

RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part V. Aragonite

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1. INTRODUCTION

IN the first four parts of this series, the author (Krishnan, 1945, 1946) reported the results obtained from a systematic investigation of the Raman spectra of calcite, gypsum, quartz and barite using the λ 2536.5 mercury resonance radiation as exciter. This paper deals with the results obtained with aragonite using the same technique. A brief review of the previous work on the Raman effect in aragonite is also given.

The Raman spectrum of aragonite was investigated by Schæfer, Matossi and Aderhold (1931), Bhagavantam (1931), Nisi (1932), Rasetti (1932) and more recently by Couture (1944, 1947). Among the earlier investigators, Rasetti who employed the ultra-violet excitation recorded ten Raman lines, Couture (1944), on the other hand, using the 4046 and 4358 radiations as exciter, succeeded in identifying seventeen Raman lines including twelve lattice or low frequency lines in the spectrum of aragonite. She studied also the effect of crystal orientation on the intensity and polarisation of the Raman lines. A more detailed reference will be made to her work later in the paper.

2: EXPERIMENTAL DETAILS AND RESULTS

The specimen of aragonite employed in the present investigation was obtained from Sir C. V. Raman's personal collection of minerals. The author is grateful to Sir C. V. Raman for the loan of the specimen. It was a colourless crystal in the form of a rod of dimensions $2.0 \times 0.5 \times 0.5$ cm., the length being parallel to the c -axis. The crystal was mounted horizontally with its b -plane facing the most intense portion of a water-cooled magnet-controlled quartz arc. The light scattered along the c -axis, *i.e.*, along the axis of the rod was focussed on the slit of a Hilger E 1 quartz spectrograph. As usual, a filter of mercury vapour at room temperature was kept in the path of the scattered light. Using a slit width of 0.04 mm., exposures of the order of two days were given to get an intense spectrogram. The frequency shifts

of the lines were estimated by comparison with the superposed iron arc spectrum. The temperature of the crystal was 45° C.

Fig. 1 (a) in Plate XXII, represents the Raman spectrum of aragonite taken with λ 2536.5 excitation, while Fig. 1 (b) in the same plate represents a lightly exposed spectrum of calcite. The position and frequency shifts of the Raman lines other than those appearing in the lattice spectrum are marked in this figure. An enlarged photograph of the lattice spectrum showing the Stokes and anti-Stokes lines is reproduced in Fig. 2. The microphotometer record of the Raman spectrum of aragonite is shown in Fig. 3. Table I gives the frequency shifts of the Raman lines of aragonite.

TABLE I
Raman Spectrum of Aragonite

	Author	Couture	Rasetti
1	105 (2)		
2	113.8 (7)	113	112.8
3	142.7 (9)	146	
4	153.3 (50)	154	154.5
5	159.0 (4)		
6	179.9 (14)	183	180.1
7	191.0 (10)	193	
8	207.1 (25)	208	207.1
9	216.3 (8)	216	
10	222 (1)	222	
11	249.1 (7)	250	246.9
12	258.8 (4)	263	261.1
13	273.0 (5)	276	
14	286.9 (3)	287	
15	702 (15)	702.9	
16	705.3 (16)	707	
17	716.4 (2)		
18	853.8 (3)		852.4
19	1058.5 (3)		
20	1086.0 (100)	1087.1	1084.9
21	1413.2 (3)		
22	1462 (12)	1464.2	1460.2
23		1466.1	
24	1574		
25	1816		
26	2163		

The second column shows the results of the present author, the relative intensities (figures given in brackets) being for the case in which the incident unpolarised beam is perpendicular to the *b*-plane and the scattered light is parallel to the *c*-axis. The third and fourth columns give the results of Couture (1944) and Rasetti (1932) respectively.

Besides confirming the appearance of 16 Raman lines reported by Couture, the author has identified nine additional lines. The photographs

reproduced here exhibit the Raman lines much more clearly than the one reproduced by Couture (1947). The doublet nature of the lines at about 705 cm.^{-1} and 1465 cm.^{-1} was established by Couture from a careful study of the polarisation photographs. In the spectrogram taken by the author and reproduced in Fig. 1 (a), the first doublet is seen clearly separated. See also the microphotometer record (Fig. 3). The companion with the smaller

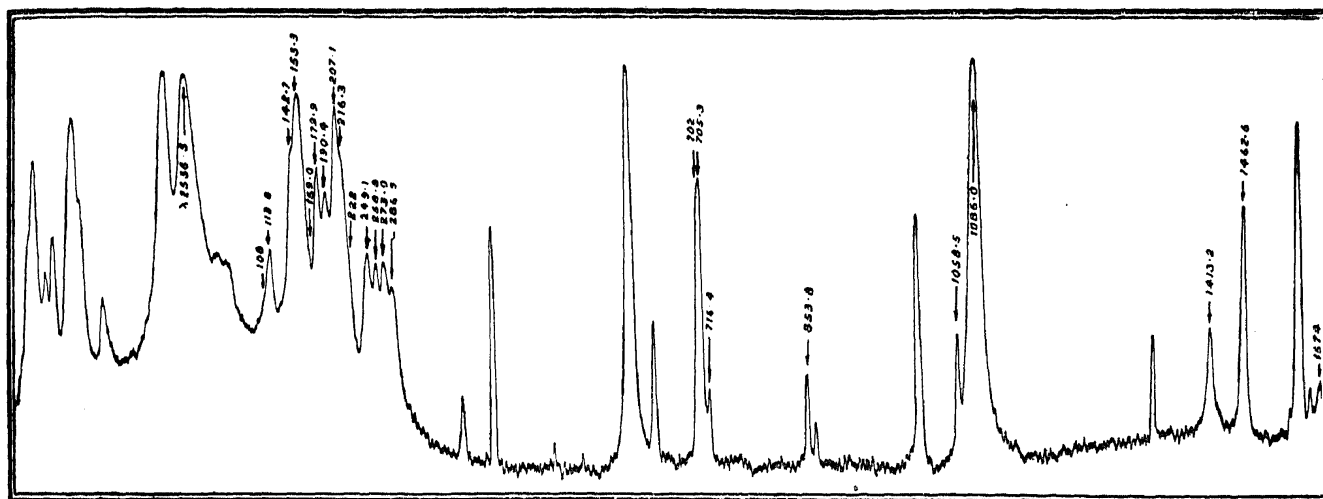


FIG. 3. Microphotometer record of the Raman spectrum of aragonite taken with E 1 quartz spectrograph

frequency shift (702 cm.^{-1}) is less intense than the other one. The second doublet reported by Couture is seen only as a single line. Even in a lightly exposed spectrogram taken with a finer slit, the line 1462.6 cm.^{-1} appeared as a single line. The appearance of a line at 852.4 cm.^{-1} observed by Rasetti has been confirmed. The most striking feature of the spectrum of aragonite is the appearance of a large number of closely spaced but sharply defined lattice lines lying in the region of frequency shifts $100\text{--}300\text{ cm.}^{-1}$. See Fig. 2 in Plate XXII. In the same region the spectrum of calcite exhibits only two lattice lines. The line at 2163 cm.^{-1} is very faint and can be seen only with some difficulty in the reproduced photograph [Fig. 1 (a)].

3. DISCUSSION

Aragonite crystallises in the orthorhombic system, the space group is V_h^{16} . The unit cell contains four molecules of CaCO_3 . The lattice is ionic and is composed of 4 CO_3 ions and 4 metal ions. The group theoretical analysis of the vibration spectrum of the aragonite structure was carried out independently by Bhagavantam and Venkatarayudu (1939, 1948) and by Couture (1944). Their results indicate that the 57 fundamental vibrations of the atoms in the unit cell are distributed into 8 types: 4 types active in Raman effect only (A_{1g} , B_{1g} , $B_{2g} + B_{3u}$), 3 types active in infra-red only (B_{1u} , $B_{2u} + B_{3u}$) and 1 type inactive in both (A_{1u}).

Internal Oscillations.—The CO_3 ion in the free state has four distinct modes of oscillation ν_1 , ν_2 , ν_3 , and ν_4 of which the last two are doubly degenerate. Due to the lower symmetry of the aragonite crystal, the degenerate modes ν_3 and ν_4 split into four non-degenerate ones ν_3' , ν_3'' , ν_4' and ν_4'' thus giving a total of six for each CO_3 group. When the crystal is taken as a whole, each of the six modes gives rise to four distinct ones, two of each set being active in Raman effect, *i.e.*, according to the theory, one should expect to observe 12 internal frequencies in the Raman spectrum of aragonite. As the recorded spectrum exhibits only six Raman shifts due to the CO_3 ions, it can be concluded that the splitting due to the multiplicity of groups in the basis of the crystal is not of much consequence in aragonite. Table II gives the assignments of the internal frequencies observed in the spectra of aragonite and calcite.

TABLE II
Raman Frequencies of the CO_3 Ion in Wavenumbers

Mode	Aragonite		Calcite
	Author	Couture	Author
ν_1 ..	1086.0	1087.1	1085.6
ν_2 ..	853.8		inactive
ν_3' ..	1462.6	1464.2	1433.8
ν_3'' ..		1466.1	
ν_4' ..	702	702.9	711.8
ν_4'' ..	705.3	707	

The mode ν_2 which is inactive in Raman effect in the case of calcite appears as a line at 853.8 cm^{-1} with feeble intensity in the aragonite spectrum. The corresponding mode appearing in the infra-red absorption spectrum of aragonite has a frequency of 866 cm^{-1} .

Lattice Oscillations.—According to the group theoretical analysis of Bhagavantam (1941) and Couture (1947), of the 33 external oscillations, 12 oscillations of the translatory type and 6 rotations of the CO_3 group are active in the Raman effect. Of the latter, two should appear with very great intensity, while three do not give any scattering moment and therefore unobservable. One should therefore expect to observe fifteen Raman shifts in the scattered spectrum. The recorded spectrum exhibits 14 lattice

lines of which the two most intense lines 153.3 and 207.1 cm.^{-1} correspond to the rotations or tilting oscillations of the CO_3 groups about the Y-axis and X-axis respectively. In the case of calcite, these two rotatory oscillations have the same frequency and appear as a single Raman line in the lattice spectrum with a frequency shift of 155.5 cm.^{-1} . The second lattice line (283.9 cm.^{-1}) observed in the case of calcite is due to the translatory type of oscillation.

Second Order Spectrum.—Beside the 6 Raman lines due to the internal oscillations of the CO_3 ion, the recorded spectrum of aragonite exhibits 6 additional feeble lines in the region of high frequency shifts. They are listed in Table III. All of them are fairly sharp and belong to the second order Raman spectrum of aragonite. These have been recorded for the first time. Proper assignments have been given to lines appearing in the second order spectrum. The frequency of ν_2 is taken as 866 cm.^{-1} , *i.e.*, the value obtained from the infra-red data. The calculated frequency shifts given in the last column agree reasonably well with the observed values. The octave of ν_2 even if present will not be detected in the spectrum taken with $\lambda 2536.5$ excitation, as it would have fallen on the triplet $\sim \lambda 2652$.

TABLE III
Second Order Raman Spectrum

Frequency shift	Assignment	Frequency shift calculated
716.4	$\nu_2 - L$ (153)	713
1058.5	$\nu_2 + L$ (191)	1059
1413.2	$2 \nu_4''$	1410.6
1574	$\nu_2 + \nu_4''$	1571.8
1816	$\nu_1 + \nu_4''$	1791.3
2163	$2\nu_1; \nu_3 + \nu_4$	2172 2167.9

L = lattice frequency

The line at 716.4 cm.^{-1} can be explained only as a differential ($\nu_2 - L$). The corresponding summational has in all probability fallen on the mercury line $\lambda 2603.2$.

SUMMARY

The Raman spectrum of aragonite crystal has been photographed using $\lambda 2536.5$ excitation. 25 Frequency shifts have been recorded as compared to 17 observed previously. They are distributed as follows: five due

to the internal oscillation of the CO_3 ion, fourteen due to lattice oscillation and six belonging to the second order spectrum. The latter have been assigned as some of the octaves and combinations of the fundamental frequencies of vibration of the aragonite structure.

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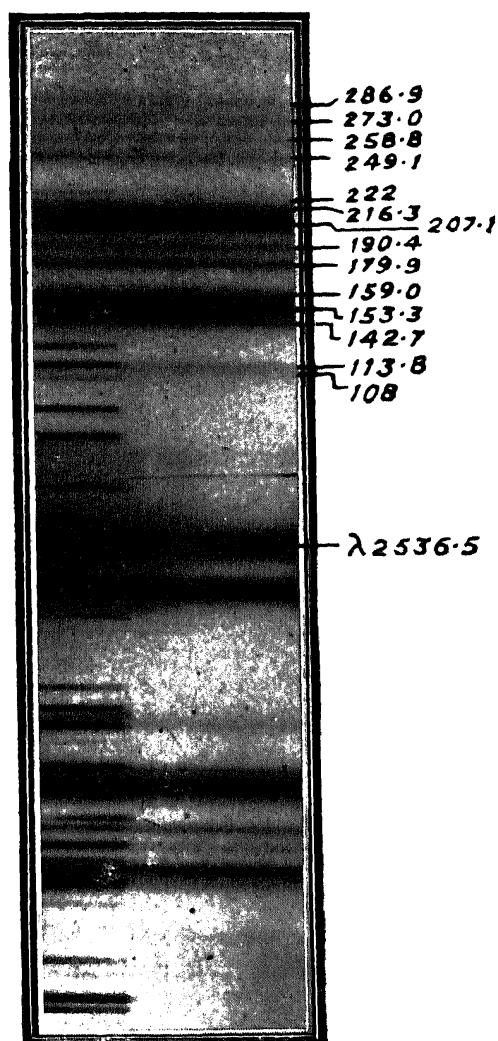
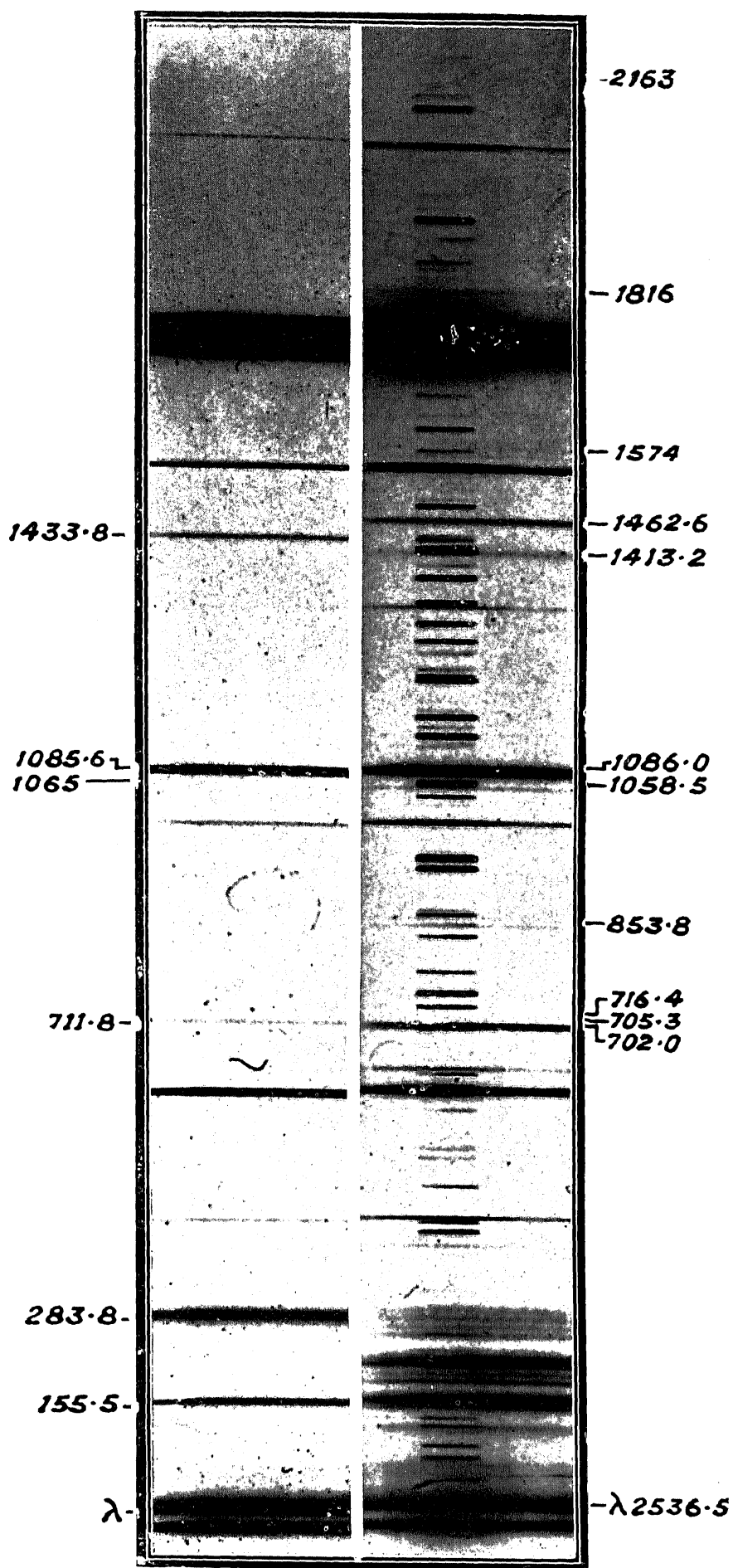


FIG. 1. (a) Raman spectrum of aragonite taken with the Elquartz spectrograph (b) Raman spectrum of calcite

FIG. 2. Lattice spectrum of aragonite