

THE RAMAN SPECTRA OF ARAGONITE, STRONTIANITE AND WITHERITE

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1. INTRODUCTION

IN view of their isomorphism a comparative study of the Raman spectra of aragonite, strontianite and witherite is of interest. The vibration spectrum of the aragonite structure was discussed theoretically by Bhagavantam and Venkatarayudu (1939) and also by Couture (1947). Amongst the earlier experimental investigations on this subject the most complete are those of Couture (1947) and of R. S. Krishnan (1950) on aragonite, of T. S. Krishnan (1956) on strontianite and of Narayanan and Lakshmanan (1958) on witherite. Nevertheless, it was thought desirable to reinvestigate the subject and the present study has in fact revealed some new features of interest and shown the necessity for a reinterpretation of some of the observed facts. The present study has also enabled the various features observed in the three cases to be correlated with the differences in detail of the crystal structures. We shall in the following first briefly summarize the results of the theoretical analysis and discuss thereafter the experimental facts.

2. THE DYNAMICS OF THE ARAGONITE LATTICE

The three substances crystallize in the holohedral class of the orthorhombic system and belong to the space-group D_{2h}^{16} and contain four molecules per unit cell. The following salient features of the structure are of interest and help in our discussion of the observed facts. The structure of these crystals can be imagined as a distorted version of a hexagonal close-packed lattice of cations by compression along the y and z axes, the carbonate group lying at the centre of the hexagonal cell and between six cations (Bragg, 1924). The structure perpendicular to the z -axis consists of a series of planes of the cations which form the hexagonal network and sandwiched between every pair of these planes are two planes of the CO_3 groups which lie almost parallel to the xy plane. The CO_3 groups on either side of any cation plane are stacked one above the other and are in a staggered configuration with respect to each other owing to the centre of inversion lying midway between

them. The structure thus differs from the case of calcite wherein there is only one CO_3 plane situated midway between two Ca planes. Besides, whereas in the calcite structure each oxygen of the CO_3 group is in contact with two cations, in the aragonite structure each oxygen is in contact with three cations. It should also be mentioned that the cations, and carbon atoms and one oxygen atom of each CO_3 group are situated on the plane of symmetry σ (yz), the two other oxygens of each CO_3 group lying symmetrically on either side of this plane.

In Table I below are shown for the three crystals the lattice constants, refractive indices for vibrations parallel to x and y axes and the shortest distance between the cations and oxygens and the sum of the cation and oxygen ionic radii. In the case of an ideal hexagonal close-packing the ratio of the lattice constants a and b should equal $1:\sqrt{3}$. Columns 5 and 6 of Table I show the calculated values of b assuming the values observed for a and the differences between b and $\sqrt{3}a$. The distances are expressed in angstrom units.

TABLE I

Substance	c	a	b	$\sqrt{3}a$	$\sqrt{3}a-b$	n_x	n_y	Minimum R-O distance	R-O ionic radii
Aragonite ..	5.72	4.94	7.94	8.56	0.62	1.681	1.686	2.39	2.38
Strontianite ..	6.08	5.12	8.40	8.87	0.47	1.664	1.666	..	2.59
Witherite ..	6.54	5.25	8.83	9.00	0.26	1.676	1.677	2.76	2.75

The data shown in Table I clearly indicate that as we pass from aragonite to witherite the structure nearly approaches that of hexagonal symmetry. It is also seen that the interionic distances increase notably; hence, the coupling forces between the cations and the carbonate groups should diminish as we pass from the case of aragonite to witherite.

The group characters, selection rules and the number of vibrations under the different species are shown in Table II. The analysis reveals that, of the total number of 57 vibrations, 30 are active in Raman effect only, 21 are active in infra-red absorption only and the rest are inactive in both. The thirty Raman-active frequencies are separable into (i) external oscillations of the translatory and rotatory types of which there are 18 in all, and (ii) internal vibrations of the CO_3 groups of which there are 12 in all. As seen from Table II, oscillations of both translatory and rotatory types occur under each of the several representations and hence it is not possible

TABLE II

D_{2h}^{16}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	T	T'	R'	n_i'	R.E.	I.R.
A_{1g}	..	1	1	1	1	1	1	1	0	4	1	4	ρ	f
B_{1g}	..	1	1	-1	-1	1	1	-1	0	2	2	2	ρ	f
B_{2g}	..	1	-1	1	-1	1	-1	1	0	2	2	2	ρ	f
B_{3g}	..	1	-1	-1	1	1	-1	-1	0	4	1	4	ρ	f
A_{1u}	..	1	1	1	1	-1	-1	-1	0	2	2	2	f	f
B_{1u}	..	1	1	-1	-1	-1	-1	1	1	3	1	4	f	ρ
B_{2u}	..	1	-1	1	-1	-1	1	-1	1	3	1	4	f	ρ
B_{3u}	..	1	-1	-1	1	-1	1	-1	1	1	2	2	f	ρ

T = Pure Translations; T' = Translatory oscillations; R' = Rotational oscillations; n_i' = internal vibrations; R.E. = Raman effect; I.R. = Infra-red; ρ = permitted; f = forbidden.

to identify any observed frequency as arising from solely a rotational or translational oscillation. A detailed description of the numerous symmetry modes can however be found in the paper by Couture (1947). The large number of eighteen lattice frequencies permitted to appear in the Raman effect in the case of the aragonite structure is in striking contrast with the case of calcite wherein only two lattice frequencies of the doubly degenerate class are allowed; this difference evidently arises from the lower symmetry of the aragonite structure and also due to the presence of the increased number of groups in the unit cell of the structure.

Finally, we may remark that the 12 frequencies of the internal type arise owing to the coupling between the four CO_3 groups and due to the removal of degeneracy in the crystalline state and are correlated to the four frequencies of the free-ion as follows:—

$$\nu_1 \text{ (Totally symmetric, } A_1', 1063 \text{ cm.}^{-1}\text{)} \rightarrow A_{1g}, B_{3g}$$

$$\nu_2 \text{ (Out of plane mode, } A_2'', 879 \text{ cm.}^{-1}\text{)} \rightarrow A_{1g}, B_{3g}$$

$$\nu_3 \text{ (Doubly degenerate, } E', 680 \text{ cm.}^{-1}\text{)} \rightarrow A_{1g}, B_{1g}, B_{2g}, B_{3g}$$

$$\nu_4 \text{ (Doubly degenerate, } E', 1415 \text{ cm.}^{-1}\text{)} \rightarrow A_{1g}, B_{1g}, B_{2g}, B_{3g}$$

Since the CO_3 groups in the case of aragonite and the other two crystals are not known to be distorted or different from the CO_3 groups in calcite, the removal of degeneracy in the cases of ν_3 and ν_4 and the Raman activity of vibrations corresponding to the Raman inactive vibration ν_2 of the free-ion have necessarily to be associated with the fact that the environment of

the CO_2 groups which are coupled to the cations lacks the trigonal symmetry. Hence, it follows that in the three crystals the splitting arising from the removal of degeneracy and the Raman activity of vibrations corresponding to ν_2 can be correlated with the fact of these structures departing from the perfect hexagonal structure to different extents as pointed out earlier.

3. EXPERIMENTAL DATA

The Raman spectra of the three crystals were recorded using the λ 2536.5 resonance radiation of the mercury arc for excitation. The details of the experimental techniques have already been described in an earlier paper by the author (1957). A medium quartz spectrograph was used to obtain intense records of the spectra. A Littrow quartz spectrograph of greater resolving power was also employed to reveal the fine structure of the lines. The crystals used were fairly small being $15 \times 10 \times 5$ mm. in size and were not altogether flawless and hence the length of useful exposure that could be given to record the spectra was limited. Exposures of the order of two days were given to record the spectra intensely. In the cases of strontianite and witherite—which were in the form of coarse lumps—the spectra recorded were for random orientations. In the case of aragonite the exciting radiation was incident on a prism face and the scattering was observed along the z-axis of the crystal. The spectrum of cerussite—which also has an isomorphous structure—could not be recorded since the specimens were opaque to the λ 2536.5 radiation. Its spectrum has however been reported and discussed in detail by Couture (1947), who used the visible radiations of the mercury arc for exciting the Raman effect.

In Plate V accompanying this paper are reproduced the spectra of the three substances, recorded with comparable intensity. The microphotometer records of the low-frequency region of the spectra recorded with the Littrow spectrograph appearing as Figs. 1, 2 and 3 in the text and those appearing in Plate VI clearly exhibit the numerous frequency shifts. Of these, 11 frequency shifts, *viz.*, 133 and 1037 cm.^{-1} in aragonite, 135, 200, 711, 855 and 2142 cm.^{-1} in strontianite, and 194, 237, 852 and 2116 cm.^{-1} in the case of witherite have emerged from the present investigation.

The frequency shifts observed in the three cases are shown in Table III. Considerations of intensity and the general pattern of the observed shifts indicate that the frequency shifts shown against each other in the three cases arise in all probability from similar normal modes of vibration. The values of the frequency shifts reported herein are in fair agreement with those reported by the earlier investigators excepting in a few cases where the lines are diffuse and weak or exhibit fine structure. The frequency shift reported by Krishnan

(1950) at 1059 cm.^{-1} in the case of aragonite is believed to be the intensely Raman active frequency of shift 1086 cm.^{-1} excited by the mercury line $\lambda 2534.8$. It may be seen from Plate VI that this mercury line has similarly

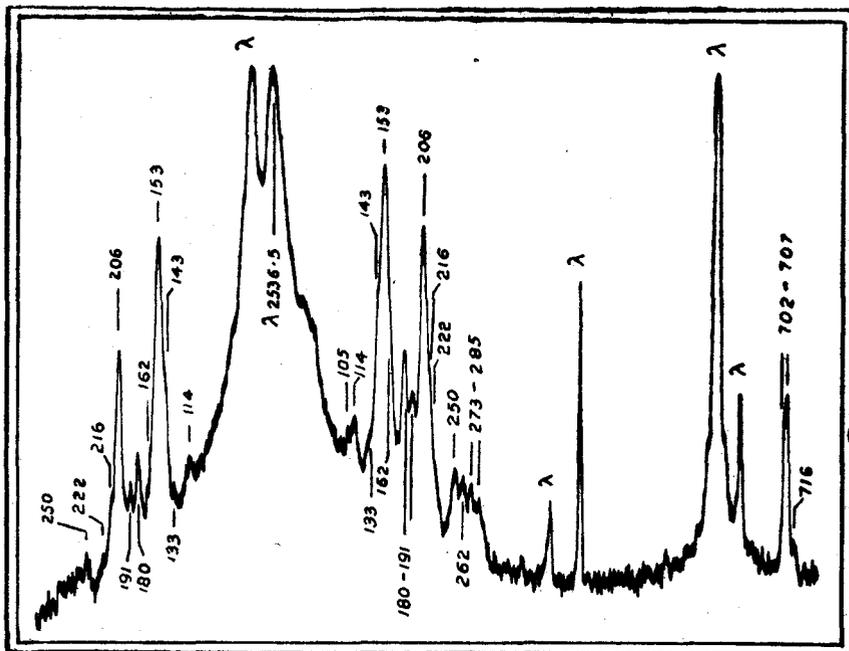


FIG. 1. Microphotometer record of the low frequency region of the Raman spectrum of aragonite.

excited the principal frequency shift in the cases of SrCO_3 and BaCO_3 as well. The frequency shift reported by him at 1574 cm.^{-1} could not be confirmed owing to the presence at about this point of the diffuse mercury line $\lambda 2642.48$.

The following principal features are strikingly evident from the reproduced spectra and their microphotometer records. (i) Barring a few exceptions there appear in all the three cases similar patterns of frequency shifts of comparable intensity. (ii) Corresponding to the degenerate modes of the free-ion there appear in the three crystals a multiplicity of components. (iii) The frequency shifts themselves and the extent of separation between corresponding groups of lines diminish as we pass from the case of aragonite to witherite. (iv) The intensity of the frequency shift at about 860 cm.^{-1} (corresponding to the Raman-inactive mode of the free-ion) diminishes as we pass from the case of aragonite to witherite. (v) The very low frequency shifts close to the exciting line show a notable increase in intensity as we

TABLE III
Observed Frequency Shifts in Cm.^{-1}

	Aragonite CaCO_3	Strontianite SrCO_3	Witherite BaCO_3
Lattice Oscillations ..	105 w. 114 m. 133 v.w.* 143 m. 153 v.s. 162 m. 180 s. 191 s. 206 v.s. 216 m. 222 v.w. 250 m. 262 m. 273 m. 285 m. 103 s. 116 s. 135 w.* 149 v.s. 184 v.s. 200 w.* 218 m. 238 m. 246 s. 260 m.	76 m. 80 s. 90 s. 101 w. 136 v.s. 153 v.s. 161 m. 178 m. 194 w.* 217 m. 227 s. 237 w.*
ν_3 ..	702 m. 707 m. 716 w.	701 m. 711 w.*	691 m. 699 w.
ν_2 ..	854 m.	855 w.*	852 v.w.*
ν_1 ..	1086 v.s.	1074 v.s.	1061 v.s.
ν_4 ..	1415 m. †1464 } 1463 s. †1466 }	1408 m. 1438 s. 1447 m.	1394 m. 1409 m. 1421 s.
$2\nu_1$..	2165 w.	2142 w.*	2116 w.*
Combinational shifts ...	1037 w*(854+180) 1815 w. (743+1078)	1510 m.(1421+90)

Note.—The frequencies marked with an asterisk are reported for the first time. 1078 and 743 appearing in the last line of the table have been observed in the infra-red (*vide* Refs. 7 and 10).

† Resolved by Couture from polarisation studies.

s = strong; v.s. = very strong; w = weak; m = moderate intensity.

pass from aragonite to witherite. (vi) In each of the three cases a well-defined frequency shift appears which is clearly the overtone of the principal frequency shift.

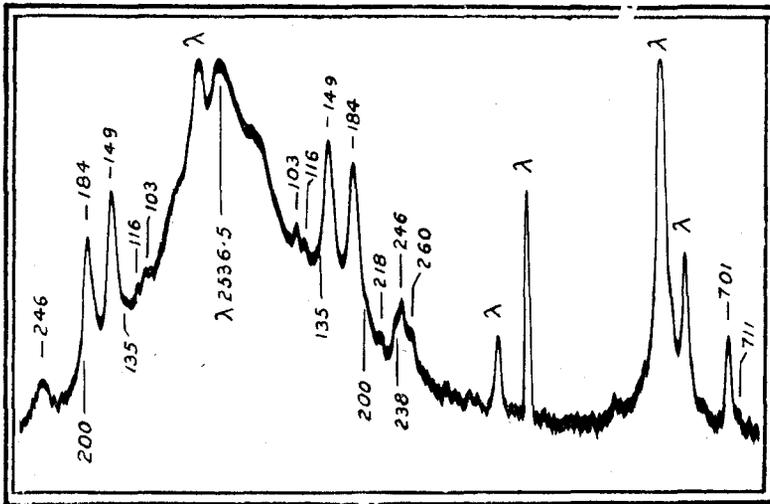


FIG. 2. Microphotometer record of the low frequency region of the Raman spectrum of strontianite.

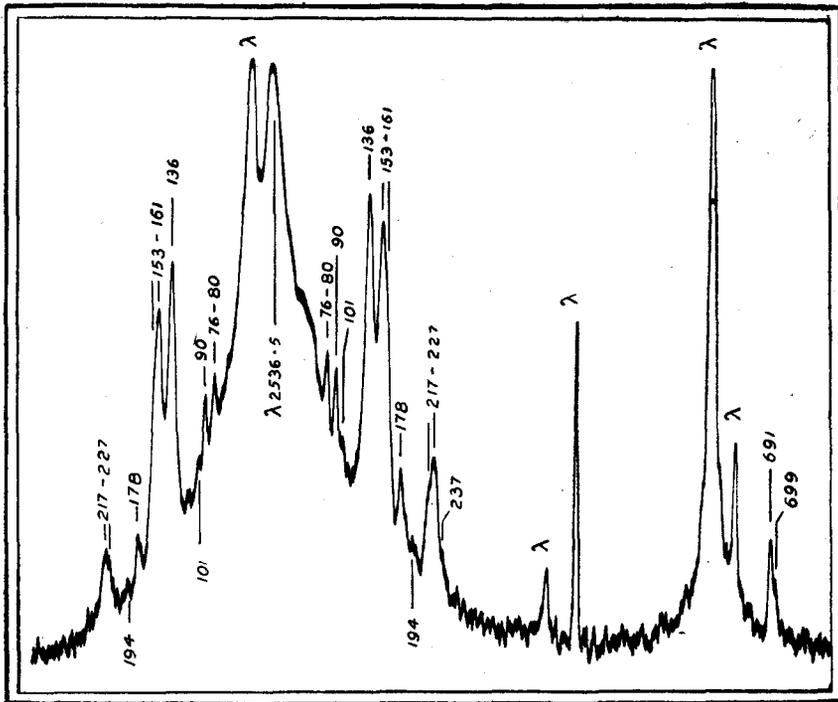


FIG. 3. Microphotometer record of the low frequency region of the Raman spectrum of witherite.

4. DISCUSSION OF THE RESULTS

The appearance in the spectrum of aragonite of 16 out of the 18 frequency shifts theoretically predicted is by itself proof of the strong coupling between the four molecules in the unit cell. Moreover, the observation in aragonite of three components in each of the cases corresponding to the degenerate modes ν_3 and ν_4 furnish further evidence of the coupling between the CO_3 groups. The earlier explanations of the frequency shifts observed at 1415 and 716 cm.^{-1} in the case of aragonite as respectively the overtone of the frequency at 707 cm.^{-1} and as a combination of the differential type, *viz.*, ($\nu_2 - 153$), are clearly untenable. Also, it may be remarked that (i) in the analogous and experimentally more favourable case of calcite the overtone of the line corresponding to ν_3 could not be observed at all and (ii) combinations of the differential type are usually too weakly Raman-active to be readily observed. The appearance of three lines corresponding to ν_4 and two lines corresponding to ν_3 in SrCO_3 and BaCO_3 also is in accordance with the splitting of ν_3 and ν_4 predicted by theory though the number of components observed is less than the predicted number.

The origin of the diminution of the internal frequency shifts and also of the diminution in the extent of splitting of the degenerate frequencies is to be sought for in the fact, that in the three cases the cations surrounding the CO_3 group are at increasingly greater distances as we pass from aragonite to witherite. Indeed, the diminution of the coupling forces are most strikingly exhibited by the shift of the principal Raman lines from a value of 1086 cm.^{-1} in the case of aragonite to a value of 1074 cm.^{-1} in strontianite and to 1061 cm.^{-1} in witherite. As already indicated in Section 2 of this paper, the splitting arising from the removal of degeneracy would diminish as the structures approach that of perfect hexagonal symmetry. This, taken in conjunction with the fact of the increasing interionic distances and correspondingly reduced coupling between the groups, explains the fact of the diminution in the extent of splitting.

We may also remark upon the fact that whereas the frequency at about 860 cm.^{-1} is observed with moderate intensity in aragonite, its intensity considerably diminishes as we pass on to the case of witherite. The frequency corresponding to the Raman inactive mode of the free-ion is actually observed in the crystalline state owing to the environment of the CO_3 group lacking the trigonal symmetry. As already mentioned the structure approaches that of hexagonal symmetry as we pass on to the case of witherite; the diminution in the intensity of this line is hence not surprising.

Polarisation studies enabled Couture to assign the two very intense Raman lines at 153 and 206 cm^{-1} in the case of aragonite to the species B_{2g} and B_{3g} respectively. The pair of intense lines observed in each of the cases of SrCO_3 and BaCO_3 also presumably belong to the species B_{2g} and B_{3g} . The analysis of the symmetry modes shows that the rotatory oscillations of the CO_3 groups about y and x axes involving large changes in polarisability fall under the classes of B_{2g} and B_{3g} respectively. The appearance of a pair of intense lines of the same species indicates that they might arise from predominantly similar movements, though coupling between them and other modes of the same species cannot be altogether excluded. The diminution in the values of these frequencies and the extent of their separation is consistent with the fact of the decreasing coupling forces and that of the structure approaching one of hexagonal symmetry as we pass on to the case of witherite.

The low-frequency lines close to the exciting line in the three cases may be attributed to mass movements of the CO_3 groups and the cations surrounding them as a whole; the pronounced diminution in the values of these frequencies because of the increase in the mass of the oscillating groups, and the gain in their intensity because of the greater refractivity of the cations as we pass from aragonite to witherite are all features consistent with each other. The lattice frequencies observed higher up in the region 220–250 cm^{-1} also diminish as we pass from the case of aragonite to witherite.

In the present study the spectra have been recorded with great intensity so as to reveal even faint lines. In spite of this it is seen from Table III that the total number of lines observed in each case is less than the number predicted by theory. The explanation that can be offered for this is that, either the frequency shifts overlap and are not resolved from each other, or that they are too weakly Raman-active to be recorded.

Finally, a few remarks may be made regarding the second order frequencies observed. There exists a small but systematic difference of the order of 4 cm^{-1} between the values of the fundamentals derived from the overtones and those of the observed Raman-active fundamentals. A simple explanation of this feature is that the observed overtone represents the combined effects of the four components theoretically permitted, *viz.*, A_{1g} , B_{3g} , B_{1u} and B_{2u} corresponding to the totally symmetric mode of the free-ion. The infra-red-active frequencies corresponding to this mode reported by Louisfert (1951) are respectively 1078 cm^{-1} in aragonite, 1072 cm^{-1} in strontianite and 1060 cm^{-1} in witherite indicating that they are indeed slightly lower than the corresponding Raman-active fundamentals. The explanations given in Table III for the combinational modes are only tentative and the

origin of their observable Raman-activity is not clear. However, it should be mentioned that the appearance of discrete well-defined frequency shifts in the second order spectrum is in consonance with the theory of lattice dynamics put forward by Sir C. V. Raman in 1943, and which predicts that the second order spectrum should exhibit the discrete character of the vibration spectra of crystals.

5. CONCLUDING REMARKS

As the crystals under discussion belong to the centro-symmetric class no exact coincidences can be expected between the data from studies on infra-red absorption and the Raman effect. The infra-red absorption spectra of these substances have been investigated by Louisfert (1951) and Narayanan and Lakshmanan (1958) and they report analogous features with regard to the splitting arising from the removal of degeneracy and the presence of a multiplicity of groups in the unit cell of the structure. However, the infra-red data for these substances are incomplete for the 7μ region of the spectrum. The striking multiplicity of frequencies observed in the Raman effect in this frequency region indicates the existence of similar effects in the infra-red also at 7μ .

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in this investigation.

6. SUMMARY

The Raman spectra of the three crystals are recorded using the λ 2536.5 radiation of mercury and eleven new lines of low intensity are reported. These include the appearance in the cases of SrCO_3 and BaCO_3 of the line corresponding to the Raman-inactive mode of the free-ion, this line being of progressively diminishing intensity in the three cases owing to the structures progressively approaching that of hexagonal symmetry. The similarities and the differences observed in the three spectra are also correlated with the details of the crystal structures.

7. REFERENCES

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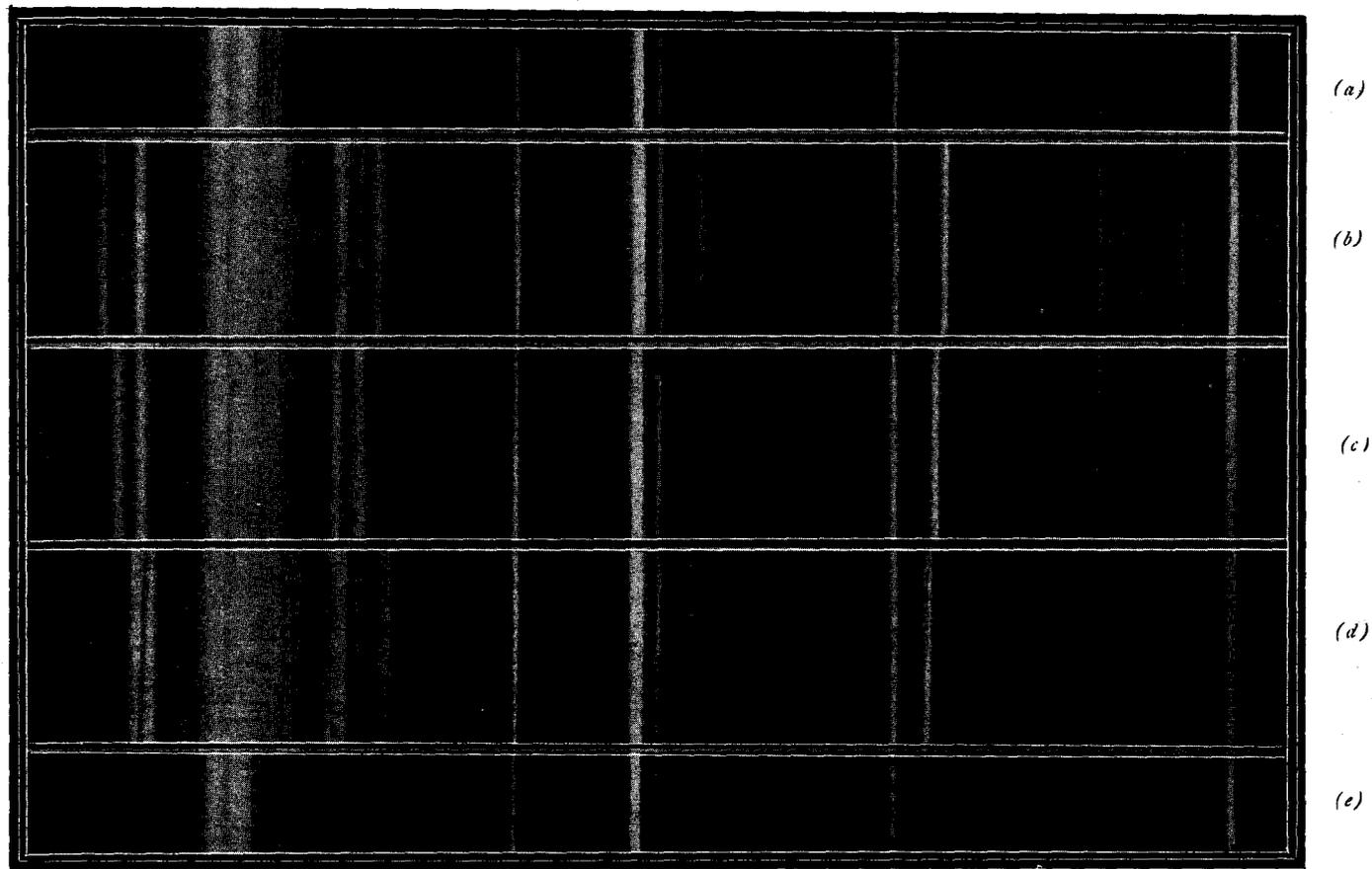


FIG. 1. The Raman spectra of the three crystals. (b). Aragonite; (c). Strontianite. (d). Witherite. (a) and (e). Spectrum of the mercury arc.

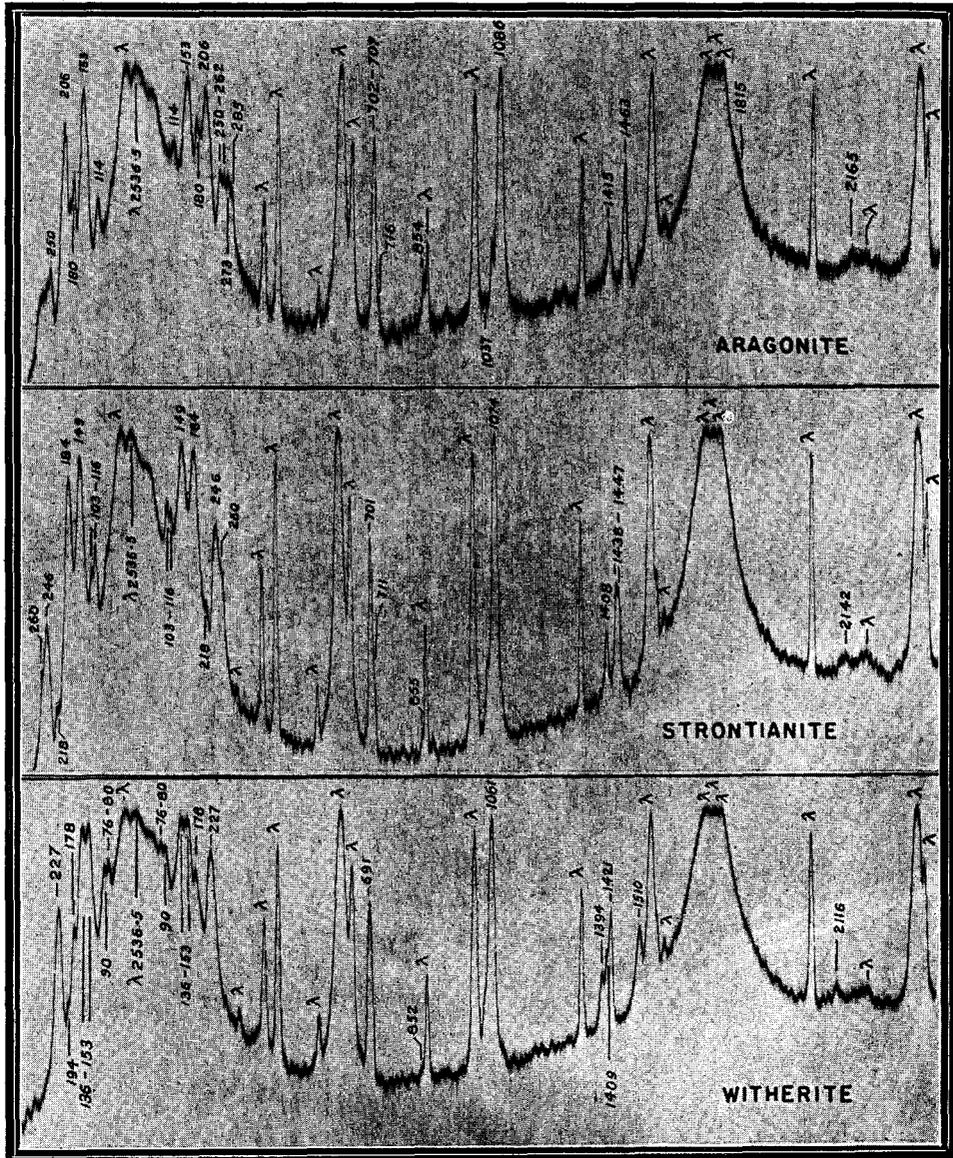


FIG. 2. Microphotometer records of the three spectra recorded with the medium quartz spectrograph.

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