

EFFECT OF CRYSTAL ORIENTATION ON THE RAMAN SPECTRUM OF CALCITE

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1. Introduction

MUCH of the experimental work so far done in the subject of Raman effect relates to either the liquid or gaseous states of matter or crystals in the form of powders. It is easily seen that the scattering unit cannot be regarded as having a definite orientation in any of these cases. On the contrary, in most of the above cases, the opposite extreme is reached as we are obliged to postulate a completely random orientation in order to interpret the observed results as average effects. This defect can only be remedied by using a suitably cut single crystal and studying the nature of the scattered light for different orientations of the crystal. Corresponding to each possible orientation of the crystal, the state of polarisation of the incident light may also be varied and such studies will undoubtedly reveal a wealth of information which was hitherto missed. The importance of obtaining such results has been stressed elsewhere.¹ The work that has so far been done on these lines is however very meagre. Reference may be made to Schæfer, Matossi and Aderhold,² Miss Osborne,³ Cabannes and Canals⁴ and Michalke.⁵ All these authors obtained some results with calcite but unpolarised incident light was generally used. Only Miss Osborne employed linearly polarised as well as unpolarised incident light and studied the case of calcite in great detail. The agreement between the results obtained by the various authors is not very satisfactory. These features have been briefly reviewed by Nedungadi⁶ in a recent publication. Nedungadi has also pointed out that the nitrates and carbonates form very favourable material for such studies and he himself has described in great detail the results obtained with NaNO_3 crystals. In the present investigation, the Raman spectrum of calcite which resembles that of NaNO_3 in many respects has been similarly studied.* The resemblance between the two cases is in fact so close that it very often becomes unnecessary to distinguish between them. The Raman spectra of these two crystals, without reference to directional excitation, have recently been studied in this laboratory by Sundara Rama Rao⁷ and a reference to this

* A preliminary note (*Curr. Sci.*, 1939, 8, 507) by the author contains some of the results of this paper.

paper will facilitate proper appreciation of the results which will be described in the following sections.

2. *Experimental Arrangements*

A one-inch cube of calcite cut in such a manner that the optic axis is parallel to one of its edges is used for obtaining the Raman spectra reproduced in Plate III. All the faces of the cube are polished. We shall designate the direction of incident light by OX and the direction of scattered light by OY. The three edges of the crystal are always along OX, OY and OZ. This notation as well as the notation that will be employed in the rest of the paper and the description of the figures in Plate III are deliberately so chosen that they conform closely to the descriptions already used by Nedungadi in order to avoid confusion. In the experimental arrangements, suitable apertures designed to minimise parasitic light are provided at appropriate places. Light from a quartz mercury lamp is focussed on the crystal by a large glass condenser involving a semi-angle of convergence of about 10° . It is found impracticable to eliminate the convergence altogether and this should at present be regarded as an inevitable defect of the experimental arrangements. A suitably oriented Polaroid disc is used for securing the desired state of polarisation for the incident light. The scattered light is separated into the horizontal and vertical components by means of a double-image prism and the two components are simultaneously photographed on Golden Iso-Zenith plates using a high light gathering power 2-prism glass spectrograph. $\lambda 4358$ is the exciting radiation. In all cases, graded intensity marks are given by the method of varying slit widths and wherever necessary, figures relating to the intensities are obtained from the density-log intensity curves. In other cases, where such an accurate study is not called for, either because the lines under comparison possess very widely different intensities or because the intensities are so small as to fall within the limits of convergence errors, only visual estimates are given. These figures are collected together in Table I. An arbitrary intensity of 100 is assigned to the strongest line in each plate and the intensities of all other lines are expressed in relation to this figure. The observed polarisation ratios are corrected for the errors introduced by oblique refraction at the surfaces of the prisms.

3. *Results*

Nedungadi has shown that 27 different spectrograms may be obtained for the case of transverse scattering with uniaxial crystals but it may easily be seen that 12 of these are the most important ones. These have been given as Figs. 4, 5 and 6 in his paper and correspond in the same order to Figs. 1, 2 and 3 of this paper. As has been done by Nedungadi, the directions

TABLE I

Serial number	Direction of vibration of incident light along	Orientation of the optic axis along	Relative Intensities of Components of Raman lines												
			155		282		709		1084		1434		1749 (overtone)		
			OX	OZ	OX	OZ	OX	OZ	OX	OZ	OX	OZ	OX	OZ	
1	OZ	OX	25	1	60	2	10	5	5	100	2	2
2	OY	"	50	..	100	..	2	..	2	5
3	OZ	OY	5	5	10	10	10	10	10	100	3	3	3	2	2
4	OY	"	50	50	100	100	3	3	20	10
5	OZ	OZ	50	0	100	3	5	10
6	OY	"	25	50	50	100	20	..	50	5	5

of the vibrations in the incident light (I.L.) as also those in the scattered light (S.L.) are indicated in the figures. Vibrations along OX and OY are represented by arrows parallel to these axes, whereas a circle with a central dot indicates that the vibrations are along OZ. The orientation of the CO_3 ion and therefore the crystal as a whole adopted in each case is also indicated by the side of the corresponding set of pictures. Results of visual estimate and quantitative measurement are contained in Table I. This corresponds to Table III of Nedungadi's paper.

A very satisfactory agreement between the general run of figures, in Table I and the results obtained by Nedungadi may be noticed. The following main conclusions may now be drawn from the results in Table I and the pictures reproduced in Plate III.

On comparing Figs. 1, 2 and 3, taking a and b components together in each case, it will be seen that the 1084 line is very weak in Fig. 3 while it is quite strong in Figs. 1 and 2. In all these cases, the incident light is polarised in the same way but the orientation of the crystal is different. This implies that the change of polarisability of the CO_3 ion due to its total symmetric oscillation is much smaller when the incident light vector is perpendicular to the plane of the ion than when it is parallel to it. The lines of frequency shifts 709 and 1434 due to the two degenerate internal oscillations of the CO_3 ion also appear to behave in a similar manner but the differences are less prominent. Similar results have been obtained by Nedungadi with NaNO_3 .

On comparing a and b taken together of Fig. 2 with c and d of the same figure taken together, it is seen that while the low frequency lines are weak and the internal oscillations are strong in the former case, the reverse is the situation in the latter. Similar results have been obtained by Nedungadi with NaNO_3 . It may be concluded from this result as has been done by Nedungadi that the behaviour of the two kinds of oscillations, namely the low frequency ones on the one hand and the internal oscillations on the other, is reciprocal in character and that the periodic changes of polarisation responsible for the former arise in a manner fundamentally different from that operative in the case of the latter.

The behaviour of the 155 and 282 lines is closely analogous. A reversal of relative intensities amongst these two lattice oscillations noticed by Nedungadi in NaNO_3 for a particular orientation (Fig. 6 c of his paper) is not confirmed by the author in CaCO_3 as may be seen from Fig. 3 c which is the corresponding figure in this paper.

The first overtone of a Raman inactive frequency (879) is recorded at 1749 in two cases and it may be noted that in both these cases, its behaviour is similar to that of the total symmetric oscillation at 1084 (see Table I).

Figs. 1 (*a* and *b*) and 2 (*a* and *b*) show that the polarisation characters of the two low frequency lines are similar to those exhibited by the degenerate internal frequencies at 709 and 1434 and opposite of those exhibited by the total symmetric oscillation at 1084. In Fig. 3 (*c* and *d*) the reciprocal behaviour of the low frequency lines on the one hand and the 1084 line on the other persists but the internal degenerate frequencies in this case appear to resemble 1084 and not the low frequency lines. Some of these results are not in conformity with those obtained by Nedungadi in NaNO_3 .

4. Comparison of the Results with Earlier Observations

It has already been pointed out that Miss Osborne had obtained some results with calcite utilising plane polarised incident light. These results which refer to the state of polarisation of the Raman lines are compared below in Table II with the values obtained in the present investigation. Excessively large values are denoted by ∞ and excessively small ones by 0. The serial number in Table II corresponds to that given in Table I and determines the crystal orientation. O stands for Miss Osborne and B for the author. *f* denotes that the line fails to appear.

TABLE II

Serial number	ρ for 282		ρ for 709		ρ for 1084	
	O	B	O	B	O	B
1	4	∞	1	>1	0	0
2	4	∞	1	>1	0	<1
3	1	1	1	1	1	<1
4	1	1	<i>f</i>	1	<i>f</i>	>1
5	>1	∞	>1	..	0	<1
6	<1	0.5	>1	>1	<i>f</i>	>1

5. Discussion of Results

Crystal Structure and Normal Oscillations.—In order to interpret the foregoing results satisfactorily, it is necessary that a reference should be made to the complete analysis of the normal oscillations of the calcite and NaNO_3 lattices carried out by the author in an earlier paper.¹ The character table given below contains all the important features and applies to both CaCO_3 and NaNO_3 .

TABLE III

D_{3d}^6	E	$2S_2^1$	$2C_2^1$	i	$3\sigma_v$	$3C_2$	n_i	External		n_i'	Activity in Raman effect	Surviving tensor components
								T	L			
A_1	1	1	1	1	1	1	1	0	0	1	p	$\alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
A_2	1	1	1	1	-1	-1	3	0	2	1	f	\dots
B_1	1	-1	1	-1	1	-1	4	1	2	1	f	\dots
B_2	1	-1	1	-1	-1	1	2	0	1	1	f	\dots
E_1	2	1	-1	-2	0	0	6	1	3	2	f	\dots
E_2	2	-1	-1	2	0	0	4	0	2	2	p	$\left\{ \begin{array}{l} (\alpha_{zz}, \alpha_{yy}) \\ (\alpha_{xy}, \alpha_{xx} - \alpha_{yy}) \end{array} \right.$
ω_R	10	2	4	2	0	4						
$h\nu_i'$	30	0	0	-6	0	-12						

The surviving tensor components are deduced by the application of the usual selection rules, the details of which will be omitted here. The trigonal axis is taken as the z -direction while the x and y axes lie in the plane of symmetry. These axes are fixed in the crystal and must be distinguished from the system fixed in space and described earlier. It may be remarked here that only one Raman-active normal oscillation (1084) comes under the total symmetric class and this is characterised by the fact that the diagonal terms of the polarisability tensor alone survive. The only other class under which Raman-active oscillations appear is E_2 . Under this category, there are two lattice oscillations (155 and 282) and two internal oscillations (709 and 1434). The surviving components are mainly the non-diagonal ones although a term involving $a_{xx} - a_{yy}$ is present. It is thus clear that the scattering moment should be of the *polarised type* in the case of the total symmetric internal oscillation (1084) only whereas the scattering moment in the case of all the other oscillations, lattice as well as internal, may be a mixture of the *polarised* and the *depolarised* types. In addition to the selection rules cited above, we have also to consider the possibility of the various tensor components that appear in each case being unequal amongst themselves such as $a_{xx} = a_{yy} \neq a_{zz}$. That such an inequality prominently exists is in fact clearly suggested by the result already noted in the foregoing section where it was observed that the change of polarisability of the CO_3 ion due to its total symmetric oscillation is much smaller when the incident light vector is perpendicular to the plane of the ion than when it is parallel to it. It may further be noted that the degree of such an anisotropy may be different for different normal oscillations. The combined effect of these two major factors, namely the selection rules and the anisotropy of the polarisation tensor will determine the ultimate characters of the Raman lines corresponding to each one of the normal oscillations. We may now deal with the various oscillations of the calcite lattice individually in the light of the above analysis.

Total Symmetric Oscillation (1084).—The set of equations (1) will determine the intensities of the various components in any general case.

$$\begin{aligned} p_x &= a_{xx} E_x + a_{xy} E_y + a_{xz} E_z \\ p_y &= a_{yx} E_x + a_{yy} E_y + a_{yz} E_z \\ p_z &= a_{zx} E_x + a_{zy} E_y + a_{zz} E_z \end{aligned} \quad (1)$$

The p 's and the E 's stand for the components of the induced moment and of the incident light vector respectively. In the case of the 1084 line, we have all $a_{j\bar{k}} = 0$ and we shall postulate that a_{xx} which is equal to a_{yy} to be about three times as large as a_{zz} . Intensities involving a_{xx} or a_{yy} will accordingly be about ten times as large as those involving a_{zz} . The results that are to be

expected may be easily calculated and these are compared below in Table IV with the observations.

TABLE IV

Serial Number	Component in the incident light	Components in the scattered light		Intensities calculated (1084)		Intensities observed (1084)	
				OX	OZ	OX	OZ
1	E_x	p_z	p_x	0	100	5	200
2	E_y	p_z	p_x	0	0	2	5
3	E_x	p_y	p_x	0	100	60	100
4	E_z	p_y	p_x	0	0	20	10
5	E_z	p_x	p_z	0	10	5	10
6	E_y	p_x	p_z	0	0	50	5

Numbers in column 1 of Table IV correspond to the numbers in column 1 of Table I. The x , y and z occurring in columns 2 and 3 of Table IV refer to the system of axes in which the z -direction is always identified with the trigonal axis of the crystal. OX and OZ occurring in columns 4 and 5 have the significance given to them earlier and refer to the space fixed co-ordinate system. With the exception of the unusually large OX intensities observed in cases 3 and 6, the experimental results may be regarded as being in excellent agreement with the theoretical expectations. A close examination of cases 3 and 6 however shows that the circumstances are particularly favourable for the presence of the proper component in the incident light due to convergence which will account for such abnormally large OX intensities.

Lattice Oscillations (155 and 282).—In this case, equations (1) still hold good but we have $\alpha_{xz} = 0$. We will also assume that α_{xy} , α_{xx} and α_{yy} are comparatively small and that α_{xy} and α_{yz} are both large and approximately equal. The expected results are shown in Table V along with observed figures.

TABLE V

Serial Number	Component in the incident light	Components in the scattered light		Intensities calculated		Intensities observed (155)		Intensities observed (282)	
				OX	OZ	OX	OZ	OX	OZ
1	E_x	p_z	p_x	large	..	25	1	60	2
2	E_y	p_z	p_x	large	..	50	..	100	..
3	E_x	p_y	p_x	5	5	10	10
4	E_z	p_y	p_x	large	large	50	50	100	100
5	E_z	p_x	p_z	large	0	50	0	100	3
6	E_y	p_x	p_z	..	large	25	50	50	100

Notation in Table V is the same as that adopted in Table IV. Agreement between the observed and the calculated characters is very satisfactory. It must be remarked here that both the lattice oscillations have been treated exactly alike both in respect of the selection rules and the degree of anisotropy of the polarisation tensor. The latter is only an assumption which is justified by the results whereas the former is a consequence of the fact that both of them come under the same irreducible representation.

Internal Degenerate Oscillations (709 and 1434).—These two oscillations also come under the irreducible representation \bar{E}_g and the selection rules are therefore the same as those that have been found to hold good for the lattice lines. It is however known that in these oscillations, the movements of the atoms are confined to the plane of the CO_3 group only (see Ref. 1) and further special considerations will therefore apply. It is easily seen that in such oscillations, the symmetry axis remains as one of the principal directions (z -direction) of the polarisability tensor during the oscillation while the x and y axes may change but being confined to the plane of symmetry only. This means that $a_{xz} = a_{yz} = 0$ and an incident light vector in which the vibrations are confined to the symmetry plane will give rise to an induced moment which is also confined to the symmetry plane. In this respect, their behaviour is akin to that of the total symmetric oscillation and reciprocal of that exhibited by the lattice lines. It may however be noted that an incident light vector which is perpendicular to the plane of the group will not give rise to any induced moment at all since a_{zz} is also equal to zero. This is in conformity with the failure to record these lines in the plate corresponding to number 5 of Table I. A more detailed correlation will not be attempted as these lines are inherently weak and their components have not been recorded in all cases.

First Overtone of the Raman Inactive Oscillation (1749).—There is a fundamental frequency at 879 arising from a non-degenerate oscillation of the lattice which is Raman inactive. The overtone in question refers to this and will accordingly be put under the total symmetric class.† It should therefore exhibit characters which are more or less similar to those exhibited by the 1084 itself. This expectation is supported by the meagre experimental results that are obtained in the present investigation.

† See reference 1 where it was shown that the representation of the overtones of all non-degenerate irreducible representations is equivalent to the irreducible representation of the total symmetric type.

6. Summary

The results of studying the Raman effect in a specially cut and polished single crystal of calcite are reported in the paper. Twelve spectrograms corresponding to different orientations of the crystal with respect to the directions of incidence and observation are obtained. The most important result of the investigation is the reciprocal behaviour of the lattice oscillations on the one hand and the total symmetric oscillation on the other. This is to be expected theoretically as the former belong to a degenerate class whereas the latter comes under an altogether different representation possessing special features. Two other degenerate internal frequencies which are Raman-active resemble the total symmetric oscillation in many important respects. The first overtone of a Raman inactive fundamental is recorded in two spectra and in these cases, it is found to resemble the total symmetric oscillation. The results of this paper are in general agreement with those already reported by Nedungadi who worked with the closely analogous case of NaNO_3 .

An attempt is made to explain the observed results by studying the selection rules in detail. The peculiar features of the recorded spectrograms indicate that the strong optical birefringence of the crystal which would naturally manifest itself in Rayleigh scattering has its parallel when we come to consider the Raman scattering. The polarisation tensor associated with each vibrational transition should accordingly be regarded as anisotropic and the type of anisotropy or the degree of anisotropy may vary from one normal vibration to another. This fact combined with the selection rules provides satisfactory explanation for most of the observed results. Small discrepancies which still remain unexplained may be attributed to errors arising from the convergence of the incident beam.

REFERENCES

1. Bhagavantam and Venkatarayudu .. *Proc. Ind. Acad. Sci.*, 1939, **9**, 224.
2. Schaefer, Matossi and Aderhold .. *Z. f. Phys.*, 1930, **65**, 289.
3. Osborne .. *Diss. Paris, Les Presses. Univ.*, 1932.
4. Cabannes and Canals .. *Comptes Rendus*, 1934, **193**, 289.
5. Heinrich Michalke .. *Z. f. Phys.*, 1938, **108**, 748.
6. Nedungadi .. *Proc. Ind. Acad. Sci.*, 1939, **10**, 197.
7. Sundara Rama Rao .. *Ibid.*, 1939, **10**, 167.