi
1	62 (4)			
2	126 (3)		122	
3	135 (6)		133	
4	151 (2)			
5	169 (8)		169	166
6	184 (1)			
7	233 (6)		233	227
8	262 (1)			
9	415·5 (8)	416		416
10	497 (10)	495	499	499
11	608 (8)	604		609
12	628 (8)	626		628
13	674 (2)	672	676	673
14	1018 (20)	1015	1019	1016
15	1108 (6)	1107	1113	1104
16	1128 (16)	1125	1129	1128
17	1160 (10)	1157	1160	1159

The relative intensities of the lines (figures given in brackets) are for the case when the light was incident normal to the *c* face and the scattered light was taken perpendicular to the *a* face. The intense Raman lines with frequency shifts 417, 608 and 1018 cm.$^{-1}$ fall very close to the three mercury lines λ 2563·9, λ 2576·3 and λ 2603·2 respectively. But their existence has been verified independently by their appearance on the anti-Stokes side of the spectrum (see Fig. 3).

3. Effect of Crystal Orientation

Three spectrograms corresponding to three different orientations of the anhydrite crystal with reference to the directions of incidence and observation were taken using the medium quartz spectrograph. They are reproduced in Fig. 3. I and S represent directions of incidence and scattering respectively. For example, the spectrum marked *ba* was taken with the incident beam parallel to *b* axis. The depth of illumination for orientation *cb* was only two-thirds of that for the other two orientations. The frequency shifts of those Raman lines which exhibit marked variations in intensity with orientation are indicated in the figure. The lines with frequency shifts 233, 417, 674, 1018 and 1128 cm.$^{-1}$ have minimum intensity for the orientation *cb*.

4. Discussion

Anhydrite belongs to the orthorhombic class with the space group V_h^{17}. A group theoretical analysis of the vibration spectrum of anhydrite was first carried out by Bhagavantam (1938) on the basis that the unit cell contained four molecules of $CaSO_4$. But according to Wasastjerna (1926) the smallest cell should contain only two molecules of $CaSO_4$. It was on this basis that Lucienne Couture (1948) made a theoretical study of the internal frequencies of the Raman spectrum of anhydrite in order to explain the observed variation in intensity of the SO_4 frequencies with orientation. The complete character table for the anhydrite structure is given in Table II. n_i, T, T′, R and n_i', represent the total number of oscillations, translations, translatory type of external oscillations, rotatory type of external oscillations and the internal oscillations respectively. The Table given here is slightly different from that given by Bhagavantam (1938) as the former is based on the fact that the unit cell contains only two molecules of $CaSO_4$. The notations A_{2g}, B_{1g}, and B_{2g} given in Table II correspond respectively to the notations B_{2g}, B_{3g} and B_{1g} adopted by Lucienne Couture.

Internal frequencies of the SO_4 ion.—The analysis shows that there are 18 internal oscillations of which nine are active in Raman effect. They arise as a consequence of the removal of degeneracies of three of the four distinct modes of oscillation appropriate to the free SO_4 ion. The nine Raman lines due to internal oscillations observed in the spectrum of anhydrite have been classified by Couture as follows: 415·5 (B_{1g}), 497 (A_{1g}), 608 (A_{2g}), 628 (B_{2g}), 674 (A_{1g}), 1018 (A_{1g}), 1108 (A_{2g}), 1128 (A_{1g}) and 1160 (B_{2g}). As is to be expected, the lines 497, 674, 1018 and 1128 cm.$^{-1}$

TABLE II

Anhydrite

V_h^{17}	E	C′	C_2(S)	C_2(S)	i	$\sigma_h(\sigma)$	σ_v	σ_v'	n_i	T	T′	R′	n_i'	Raman	Infra-red
A_{1g} ..	1	1	1	1	1	1	1	1	6	0	2	0	4	P	F
A_{2g} ..	1	−1	1	−1	1	−1	1	−1	5	0	2	1	2	P	F
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	2	0	0	1	1	P	F
B_{2g} ..	1	−1	−1	1	1	−1	−1	1	5	0	2	1	2	P	F
A_{1u} ..	1	1	1	1	−1	−1	−1	−1	2	0	0	1	1	F	F
A_{2u} ..	1	−1	1	−1	−1	1	−1	1	5	1	1	1	2	F	P
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	6	1	1	0	4	F	P
B_{2u} ..	1	−1	−1	1	−1	1	1	−1	5	1	1	1	2	F	P
U_R(S) ..	4	4	0	0	0	0	4	4							
U_R(S-ν) ..	2	2	0	0	0	0	2	2							
$h_\rho\chi_\rho'$(T)	3	−1	−1	−1	−3	1	1	1							
$h_\rho\chi_\rho'$(T′)	9	−3	1	1	3	−1	3	3							
$h_\rho\chi_\rho'$(R′)	6	−2	0	0	0	0	−2	−2							

coming under A_1 (symmetric) class exhibit marked variations in intensity with orientation (see Fig. 3).

Lattice Oscillations.—Of the fifteen external oscillations, 6 of the translatory type and 3 of the rotatory type should be active in Raman effect. Actually, 8 lattice lines with the frequency shifts 62, 126, 135, 151, 169, 184, 233 and 262 cm.$^{-1}$ have been recorded. The ninth oscillation may have been too weak to be recorded with the small specimen of anhydrite used in the present investigation. Of the six Raman-active translatory oscillations, two come under the symmetric (A_{1g}) class. They may be expected to exhibit marked variations in intensity with orientation. The two lattice lines which behave in this manner are 126 and 233. (See Fig. 3) They should therefore be identified as the translatory oscillations coming under the symmetric class. Besides these, there are three sharp lines with frequency shifts 62, 135 and 169 cm.$^{-1}$ which are fairly intense (see Fig. 1). They may be assigned as the three rotatory oscillations which are allowed in the Raman effect. Further detailed classification and identification of the modes

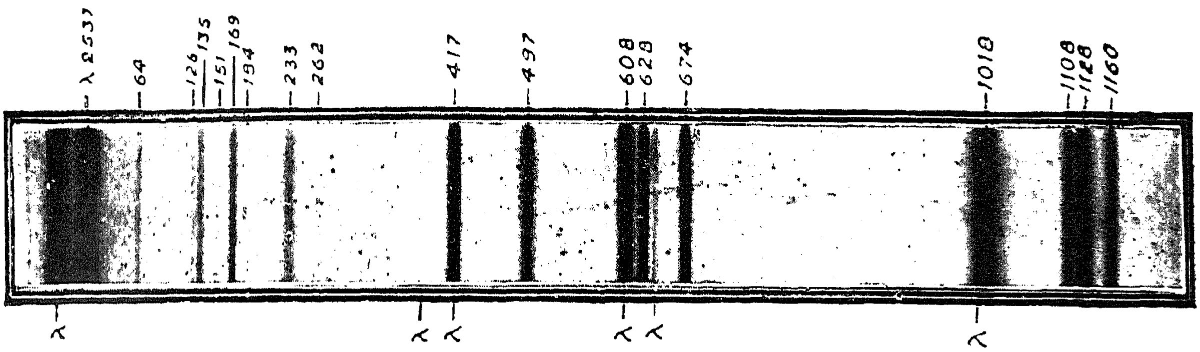

FIG. 1. Raman spectrum of anhydrite taken with E 1 quartz spectrograph

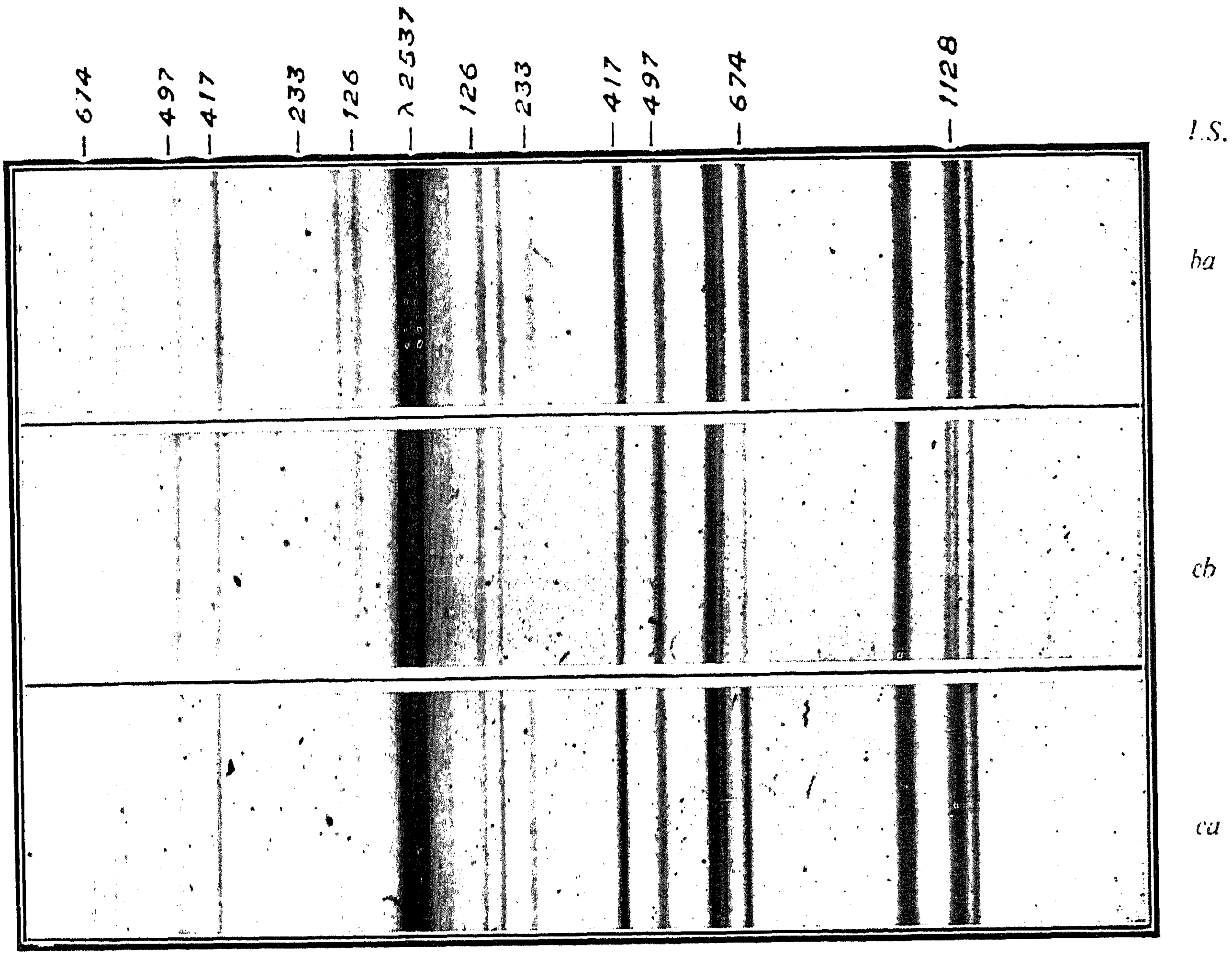

FIG. 3. Raman spectra of anhydrite in different orientations

could be made only after obtaining data concerning the polarisation characteristics of the lattice lines.

5. Summary

Using λ 2536·5 mercury resonance radiation as exciter, the Raman spectrum of a single crystal of anhydrite has been investigated for three different orientations. Besides the nine Raman lines due to the sulphate ion, the recorded spectrum exhibits eight of the nine lattice lines to be expected theoretically. Their frequency shifts are 62, 126, 135, 151, 169, 184, 233 and 262 $cm.^{-1}$ From the observed variations in intensity with orientation, tentative assignments have been given to the lattice lines.

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