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INFRARED AND RAMAN SPECTRA OF WITHERITE ($BaCO_3$) AND STRONTIANITE ($SrCO_3$)

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Abstract

The infrared and Raman spectra of witherite ($BaCO_3$) have been experimentally investigated and discussed in relation to the other orthorhombic carbonates. Using the large quartz spectrograph and λ 2537, 16 Raman lines have been recorded and a splitting of the degenerate modes ν_3 and ν_4 is found. But it is the infrared absorption maxima, analysed taking into account the selection rules that provide any proof for the coupling of the vibrations of the 4 CO_3 ions in the unit cell. The infrared absorption spectrum of strontianite ($SrCO_3$) has also been examined in the light of the theories of vibration spectra of these carbonates.

1. Introduction

Among the orthorhombic carbonates of the series XCO_3 ($X = Ca, Sr, Ba, Pb$) only those of Ca and Pb have come in for exhaustive study, notably by Couture (1944, 1947), Bhagavantam and Venkatarayudu (1939), Bhagavantam (1941), R. S. Krishnan (1950). Of the remaining two carbonates, the Raman spectrum of strontianite was investigated by T. S. Krishnan (1956) using the resonance radiation of mercury as exciter. Although the Raman spectrum of witherite has been recorded by Roop Kishore (1942), from an examination of his results, it was obvious that the spectrum obtained by him was by no means complete and this expectation was fully justified as will be seen from the results presented here. On the other hand, the infrared spectra of strontianite and witherite have been examined in the powder form by Duval, M. C. Duval and J. Lecomte (1943), J. M. Hunt, M. P. Wisherd and L. C. Bonham (1950), Miller and Wilkins (1952) and

Jeannie Louisfert (1951) and in the form of single crystals only by Schaeffer, Bormuth and Matossi (1926) (see also Schaeffer and Matossi, 1930). However, it is only Louisfert (1951) who has considered in any detail the theoretical predictions based on the known symmetry and structure of these carbonates in relation to infrared absorption and that too only for the fundamentals of three of the internal vibrations. In view of these and also because of the fact that in these carbonates the infrared and Raman spectra are complementary, it was considered desirable to study the infrared absorption also over the range 2–15 μ.

2. EXPERIMENTAL DETAILS

Witherite ($BaCO_3$) which occurs as a mineral was available for study only in the form of lumps and was of Kahlbaum supply. By scrutiny a small piece which was a little milky white but semi-transparent, was selected and cut and polished in the form of a rectangular parallelepiped with its edges roughly parallel to the axes of the refractive index ellipsoid. However, the X-ray diffraction photograph, which was taken to identify the Z-axis, revealed a number of multiple spots and the slight polycrystalline nature of the specimen. As such no polarisation studies could be made. For recording the Raman spectrum use was made of λ 2537 excitation described in earlier papers. The infrared spectra were obtained with a Perkin Elmer Model 112 double-pass infrared spectrometer equipped with NaCl prism. Witherite was studied in the form of three specimens of different thicknesses and also in the power form mulled in paraffin oil. Strontianite, however, was studied only as a mull in paraffin oil.

3. RESULTS

The recorded Raman spectrum of witherite reveals the existence of at least 16 frequency shifts (see Fig. 1 on Plate I). To study the lattice spectrum in greater detail, the spectrum was also examined with the large quartz spectrograph (El) (see Fig. 2). The microphotometer record of the lattice spectrum has also been included in the same figure. The measured frequency shifts of the Raman lines are 75 (4), 79 (7), 90 (6), 100 (2), 136 (16), 154 (12), 161 (4), 176 (4), 218 (5), 226 (8), 694 (4), 700 (1), 1063 (20), 1410 (1), 1422 (4) and 1520 (0). In one orientation of the crystal, there was an indication of one additional line at 1400 cm.$^{-1}$ The figures within brackets indicate roughly the relative intensity of the lines. The lines 85, 135, 164, 221, 699 and 1416 cm.$^{-1}$ reported by Roop Kishore (1942) coincide roughly with the mean of the values given by the authors, because the doublet nature of each one of these lines has been brought out only in the present study. The Raman lines 54 (3) and 186 (3) reported by Roop Kishore are most probably spurious. Figures 1 and 2 represent the infrared spectrum of witherite for two different thicknesses while Fig. 3 represents the infrared absorption spectrum of strontianite powder mulled in oil. In the latter case a cell of suitable thickness containing paraffin alone was employed to compensate almost fully the influence of paraffin absorption. The absorption maxima given in

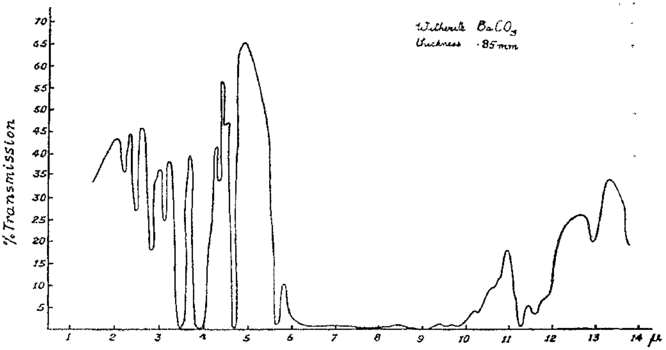
Witherite BaCO3
thickness ·85 mm
% Transmission
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1
2
3
4
5
6
7
8
9
10
11
12
13
14 μ

FIG. 1

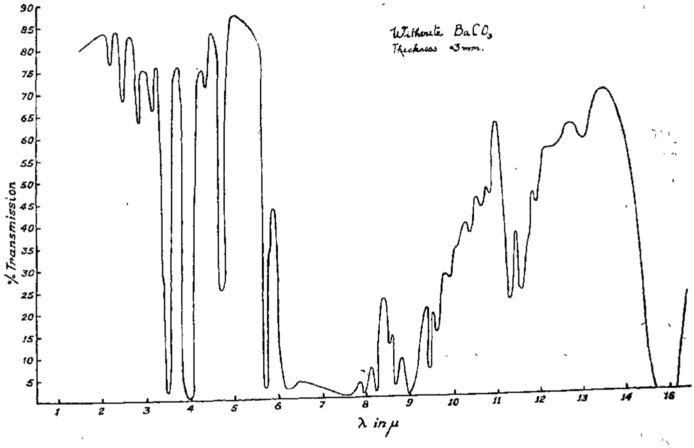
Witherite BaCO3
Thickness ·3 mm.
% Transmission
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
λ in μ

FIG. 2

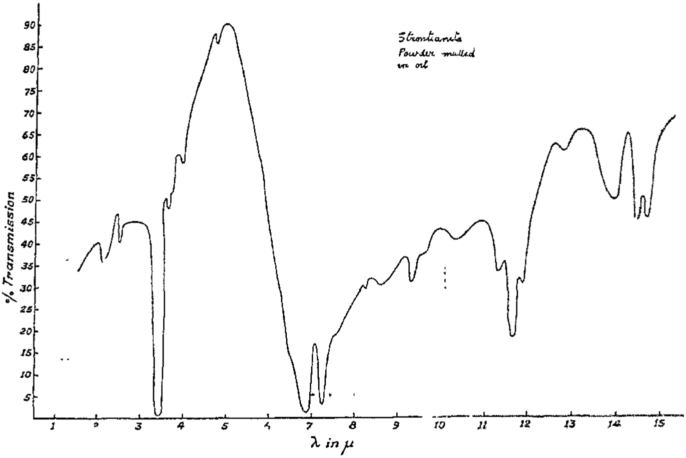

FIG. 3

Tables III and IV were arrived at by a comparative study of the spectra for different thicknesses and therefore only one set of values has been given in each case.

4. DISCUSSION

Witherite and strontianite belong to the orthorhombic system and have the same structure as aragonite (Huggins, 1922; Wilson, 1928). However, all the parameters are available accurately only for aragonite and cerussite and not in any great detail for witherite and strontianite. The theory of the vibration spectra of these carbonates has been examined and worked out in detail by Bhagavantam and Venkatarayudu (1939), Bhagavantam (1941) and Couture (1944, 1947) and only the conclusions relevant to the present investigation will be given here.

External Vibrations.—These carbonates have the space group symmetry of V_h^{16} and the unit cell contains 4 X (Ca, Sr, Ba, Pb) ions and 4 CO_3 ions. In the crystal, the CO_3 ion no longer possesses its full symmetry D_{3h}; the 4 CO_3 ions occupy positions in the unit cell such that they retain only a true plane of symmetry σ_z with one O and the C atom of each group in that plane. The other two O atoms of each ion are symmetric with respect to this plane. The metal ions are also in this plane of symmetry. The 57 fundamental vibrations of the unit cell fall under 8 symmetry types, 4 of which are active in Raman effect, 3 in infrared absorption and one inactive in both. Of the Raman active vibrations, 12 are due to translatory type of lattice oscillations and 6 arise from rotatory type of oscillations or 'librations' of the CO_3 ions, about their principal axes of inertia which in this case coincide with the crystallographic axes. It has been shown, however, that in three of these librations the phases of oscillations of the 4 CO_3 groups in the unit cell are such that on the whole the resulting variation in polarisability is zero. Of the remaining three, the one which is due to libration of the CO_3 groups in phase about the Z-axis, which is normal to the plane of the CO_3 ions, obviously should be of very small intensity on account of the symmetry of the ion. On the other hand, the librations around the X- and Y-axes lead to large changes of polarisability. In fact they give rise to very intense lines in aragonite, strontianite and witherite. In the case of witherite the lines 136 cm.$^{-1}$ and 154 cm.$^{-1}$ may be identified with the modes B_{2g} and B_{3g} which correspond to librations around the Y- and the X-axes. It is probable that the weak line 161 cm.$^{-1}$ arises from the rotatory oscillation about the Z-axis. It is interesting to note that as we go from Ca to Sr and then to Ba the frequency separation between these two librations (X and Y) becomes smaller and smaller and in the case of witherite the ratio of I_x/I_y is nearer to ν_y^2/ν_x^2 (·75 and ·78 respectively) than in the case of aragonite and strontianite. As has been pointed out by Couture (*loc. cit.*) it is surprising to find a difference in frequency between these two modes contrary to what one would expect from the quasi-three-fold symmetry of arrangement of the metal ions around any CO_3 group. In the case of aragonite, Couture has sought to explain the observed facts by considering the slight differences in the Ca-O distances around a CO_3 group. Although data on the interatomic distances are not available to the same accuracy in strontianite and witherite, one can easily see that in the sequence of carbonates studied as we proceed to higher mol. wt. the forces around a CO_3 group become more symmetric.

Though theoretically one should expect as many as 12 Raman lines due to translatory type of lattice oscillations, one actually finds only seven lines in the low frequency region. This is essentially because these lines result only from variations in the induced polarisability in each ion due to the displacement of the neighbouring ions. As in the other three orthorhombic carbonates, in witherite also one finds a crowding of the lattice lines in the high frequency region of the lattice spectrum, *viz.*, 190–230 cm.$^{-1}$ Moreover the lattice lines in this region which are clearest in aragonite become increasingly diffuse as the polarisability of the metal ion increases. A comparison of the frequencies of the same modes in aragonite and witherite (after making allowance for the mass of vibrating unit) shows that the forces of restitution brought into play are nearly the same in both these, unlike the large difference found between aragonite and cerussite (Couture, *loc. cit.*, p. 55). An assignment of the observed Raman lines to the different symmetry types is not made for want of polarisation data.

Internal Vibrations.—The CO_3 ion in the free state has four distinct modes of oscillation ν_1 ($\sim$ 1080 cm.$^{-1}$), ν_2 ($\sim$ 850 cm.$^{-1}$), ν_3 ($\sim$ 700 cm.$^{-1}$) and ν_4 ($\sim$ 1450 cm.$^{-1}$), the last two being doubly degenerate. Since in the crystal the proper symmetry of the CO_3 ion is no more than C_s one should expect the degeneracies to be removed and hope to find six normal modes for each CO_3 ion.

Further, each of these vibrations by the coupling of the vibrations of four such ions in the unit cell lead to four distinct ones, two of each set being Raman active (ν's), while the other two are infrared active (ω's) (see Table I). The intensities of these vibrations have been worked out by Couture to the zero order as well as first order approximation.

The loss of the three-fold axis of symmetry by the CO_3 ion is therefore to be revealed by a splitting of ν_3 and ν_4. However, experimentally one finds in aragonite ν_3 splitting into two components with a separation of 4 cm.$^{-1}$ while no observable splitting of ν_3 takes place in strontianite and cerussite. In witherite the two Raman lines have a frequency separation 6 cm.$^{-1}$ The additional Raman lines expected on the basis of theoretical considerations due to the coupling of the internal vibrations of the CO_3 ions are not observed experimentally in the case of ν_1, ν_2 and ν_3 and it is only in regard to ν_4 and that too only in strontianite and cerussite (Raman lines 1377 cm.$^{-1}$ and 1438 cm.$^{-1}$ respectively) there is any evidence from existing Raman spectral data of the carbonates for any appreciable coupling of the vibrations. But infrared spectra, dealt with below, appear to be much more sensitive from this point of view.

Table I

Free CO_2 ion symmetry D_{3h}	Local symmetry C_s	Unit cell symmetry			
ν_1 (A_1')	ν_1 (A')	ν_1^1 (A_{1g})	ν_1^2 (B_{3g})	ω_1^1 (B_{1u})	ω_1^2 (B_{2u})
ν_2 (A_2'')	ν_2 (A')	ν_2^1 (A_{1g})	ν_2^2 (B_{3g})	ω_2^1 (B_{1u})	ω_2^2 (B_{2u})
ν_3 (E')	ν_3^1 (A')	ν_3^2 (A_{1g})	ν_3^3 (B_{3g})	ω_3^1 (B_{1u})	ω_3^2 (B_{2u})
	ν_3^2 (A'')	ν_3^2 (B_{1g})	ν_3^4 (B_{2g})	ω_3^3 (A_{1u})	ω_3^4 (B_{3u})
ν_4 (E')	ν_4^1 (A')	ν_4^1 (A_{1g})	ν_4^3 (B_{3g})	ω_4^1 (B_{1u})	ω_4^2 (B_{2u})
	ν_4^2 (A'')	ν_4^2 (B_{1g})	ν_4^4 (B_{2g})	ω_4^3 (A_{1u})	ω_4^4 (B_{3u})

Infrared Absorption.—Though the infrared spectra of all these carbonates in the powder form were examined in detail with a Perkin Elmer Model 12 C infrared spectrometer by J. Louisfert (*loc. cit.*), she restricted herself to a study of the region 600–1100 cm.$^{-1}$ The absorption maxima reported by her are included in Table II. The absorption maxima reported by Schaeffer, Bormuth and Matossi agree well with some of those of the present study and may be found in Table III.

The infrared maxima due to the external oscillations, which fall in the long wavelength infrared are at 215 cm.$^{-1}$ ($\perp$ band) and 182 cm.$^{-1}$ ($\parallel$ band) for witherite and at 238 cm.$^{-1}$ ($\perp$ band) and 212 cm.$^{-1}$ ($||$ band) for strontianite (Schaeffer and Matossi). These intense maxima are due to the anti-translatory vibrations of the lattice in which all the CO_3 ions of the unit cell vibrate in a phase opposite to that of all the Ba or Sr ions. The high frequency Raman active lattice vibrations which correspond to modes similar to the above are naturally of frequencies very close to the infrared maxima. The small frequency difference (20 cm.$^{-1}$) between the $||$ and $\perp$ bands in aragonite has been taken by Couture to indicate the ionic character of the forces and the almost isotropic nature of these cohesive forces. On the basis of this the increasing frequency separation between the $||$ and $\perp$ bands as we proceed from aragonite to strontianite and witherite would seem to indicate clearly that the forces are no longer fully ionic when the polarisability of the metal ion is large.

TABLE II

Infrared Maxima

J. Louisfert				Authors	
$CaCO_3$	$SrCO_3$	$BaCO_3$	$PbCO_3$	$SrCO_3$	$BaCO_3$
697 *v.s.*	696 *s.*	673 *w.*	672 *m.*	681 *s.*	
707 *v.s.*	705 *s.* 721 *m.*	689 *v.s.* 720 *w.*	689 *m.* 720 *w.*	691 *s.* 715 *s.*	672 *v.s.*
850 *v.s.*	860 *v.s.*	858 *v.s.*	838 *v.s.*	842 *s.*	843 *w.*
840 *s.*	844 *m.*	840 *s.*	821 *w.*	857 *v.s.* 880 *s.*	864 *v.s.* 886 *s.*
1078 *v.s.*	1072 *v.s.*	1060 *v.s.*	1050 *v.s.*	1042 *s.* 1072 *s.*	1043 *s.* 1065 *v.s.* 1013 *w.*

w. = weak; *m.* = medium; *s.* = strong; *v.s.* = very strong.

In the region of the fundamental infrared absorption due to the internal vibrations of the free CO_3 ion of symmetry D_{3h} it is known that ν_1 is inactive while ν_2 gives rise to an absorption parallel to its three-fold axis ($m_{||}$). The doubly degenerate oscillations ν_3 and ν_4 are active in absorption with moment perpendicular to this axis ($m_{\perp}$). On the other hand in the orthorhombic carbonates under study, the diminution in the symmetry results in the activation of ν_1 with a moment in the plane ZOY and also in ν_2 having similarly a moment in this plane. The degeneracy of ν_3 and ν_4 is removed, one of the resulting moments being in the plane

ZOY and the other along OX. Thus the theoretically expected first order infrared activity of the internal modes may be summarised as follows:—

Free ion

$$\nu_1 \rightarrow \omega_1{}^1\,(\mathrm{B}_{1u}) : m_z{}' \quad \omega_1{}^2\,(\mathrm{B}_{2u}) : m_y{}'$$

$$\nu_2 \rightarrow \omega_2{}^1\,(\mathrm{B}_{1u}) : m_z \quad \omega_2{}^2\,(\mathrm{B}_{2u}) : m_y{}''$$

$$\nu_3 \rightarrow \begin{cases} \omega_3{}^1\,(\mathrm{B}_{1u}) : m_z{}'' \quad \omega_3{}^2\,(\mathrm{B}_{2u}) : m_y \\ \omega_3{}^4\,(\mathrm{B}_{3u}) : m_x \end{cases}$$

$$\nu_4 \rightarrow \begin{cases} \omega_4{}^1\,(\mathrm{B}_{1u}) : m_z{}'' \quad \omega_4{}^2\,(\mathrm{B}_{2u}) : m_y \\ \omega_4{}^4\,(\mathrm{B}_{3u}) : m_x \end{cases}$$

The dashed moments are small compared to the undashed quantities and the subscript of *m* indicates the direction of the moment.

It is to be pointed out that the observed splitting of the mode ν_3 ($\sim$ 700 cm.$^{-1}$) is in agreement with the theoretical predictions. In the case of ν_2 while one should find an additional absorption maximum on the lower frequency side of 850 cm.$^{-1}$ due to the lowering of the symmetry and the observations fully bear this out, it should be mentioned that J. C. Decius (1954) has been able to explain the subsidiary maxima and the contour of the absorption band in the neighbourhood of 850 cm.$^{-1}$ in Ca, Sr and Ba carbonates on the basis of intermolecular coupling of the out of plane bending mode and the isotopic influence of C^{13}. More recently C. Haas and D. F. Hornig (1957) calculating $\partial\mu/\partial Q$ (change of moment μ in the normal co-ordinate Q) for calcite from infrared reflection measurement found a value close to that obtained by Decius on the basis of the coupling of the internal vibrations of the CO_3 ions in aragonite and this has been taken to indicate the essentially correct nature of the Decius model. However it is the activity of ν_1 in absorption that is of great significance because it indicates unambiguously not only the loss of the three-fold axis of symmetry of the CO_3 ion but also the plane of symmetry perpendicular to it in all these orthorhombic carbonates. The region of ν_4 ($\sim$ 1450 cm.$^{-1}$) is one of intense and wide absorption and as such for investigating the effect of the crystalline field on this in great detail, one should use films much thinner than those employed here (·1 mm.–1 mm.). The reason for the intense absorption in this region will be clear when we consider the infrared activity of the combinations and overtones.

The infrared absorption maxima in the region 4000–1400 cm.$^{-1}$ have previously been explained by Schaeffer and Matossi as combinations and overtones of the internal frequencies and lattice vibrations without considering the crystal symmetry and selection rules. In fact, exact numerical coincidence of the frequencies of the maxima with the sums or differences of the fundamentals is not to be regarded as a justification for an assignment because the effect of crystalline field is to lower the first vibrational level alone predominantly (C. Haas and J. A. A. Ketelaar, 1956). Further, Rawlins and Taylor (1929) have also questioned the validity of the explanation in terms of the inactive frequencies of the free CO_3

ion and have regarded anharmonicity alone as sufficient to explain the observed maxima. In view of these, it is of special interest to examine the activity of the

TABLE III

Infrared Spectrum of Witherite ($BaCO_{43}$)

'A' Absorption maxima	'B' Absorption maxima		Intensity	Assignment
μ	μ	cm.$^{-1}$		
2·54	2·21	4529	w.}	$2\nu_4 + \omega_1{}^1$
2·595	2·48	4021	w.}	$2\nu_4 + \omega_1{}^2$
2·84	2·8	3567	w.	$2\nu_4 + \omega_3$
2·855				
3·16	3·13	3196	w.	$2\nu_1 + \omega_1$; $\omega_1 + \nu_3 + \nu_4$
3·17				
3·455	3·5	2854	v.s.	$\nu_4 + \omega_4$
3·525	3·97	2518	v.s.	$\nu_1 + \omega_4$
3·92				
3·99	4·33	2311	w.	$\nu_2 + \omega_4$
4·33				
4·75	4·70	2129	s.	$\nu_4 + \omega_2$
5·12	5·70	1754	v.s.	$\nu_1 + \omega_2$
5·66				
	6·27	1591	v.s.	| $\omega_4 + \nu$ (Lattice)
	↓ 7·65	1307	v.s.	↓ $\omega_4 + \nu$ (Lattice)
7·91	7·95	1258	v.s.	$\nu_1 + \omega$ (Lattice)
8·15	8·23	1215	v.s.	|
8·47	8·53	1172	s.	|
8·57				↓
	8·67	1153	v.s.	$\nu_1 + \omega$ (Lattice)
	8·69	1115	v.s.	$\omega_2 + \nu$ (Lattice)
8·95	9·39	1065	v.s.	ω_1
9·4	9·58	1043	s.	$\nu_2 + \omega$ (Lattice)
	9·76	1013	w.	|
	10·06	994	w.	|
	10·36	965	w.	|
	10·63	941	w.	↓
	10·78	928	w.	$\nu_2 + \omega$ (Lattice)
11·2	11·28	886	s.	$\omega_2 + \nu$ (Lattice)
11·4	11·57	864	v.s.	ω_2
	11·86	843	w.	ω_2 (C^{13})
	12·24	817	w.	$\omega_3 + \nu$ (Lattice)
	12·96	771	w.	$\omega_3 + \nu$ (Lattice)
14·32				
	14·88	672	v.s.	ω_3

'*A*' = Schaeffer and Matossi. 'B' = Authors.

w. = weak; *s.* = strong; *v.s.* = very strong; ν's = Raman active; ω's = Infrared active.

overtones and combinations. The symmetry types of the higher vibrational levels for V_h, *i.e.*, the unit cell symmetry of the orthorhombic carbonates, are easily worked out from the following:—

$a.b_i = B_i$; $b_1.b_2 = B_3$; $b_1.b_3 = B_2$; $b_2.b_3 = B_1$ taking into account also the g, u rule in the usual way. The subscript i may be 1, 2 or 3 and the small letters stand for the component vibrations and the capital letter for the resulting state [Herzberg (1945), p. 126]. Consequently, the even harmonics of infrared active fundamentals, both odd and even harmonics of Raman active fundamentals and combinations of any two infrared active fundamentals are forbidden in infrared absorption from purely symmetry considerations. One can now easily see that while some of the assignments of Schaeffer and Matossi are definitely in con-

TABLE IV

Infrared Spectrum of Strontianite ($SrCO_3$)

Absorption maxima		Intensity	Assignment
μ	cm.⁻¹		
2·13	4694	*w.*	$2\nu_4 + \omega_1{}^1$
2·50	3994	*w.*	$2\nu_4 + \omega_1{}^2$
2·82	3550	*w.*	$2\nu_4 + \omega_3$
3·13	3200	*w.*	$2\nu_1 + (\omega_1{}^1;\ \omega_1{}^2)$
3·43	2920	*v.s.*	$\nu_4 + \omega_4$
3·64	2750	*w.*	$\nu_4 + \nu_1 + \omega\,(L)$
3·69	2710	*w.*	$\nu_4 + \nu_1 + \omega\,(L)$
3·96	2525	*w.*	$\nu_4 + \omega_1{}^1$
4·82	2076	*w.*	$\omega_4 + \nu_2$
6·90	1450	*v.s.*	$\omega_4{}^4;\ \omega_4{}^2$
7·26	1377	*v.s.*	$\omega_4{}^1;\ \omega_4{}^3;\ \nu_2 + \omega_3$
8·26	1210	*s.*	$\omega_1 + \nu\,(L)$
8·65	1156	*s.*	$\omega_1 + \nu\,(L)$
9·35	1072	*s.*	$\omega_1{}^1$
9·62	1040	*s.*	$\omega_1{}^2$
10·31	970	*s.*	$\omega_2 + \nu\,(L)$
10·71	934	*s.*	$\omega_2 + \nu\,(L)$
10·91	917	*s.*	$\omega_2 + \nu\,(L)$
11·67	857	*v.s.*	ω_2
11·89	841	*w.*	$\omega_2\,(C^{13})$
12·99	770	*w.*	$\omega_3 + \nu\,(L)$
14·04	712	*s.*	$\omega_3{}^2$
14·49	690	*s.*	$\omega_3{}^4$
14·75	678	*s.*	$\omega_3{}^1$

w. = weak; *s.* = strong; *v.s.* = very strong.

$\omega\,(L)$ = 238, 213 cm.⁻¹ (Schaeffer and Matossi).

$\nu\,(L)$ = 103, 115, 218, 238, 244, 254 (T. S. Krishnan).

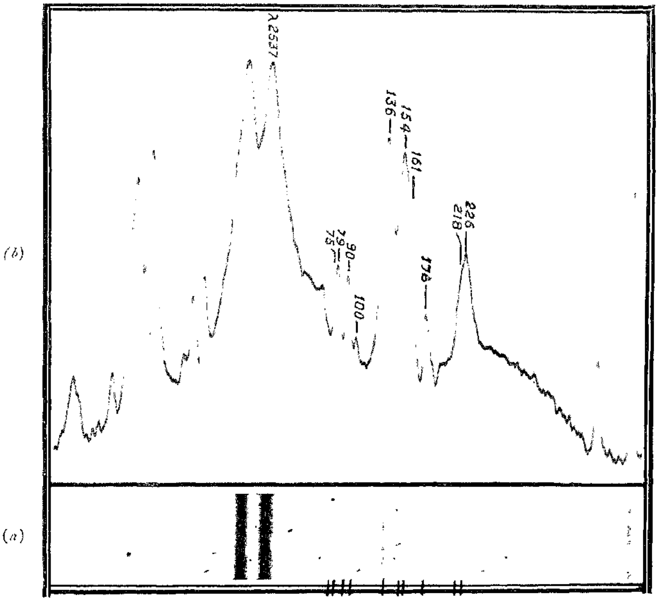

FIG. 2

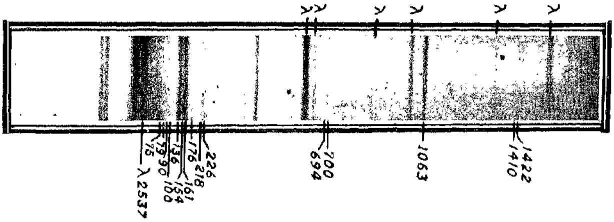

FIG. 1

Raman Spectrum of Witherite $BaCO_3$.

tradiction with this, a few others involving the internal frequencies which have become active on account of the lowering of the symmetry and coupling of the vibrations of the CO_3 ions, are essentially correct. It is true, however, that anharmonicity, as suggested by Rawlins and Taylor, may account for the large intensity of the bands and also the excitation of some weak combinations not permitted by the selection rules. The assignment of the infrared absorption maxima in the light of the selection rules is indicated in Table III for witherite and in Table IV for strontianite. The large intensity and width of the absorption at about 1,400 cm.$^{-1}$ is due to the crowding in this region of all the allowed combinations of ω_4 and ω_1 with Raman active lattice vibrations and ν_1 with the infrared active lattice vibrations. This feature in absorption is the infrared counterpart of the intense group of second order lines observed in the Raman spectra of carbonates in the neighbourhood of 2170 cm.$^{-1}$ (Krishnan, 1945, 1947).

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