

RAMAN EFFECT IN RELATION TO CRYSTAL STRUCTURE: LATTICE OSCILLATIONS

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1. Introduction

It may easily be shown that when radiation falls on a block of *perfectly homogeneous* matter, there is no scattering of either the diffuse or the specular type. The validity of this statement rests on our being able to divide the entire block into a large number of volume elements which are identical with each other in all respects and each of which is quite small in comparison with the wave-length of the incident radiation. This result is, however, considerably modified in actual application as it rests on a hypothesis that can never be realized in practice. A perfect crystal, provided the temperature is sufficiently low and the incident radiation has a wave-length which is quite large in comparison with the interatomic distances, has often been given as an example closely approaching such an ideal. A little consideration will show that even this case falls short of the ideal in several respects. One of these is intimately connected with the experimental result that in crystals, Raman lines characterized by large frequency shifts are easily recorded even at very low temperatures. This implies that we cannot ignore the effect on radiation of the kinetic motions, even after eliminating them by reducing the temperature, because we have always to reckon with the possibility of the incident radiation itself inducing them.

There have been some suggestions as regards the actual condition in which the crystal should find itself, if it is to give rise to a scattered beam of an appreciable intensity. Mention may be made here of a working hypothesis, adopted by the author and Venkatarayudu (1939) in their earlier investigations, which states that only those lines which correspond to the mutual vibrations of the elementary lattices that constitute the structure have a chance of being observed in Raman scattering.

Raman and Nagendra Nath (1940) and Raman (1941) have, on the other hand, given a slightly different picture in their recent investigations. That the relation (1), originally enunciated by Brillouin (1922), is of fundamental importance in this connection as well, is an important feature of their work. λ is the wave-length of the incident light and

$$\lambda = 2 \lambda^* \sin \theta \quad (1)$$

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λ^* is the wave-length of the stratification that causes a scattered beam in a direction which deviates from the incident direction by 2θ . In this picture, all diffuse scattering by crystals is in the nature of specular reflection. If λ is large, a suitable λ^* is always available for any value of θ and specular reflection, because it is thus present in all directions, may be called diffuse scattering.

In the present paper, it is proposed to briefly examine the relation between these two ways of looking at the phenomenon and extend the author's earlier work to some crystals with special reference to certain aspects that had not been dealt with in detail at that time.

2. The Dynamic Condition of a Crystal

If we are dealing with a crystal made up of N unit cells, there being n atoms in each of these unit cells, the well-known work of Born shows that the $3nN$ degrees of freedom may be distributed over the various normal modes of oscillation of the crystal which fall into $3n$ series. Of these $3n$ series, 3 are of the acoustic class and the rest belong to the optical class. In all these cases, stratifications which are periodic both in time and in space are caused in the medium.

In order to bring out the mutual relationships that exist between the various parameters that characterize such stratifications, we consider, for simplicity, a linear chain structure shown in Fig. 1. In this structure, each

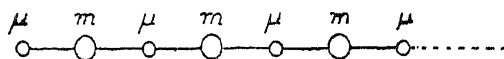


FIG. 1

one of the atoms is confined to move along the chain and has only one degree of freedom. The distance between two consecutive atoms is a and α is the restoring force called into play when this distance changes by one unit. The unit pattern in this model has a length $2a$ and contains two atoms, one of mass μ and the other of mass m . Fig. 2, taken from Born's

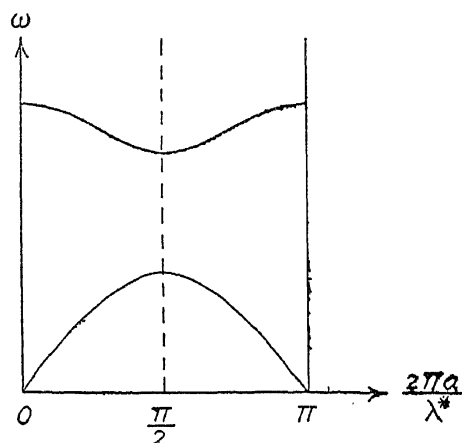


FIG. 2

work, illustrates some of the important features. The angular frequency ω or $2\pi\nu$ is plotted against the parameter $\frac{2\pi a}{\lambda^*}$. λ^* is the wave-length of the stratification. In this case, there is only one series of the optical type and one of the acoustic type. In the neighbourhood of the origin, the optical series shown by the upper curve in Fig. 2 is represented by equation (2) and the acoustic series shown by the lower curve is represented by equation (3).

$$\omega_1^2 = 2a \cdot \frac{m+\mu}{m\mu} - \left(\frac{2\pi a}{\lambda^*}\right)^2 \cdot \frac{2a}{m+\mu} + \dots \quad (2)$$

$$\omega_2^2 = \left(\frac{2\pi a}{\lambda^*}\right)^2 \cdot \frac{2a}{m+\mu} + \dots \quad (3)$$

The lowest acoustic frequency which is equal to zero and the highest optical frequency which is equal to $\left[2a \cdot \frac{m+\mu}{m\mu}\right]^{\frac{1}{2}}$ correspond to a stratification whose wave-length is the length of the chain itself and this may be regarded as infinitely large in comparison with the interatomic distances. These modes may conveniently be referred to as the limiting oscillations of the structure. The limiting optical oscillation, in particular, may be described as a motion of the whole chain of μ atoms against the whole chain of m atoms. Confining ourselves to equations (2) and (3), which are strictly valid only in the neighbourhood of the origin where λ^* is very large, it is easily seen from (3) that the velocity of the acoustic waves in the medium is about 10^6 cm. per second if the restoring force is assumed to be of the order of 10^4 dynes per cm. extension. This is of the right order of magnitude. More important than this, for our present purpose, is the fact that while the limiting optical frequency is of the order of 10^{13} , the diminution caused in it, even as we come down from $\lambda = \infty$ to $\lambda = 10^{-5}$ cm.; is only of the order of 10^{10} . This result is easily obtained from (2) and implies that the upper curve in Fig. 2 is so flat in the neighbourhood of the origin that stratifications possessing wave-lengths comparable to the wave-length of light in the visible region are characterized by frequencies which differ from the limiting frequency by only about one in a thousand.

Although the above arguments relate to the simple case of a chain, the general conclusions relating to the division of the series into the optical and the acoustic classes, the existence of the limiting oscillations corresponding to $\lambda = \infty$ characterized by special features and the flatness of the curves showing the variation of the optical frequencies with wave-length in the neighbourhood of the origin remain unaffected when the analysis is extended to three dimensional lattice structures, provided the interatomic forces continue to be of the order of 10^4 dynes per cm. extension. As a result of the

temperature which the crystal may possess, there will be thermal energy and this will be distributed amongst the various degrees of freedom in accordance with the Boltzmann law. As has already been remarked, we cannot ignore the degrees of freedom which have a low *a priori* probability as per this law, because when radiation is incident, just those may be induced if they happen to be the appropriate ones. Thus, incident radiation possessing a large wave-length, is specularly reflected in all directions in accordance with relation (1), irrespective of the temperature of the crystal being high or low. It may, however, be noted that different stratifications possessing different values of λ^* will be effective for different values of 2θ . As 2θ ranges from being 0 in the case of forward scattering to being 180° in the case of backward scattering, the effective value of λ^* will range from ∞ in the former case to $\frac{\lambda}{2}$ in the latter. In this general case, there are $3n$ series of stratifications and one stratification possessing the required λ^* for a given λ and θ can be picked up from each of the $3n$ series. Three of these, belonging to the acoustic class, give rise to six Brillouin components whose positions are given by the well-known relation (4)

$$d\nu = \pm 2 \frac{v}{c} \cdot v \sin \theta \quad (4)$$

v , the velocity of sound in the medium, can take the three appropriate values which are generally different from each other. Each of the remaining $3n-3$ optical series will furnish one stratification having that particular value λ^* which will fit in with the direction of observation and the wave-length of the incident light used. In each case, provided consequent changes in the optical properties of the medium are brought about, two Raman lines given by (5) are produced

$$d\nu = \pm \nu^* \quad (5)$$

ν^* is the optical frequency corresponding to λ^* and will be quite different for different series. The important point is that while $d\nu$ in (4) depends very much on θ , $d\nu$ in (5) depends on θ only inasmuch as λ^* depends on θ . It has already been shown that even when the wave-length of the optical stratifications changes from ∞ to a dimension comparable to that of the wave-length of light in the visible region—which is indeed the range of λ^* as θ goes through all possible values—the frequency changes only by about one in a thousand. This enables us to overlook in practice, any possible dependence of the frequency of a Raman line on the direction of observation. We are further enabled to state that, while the limiting oscillation itself does not cause the diffuse scattering in any case, yet it may be chosen as a representative of a whole series, different members of which cause the

Raman line in question in practically the same position for different directions of observation.

3. *External and Internal Oscillations*

Reasons have been given to show why the limiting oscillations in a crystal may be studied as representative members of the various series. The first problem that confronts us, when we attempt to interpret the Raman spectrum of a crystal, is therefore, to find the correct unit cell.

For simplicity, let us consider in the first instance, a lattice and not a structure.† One way of choosing the unit cell, which is commonly employed in the crystallographic literature, is to choose a cell whose axes coincide with the crystallographic axes. Such a choice has the merit of clearly showing up the crystal system to which the lattice belongs. There is, however, a serious drawback in such a description because, the unit cell so chosen is not always of the smallest possible size. When the unit cell chosen is not of the smallest possible size, the labour involved in putting down the normal co-ordinates corresponding to the various limiting oscillations becomes considerable. On the other hand, if the unit cell is so chosen that its axes coincide with the primitive translations of the lattice, it is always of the smallest possible size and contains only one atom. It is immediately evident that there are no oscillations of the optical type and that no Raman scattering will be exhibited by a simple lattice.

If a crystal has a constitution which is to be regarded as a structure or a set of inter-penetrating lattices, it is easily seen that the unit cell of the smallest possible size will contain as many atoms in it as there are inter-penetrating lattices in the structure. These points may be referred to as the non-equivalent points of the structure, for no one of these points may be reached from any other by performing the primitive translations characteristic of the lattice. If there are n non-equivalent points in a structure, there will be $3n - 3$ optical series and in order to study the limiting oscillations of the whole crystal, we merely have to study the $3n - 3$ normal oscillations of the point group constituted by the n non-equivalent points. The three excluded degrees of freedom relate to the translations of the group as a whole.

We have now to classify the $3n - 3$ optical oscillations as external and internal ones. The external ones are sometimes referred to as the lattice

† The word lattice is used to denote an arrangement in which only one atom is located at each of the lattice points. A structure, on the other hand, denotes an arrangement in which a group of two or more atoms is located at each of the lattice points and has, therefore, to be looked upon as made up of a set of interpenetrating lattices.

oscillations. The distinction is not a very clear-cut one but the following may serve as useful criteria in the two cases. The possibility of the oscillations being classified in this manner rests on our being able to divide the n non-equivalent points into s groups such that the forces between one group and the other are comparatively feeble whereas the forces that exist between the members of any one group, are quite strong. In such a case, all the oscillations involving a movement of the s groups, only as entities, will generally exhibit low frequencies and may be termed external. The others, involving also movements of the individual members in each of the groups against themselves, will generally exhibit high frequencies and may be termed internal. The external oscillations may further be sub-divided into two classes, namely, rotational and translational, according as the movements of the groups are of a rotatory type or translatory type. In complicated crystals, where a full and detailed analysis is very difficult to carry through, a classification in this manner is likely to be of great help in explaining the results. In fact the purpose of the present paper is to show that the application of the group theory to a study of the limiting oscillations in a crystal enables us to classify them in the above manner and thus arrive at fruitful results even when the crystal structure is somewhat complicated. The foregoing sections constitute the necessary background and we shall now derive some important theorems and apply them to specific cases of practical interest.

4. Application of Group Theory

In all that follows, we need consider only the group of n non-equivalent points that are contained in the unit cell formed by taking for its sides, the primitive translations of a lattice or a structure as the case may be. The covering operations constitute a group and the Character Table with the irreducible representations of the group may easily be written out. Relation (6) enables us to find n_i , the number of times a particular irreducible representation Γ_i is contained in another representation Γ , if the group characters in both the representations are known.

$$n_i = \frac{1}{N} \sum_j h_j \chi_i(\mathbf{R}) \chi_j'(\mathbf{R}) \quad (6)$$

$\chi_i(\mathbf{R})$ and $\chi_j'(\mathbf{R})$ are respectively the characters of the group operation \mathbf{R} in the representations Γ_i and Γ and N is the order of the group and h_j is the number of group operations falling under the j th class. One of the main results of the present investigation follows from the fact that by suitably choosing the representation Γ and utilizing the characters $\chi_j(\mathbf{R})$ appropriate to it, we can confine ourselves to one or other of the several types of normal oscillations.

For example, if Γ is a representation defined by all the $3n$ cartesian co-ordinates which account for the entire freedom possessed by the n non-equivalent points in the unit cell, then

$$\chi_j'(\mathbf{R}) = \omega_{\mathbf{R}} (\pm 1 + 2 \cos \phi_{\mathbf{R}}) \quad (7)$$

and n_i , obtained by substituting (7) in (6), will include all types of normal modes, namely, translations, translatory and rotatory types of external oscillations and internal oscillations. (7) is a relation which is now well known and the method of deriving it has been given in the earlier literature already referred to. It will be evident from the linear transformation given below:

$$x \rightarrow x \cos \phi + y \sin \phi; \quad y \rightarrow -x \sin \phi + y \cos \phi; \quad z \rightarrow \pm z.$$

$\omega_{\mathbf{R}}$ is the number of atoms that remain invariant under the operation \mathbf{R} and the plus or the minus sign is to be used according as \mathbf{R} is a pure rotation through ϕ or a rotation through ϕ accompanied by a reflection. The atoms that change position under the operation \mathbf{R} do not contribute to the character.

If we want to confine ourselves only to translations (acoustic series), it is clear that $\omega_{\mathbf{R}}$ is to be put equal to unity for all \mathbf{R} because the whole group moves as one entity in these modes. In other words, Γ is defined by only three cartesian co-ordinates and it is easily seen that

$$\chi_j'(\mathbf{R}) = \pm 1 + 2 \cos \phi_{\mathbf{R}} \quad (8)$$

n_i obtained by substituting (8) in (6) may be denoted as $n_i(\mathbf{T})$, as the results now refer to translations or the acoustic series only.

Relation (9) gives the value of $\chi_j'(\mathbf{R})$, if we confine ourselves to the translatory type of external oscillations. As has already been explained in section 3, s is the number of groups into which the non-equivalent points may be divided, with due regard to the magnitudes of the forces that exist between them.

$$\chi_j'(\mathbf{R}) = [\omega_{\mathbf{R}}(s) - 1] (\pm 1 + 2 \cos \phi_{\mathbf{R}}) \quad (9)$$

$\omega_{\mathbf{R}}(s)$ represents the number of such groups that remain invariant out of the number s under an operation \mathbf{R} . The derivation of (9) is quite simple. Each one of the groups s has 3 degrees of translational freedom and the representation Γ in this case is defined by $3s$ cartesian co-ordinates. $\omega_{\mathbf{R}}(s) (\pm 1 + 2 \cos \phi_{\mathbf{R}})$ will be the character of an operation \mathbf{R} in such a representation. If the pure translations that have already been taken account of in (8) are to be excluded from this, we have to subtract $\pm 1 + 2 \cos \phi_{\mathbf{R}}$ from $\omega_{\mathbf{R}}(s) (\pm 1 + 2 \cos \phi_{\mathbf{R}})$ and we get (9).

Relation (10) gives the value of $\chi_j'(\mathbf{R})$, if we confine ourselves to the rotatory type of external oscillations. p in (10)

stands for the number of groups in s , which are constituted by

$$\chi_j'(\mathbf{R}) = [\omega_{\mathbf{R}}(s-p)] (1 \pm 2 \cos \phi_{\mathbf{R}}) \quad (10)$$

single atoms only. Such monatomic groups have no rotational degrees of freedom and $s-p$ is, therefore, the number of groups with each of which we have to associate three degrees of rotational freedom. $\omega_{\mathbf{R}}(s-p)$ represents the number that remain invariant out of the number $s-p$ under an operation \mathbf{R} . The derivation of (10) is also quite simple. It has already been shown by Rosenthal and Murphy (1936) that the character of an operation \mathbf{R} , in a representation defined by the three components of an angular momentum vector, is $1 \pm 2 \cos \phi_{\mathbf{R}}$ according as \mathbf{R} is a pure rotation through ϕ or a rotation through ϕ accompanied by a reflection. This is evident from the transformations given below:

$$l_x \rightarrow \pm l_x \cos \phi \pm l_y \sin \phi; \quad l_y \rightarrow \mp l_x \sin \phi \pm l_y \cos \phi; \quad l_z \rightarrow l_z$$

l_x, l_y and l_z are the components of the angular momentum and the series of signs given on the top are to be taken when the operation \mathbf{R} is a pure rotation around the Z axis. The alternative set relates to the case where \mathbf{R} is a rotation accompanied by a reflection. If there are $\omega_{\mathbf{R}}(s-p)$ separate units, each of which has three degrees of rotational freedom, the representation will be that defined by $3 \omega_{\mathbf{R}}(s-p)$ components of angular momentum and the character of an operation \mathbf{R} in such a representation is that given by (10). Those groups which are not invariant under the operation \mathbf{R} do not contribute to the character.

In order to get n_i' , the number of internal oscillations under each representation, we merely have to eliminate those given under the categories (8), (9) and (10) from n_i obtained by using (7). This is formally achieved by writing out the character as given by (11) and using it in the formula (6). The result may also be obtained by direct subtraction of the numbers under the categories of translation and translatory and rotatory types of external oscillations from the total number under each representation.

$$\chi_j'(\mathbf{R}) = [\omega_{\mathbf{R}} - \omega_{\mathbf{R}}(s)] (\pm 1 + 2 \cos \phi_{\mathbf{R}}) - \omega_{\mathbf{R}}(s-p) (1 \pm 2 \cos \phi_{\mathbf{R}}) \quad (11)$$

5. Calcite and Sodium Nitrate

In order that the utility of the above method may be fully appreciated, we shall first apply it to the well-known cases of calcite and sodium nitrate in this section. These two substances have the same crystal structures and their space group is D_{3d}^6 . Exactly similar considerations apply to both. The unit cell which is shown in Fig. 3 is an elongated rhombohedron and contains two molecules. The lattices are ionic and the co-ordinates of the atoms in the case of calcite are given below,

$$\begin{array}{l} \text{Ca (1, 2): } \frac{1}{4} \frac{1}{4} \frac{1}{4}; \quad \frac{3}{4} \frac{3}{4} \frac{3}{4} \\ \text{C (3, 4): } 0 \ 0 \ 0; \quad \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2} \\ 0 \quad (5 \text{ to } 10) \end{array}$$

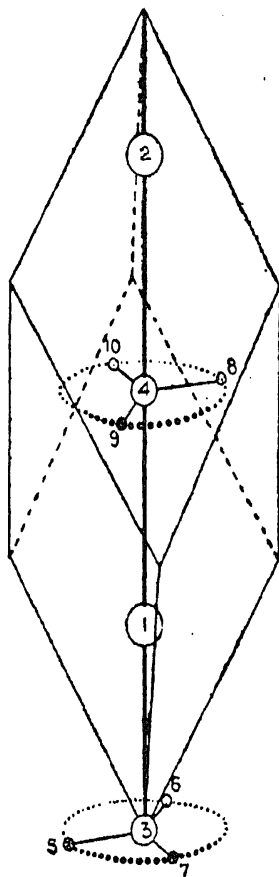


FIG. 3

In the notation of the present paper, $n=10$, $s=4$ (two CO_3 groups and two Ca atoms) and $p=2$ (two Ca atoms).

The operations of this group may be expressed as follows:

E (Identity)

$$2 S_{\frac{1}{2}} \begin{cases} (1) (2) (3, 4) (5, 9, 7, 8, 6, 10) \\ (1) (2) (3, 4) (5, 10, 6, 8, 7, 9) \end{cases}$$

$$2 C^1 \begin{cases} (1) (2) (3) (4) (8, 10, 9) (5, 7, 6) \\ (1) (2) (3) (4) (8, 9, 10) (5, 6, 7) \end{cases}$$

$$i \quad (1) (2) (3, 4) (5, 8) (6, 9) (7, 10)$$

$$3\sigma_v \text{ (glide)} \begin{cases} (1, 2) (3, 4) (5, 8) (6, 10) (7, 9) \\ (1, 2) (3, 4) (5, 10) (6, 9) (7, 8) \\ (1, 2) (3, 4) (5, 9) (6, 8) (7, 10) \end{cases}$$

$$3 C_2 \begin{cases} (1, 2) (3) (4) (5) (8) (6, 7) (9, 10) \\ (1, 2) (3) (4) (6) (9) (5, 7) (8, 10) \\ (1, 2) (3) (4) (7) (10) (5, 6) (8, 9) \end{cases}$$

The Character Table and the values of n_i , n_i' , etc., are given below :

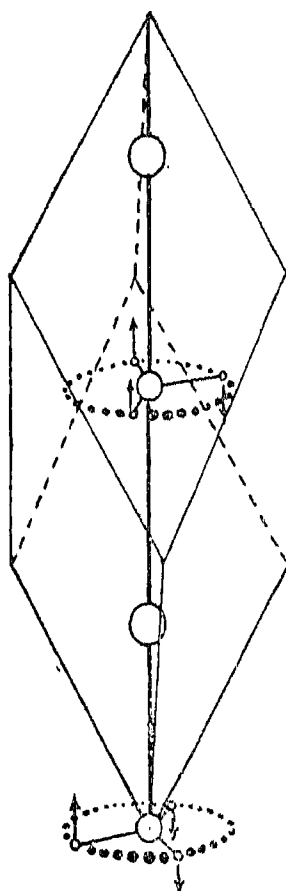
D_{2d}^6	E	$2S^{\frac{1}{2}}$	$2C^1$	i	$3\sigma_v$	$3C_2$	External						
							n_i	T	T'	R'	n_i'	Raman	Infra-red
A_1	..	1	1	1	1	1	1	0	0	0	1	p	f
A_2	..	1	1	1	-1	-1	3	0	1	1	1	f	f
B_1	..	1	-1	1	-1	1	4	1	1	1	1	f	p
B_2	..	1	-1	1	-1	-1	2	0	1	0	1	f	f
E_1	..	2	1	-1	-2	0	6	1	2	1	2	f	p
E_2	..	2	-1	-1	2	0	4	0	1	1	2	p	f
$\omega_R(n_i)$..	10	2	4	2	0	4						
$\omega_R(s)$..	4	2	4	2	0	2						
$\omega_R(s-p)$..	2	0	2	0	0	2						
$h_j\chi_j'(n_i)$..	30	0	0	-6	0	-12						
$h_j\chi_j'(T)$..	3	0	0	-3	3	-3						
$h_j\chi_j'(T')$..	9	0	0	-3	-3	-3						
$h_j\chi_j'(R')$..	6	0	0	0	0	-6						

In this and other tables that follow, n_i , T, T', R' and n_i' stand for the total number of oscillations, translations, translatory type of external oscillations, rotatory type of external oscillations and the internal oscillations respectively. $\chi_j'(n_i)$, $\chi_j'(T)$, $\chi_j'(T')$ and $\chi_j'(R')$ have been obtained in accordance with the values given for them in the relations (7), (8), (9) and (10) respectively. The method of finding out whether the lines coming under a certain representation are Raman active or infra-red active has been described in the earlier literature and we need not go into it here. p denotes that all the oscillations coming under that representation are permitted to appear and f denotes that they are forbidden. The following features may now be noted. Because there are two CO_3 ions in the unit cell, each internal oscillation of the free CO_3 ion splits into two in the crystal. The extent of splitting will naturally depend upon the forces that are present in the crystal. Since $s=4$, besides the translations which represent the acoustic series, there are present a large number of external oscillations, both of the rotatory type and the translatory type. If we are not immediately interested in the internal oscillations, it is quite easy to picture the external modes coming under each representation in them, because all the four groups are to be regarded as entities. Only the CO_3 ions take part in the rotatory type of external

oscillations as the calcium ions (monatomic groups) come under the p class. As an example, we give below the symbolic representation of the two external modes coming under the representation E_2 and which are Raman active.

$$\left. \begin{aligned} T'(a) &= x_3 - x_4 \\ T'(b) &= y_3 - y_4 \\ R'(a) &= l^3_x + l^4_x \\ R'(b) &= l^3_y + l^4_y \end{aligned} \right\} \dots \dots \dots E_2$$

$T'(a)$ and $T'(b)$ and similarly $R'(a)$ and $R'(b)$ are degenerate. Z axis is taken along the trigonal axis and the X and Y axes may lie anywhere in the plane perpendicular thereto. x_3 indicates that the group containing atom 3 undergoes a displacement of one unit in the direction of the X axis. x_4, y_3 , etc., occurring in the normal co-ordinates relating to the T' type are to be similarly interpreted. l^3_x indicates that the group containing atom 3 undergoes a rotation such that it possesses unit angular momentum around the X axis. l^4_x, l^3_y , etc., occurring in the normal co-ordinates relating to the R' type are to be similarly interpreted. The method of writing down these normal co-ordinates is quite easy and is explained elsewhere. With the help of the group operations and the transformation matrices for x, y, z and l_x, l_y, l_z already given in a foregoing section, it may be verified that the characters of the normal co-ordinates given above for various R are just those given under the irreducible representation E_2 . One of these modes is represented diagrammatically in Fig. 4. They are identical with the modes



obtained by a more elaborate method and described in an earlier paper by the author and Venkatarayudu (1939) as Q_{15} and Q_{17} .

In a similar manner, we can write down the normal co-ordinates relating to all the external oscillations without much labour and without reference to the internal modes. Such an investigation need not be pursued for this case as the results are already well known. In fact, if only the external modes and their classification are needed, the group operations also could have been written in a much simpler manner as will be evident from the cases that are dealt with in the following sections.

6. *Some Special Cases*

Such a simplification will be particularly useful, when experimental results show that the intermolecular forces in the crystal are not very important. This may easily be inferred, especially in cases where there is no degradation of symmetry from the free molecule to the crystal, if we find that the Raman lines obtained in the liquid exhibit a general one to one correspondence with those obtained in the same substance in the crystalline state even though there may be two or more molecules per unit cell in the latter.* In such cases, no more information will be obtained by making a detailed study of the internal frequencies for a group of molecules than that available from a study of the single molecule. On the other hand, much of the interest will centre round the lattice oscillations and the special methods outlined in the foregoing pages will be particularly useful. The classification of the lattice oscillations into the translatory and the rotatory types is also of some help, if the following principles are borne in mind in interpreting the experimental results. The translatory type of oscillations are likely to give rise to relatively low frequencies in most cases and even these will be of low intensity in Raman scattering as the changes caused in the polarizability of the crystal cannot be appreciable. On the other hand, the rotatory type of oscillations will result in intense Raman lines, if the rotating groups are strongly optically anisotropic.

1. *If there is only one molecule per unit cell and if centre of inversion is a covering operation of the structure, the crystal may exhibit three lattices oscillations of the rotatory type if there is no degeneracy.*

This statement is almost self-evident and follows from the fact that the three oscillations of the rotatory type are symmetric to the operation of

* The resemblance referred to is of a general nature. One or two of the lines that occur in the crystal may not appear in the liquid and *vice versa* on account of the different symmetries in the two cases. The essential point is that there is no splitting of the majority of the lines as we pass from the liquid to the crystal.

inversion. For crystals of trigonal, tetragonal and hexagonal classes, this number reduces to two and for crystals of the cubic class, it reduces to one merely as a result of the symmetry. As the intensity will also be governed by the optical anisotropy of the molecule, the only lattice line in the case of cubic crystals will have zero intensity because the molecule itself should possess cubic symmetry and one of the lattice lines (non-degenerate one) in the trigonal, tetragonal and hexagonal classes will also have zero intensity.

2. *If there are two molecules per unit cell and if the centre of inversion, as a covering operation of the structure, is located at one of the molecules, all lattice oscillations of the translatory type will be Raman inactive. Some of them may be infra-red active.*

This follows from the fact that the normal co-ordinates relating to such oscillations, are always anti-symmetric to the operation of inversion.

3. *If in the above case, the centre of inversion is located midway between the two molecules, all lattice oscillations of the translatory type will be symmetric to the operation of inversion and some of them may be Raman active. All of them will be infra-red inactive.*

7. *Naphthalene, Diphenyl, Anthracene, etc.*

All the substances discussed in this section crystallize in the monoclinic prismatic class having the space group C_{2h}^6 . The unit cell in each case contains two molecules. They have been specially chosen here with a view to bring out the fact that the crystal structure plays a major part in determining the character of the low frequency Raman spectrum while the exact chemical nature of the substance has no appreciable influence on it. We start by stating that these crystals melt at comparatively low temperatures and that the Raman lines of naphthalene in the liquid state show a one to one correspondence with those obtained in the crystal (Nedungadi, 1941). Lines do not show any systematic doubling even though there are two molecules in the unit cell. A study of the internal oscillations may, therefore, be confined with advantage to the free molecule. We shall now apply the methods of the foregoing sections to these cases and obtain the results that are to be expected in the low frequency region of the Raman spectrum. Fig. 5 represents the unit cell for naphthalene which is a typical representative of this class. The two molecules are numbered 1 and 2. In the notation of the present paper, $s=2$ and $p=0$. These molecules have their lengths roughly parallel to the C axis and their planes making angles of about $+65^\circ$

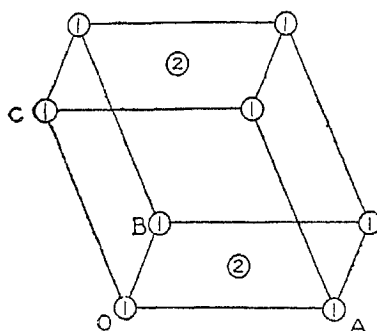


FIG. 5

and -65° with the (010) plane. The group operations may be written out as

$$\begin{aligned} E & \text{ (Identity)} \\ C_2 & \text{ (screw) } \dots \dots (1, 2) \\ i & \dots \dots \dots (1) (2) \\ \sigma_h & \text{ (glide) } \dots \dots (1, 2) \end{aligned}$$

The Character Table and other relevant features are given below :—

C_{2h}^5	E	C_2	i	σ_h	External				
					T	T'	R'	Raman	Infra-red
A_1 ..	1	1	1	1	0	0	3	p	f
A_2 ..	1	-1	1	-1	0	0	3	p	f
B_1 ..	1	1	-1	-1	1	2	0	f	p
B_2 ..	1	-1	-1	1	2	1	0	f	p
$\omega_R (s)$..	2	0	2	0					
$\omega_R (s-p)$	2	0	2	0					
$h_j \chi_j' (T)$..	3	-1	-3	1					
$h_j \chi_j' (T')$..	3	1	-3	-1					
$h_j \chi_j' (R')$	6	0	6	0					

Centre of inversion in this case is located at the molecule 1 and it comes under special case number 2 of the previous section. We do not get any Raman active lattice oscillations of the translatory type. We should, however, expect six oscillations of the rotatory type. The corresponding normal co-ordinates may easily be written out in the following manner:—

$$\left. \begin{array}{l} l_x^1 - l_x^2 \\ l_y^1 - l_y^2 \\ l_z^1 + l_z^2 \end{array} \right\} \dots \dots A_1; \quad \left. \begin{array}{l} l_x^1 + l_x^2 \\ l_y^1 + l_y^2 \\ l_z^1 - l_z^2 \end{array} \right\} \dots \dots A_2$$

directions parallel to the Z axis and any two mutually perpendicular directions in the XY plane may be chosen as the X and Y axes. It may be noted that the three modes, A_1 , A_2 and A_3 , differ from those coming under A_1 in the case of a diatomic crystal in relative phase difference between the two molecules. For example, when A_1 and A_2 both molecules are rotating about the Z axis in phase, in A_3 they do so in opposite phases. As has already been pointed out, however, the mass factors are not appreciable, the frequencies of these two groups of modes are not far apart and we can not expect to record sharp sound bands. Results are not available for naphthalene. The lattice oscillations observed in naphthalene, diphenyl, and chlorobenzene and *p*-dibromobenzene, all of which belong to this class, are given below.

Naphthalene	47	73	109 and 124
Diphenyl	47	75	150
<i>p</i> -Dibromobenzene	41	55	82
Chlorobenzene	38	..	93

The Raman lines are in general broad in most cases, the lines are broad. The most prominent is that at 20 cm.^{-1} , recorded by Vuks (1937) in the latter two substances, is not included in the above table as it has not been confirmed by other investigation. The highest frequency in naphthalene has split into two, apparently because of its nearness to the sum of the other two frequencies at 47 and 73. Since all the three lines are expected to be of the same structure and as they all come under the same representation, it is difficult to assign any one of the frequencies to a particular mode. It is not, however, too easy to predict their behaviour under directional irradiation. Consequently, one may not expect in these cases, such a clear-cut identification of the lattice oscillations into the symmetric, the anti-symmetric and the degenerate types as has been obtained in simpler structures like diatomic and diatomic crystals. The high intensity of the Raman line at 20 cm.^{-1} in naphthalene suggests that it arises from rotatory movements of the molecules about the Z axis of C_{2v} because the largest optical anisotropy in the naphthalene crystal is in the XY plane.

Effect of Crystal Modification on the Low Frequency Spectrum

Several attempts have been made to detect changes in the Raman spectrum of a substance as we pass from one crystalline modification to another. On account of experimental difficulties these have been mostly

confined hitherto, to the internal oscillations although prominent changes are not to be expected in that region but should be looked for only in the low frequency region. In order to illustrate this point, we shall consider here the cases of aragonite and potassium nitrate. The crystal structure of aragonite bears to that of calcite, the same relationship as that existing between the structures of potassium nitrate and sodium nitrate. Unfortunately, the lattice oscillations of these substances have not been studied in detail in their Raman spectra and only meagre and conflicting results are available. Hence it is not proposed to compare the conclusions with the experimental data. Nevertheless, the analysis is given here as the structures are of great importance.

The space group is V_h^{16} and the unit cell of the smallest size, a projection of which is shown in Fig. 6, contains 4 molecules of CaCO_3 . Since we are interested only in the lattice oscillations, we need consider 8 groups ($s=8$) on the whole, of which 4 ($p=4$) are monatomic.*

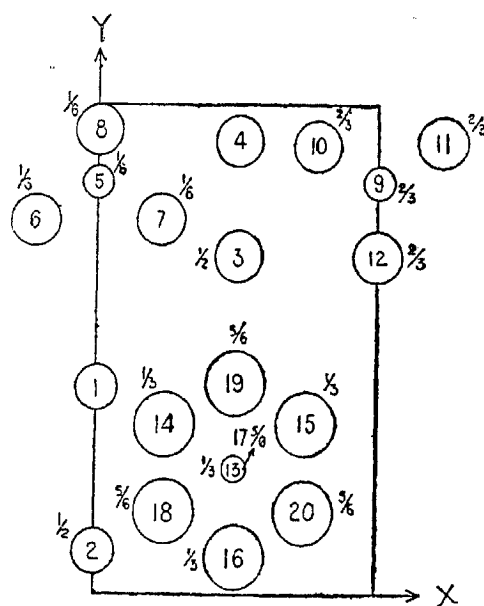


FIG. 6

The groups are numbered as follows:

Ca .. 1, 2, 3 and 4

CO_3 .. 5, 9, 13 and 17

Atoms numbered, 6, 7, 8, 10, 11, 12, 14, 15, 16, 18, 19, 20 are the oxygens and they need not be considered separately as they go with the corresponding carbons.

* The internal oscillations in this case have been considered in an earlier paper.

The operations of the group are:

E	(Identity)										
C ¹	(screw $\frac{1}{2}$ to Z)	(1, 2)	(3, 4)	(5, 9)	(13, 17)						
C ₂	(screw $\frac{1}{2}$ to Y)	(1, 4)	(2, 3)	(5, 17)	(9, 13)						
C ₂ '	(screw $\frac{1}{2}$ to X)	(1, 3)	(2, 4)	(5, 13)	(9, 17)						
<i>i</i>		(1, 2)	(3, 4)	(5, 9)	(13, 17)				
σ_h		(1)	(2)	(3)	(4)	(5)	(9)	(13)	(17)
σ_{η}	(glide)	(1, 3)	(2, 4)	(5, 13)	(9, 17)				
σ_{η}'	(glide)	(1, 4)	(2, 3)	(5, 17)	(9, 13)				

The Character Table and other relevant features are given below:

V_h^{11}	E	C ¹	C ₂	C ₂ '	<i>i</i>	σ_h	σ_{η}	σ_{η}'	External				
									T	T'	R'	Raman	Infra-red
A _{1g}	..	1	1	1	1	1	1	1	0	4	1	<i>p</i>	<i>f</i>
A _{2g}	..	1	-1	1	-1	1	-1	-1	0	2	2	<i>p</i>	<i>f</i>
B _{1g}	..	1	1	-1	-1	1	1	-1	0	4	1	<i>p</i>	<i>f</i>
B _{2g}	..	1	-1	-1	1	1	-1	1	0	2	2	<i>p</i>	<i>f</i>
A _{1u}	..	1	1	1	1	-1	-1	-1	0	2	2	<i>f</i>	<i>f</i>
A _{2u}	..	1	-1	1	-1	-1	1	-1	1	3	1	<i>f</i>	<i>p</i>
B _{1u}	..	1	1	-1	-1	-1	-1	1	1	1	2	<i>f</i>	<i>p</i>
B _{2u}	..	1	-1	-1	1	-1	1	-1	1	3	1	<i>f</i>	<i>p</i>
$\omega_R(s)$..	8	0	0	0	0	8	0	0				
$\omega_R(s-p)$..	4	0	0	0	0	4	0	0				
$h_j \chi_j'$ (T)	..	3	1	-1	-1	-3	1	1	1				
$h_j \chi_j'$ (T')	..	21	1	1	1	3	8	-1	-1				
$h_j \chi_j'$ (R')	..	12	0	0	0	0	-4	0	0				

We see from the table that, besides a large number of translatory type of oscillations, we should expect to get in the Raman spectrum, six oscillations of the rotatory type under different classes. These six normal co-ordinates are easily written down in the following manner:

$$\begin{array}{rcl}
 l_z^5 + l_z^9 - l_z^{13} - l_z^{17} & \dots\dots\dots & A_{1g} \\
 \left. \begin{array}{l} l_z^5 + l_z^9 - l_z^{13} - l_z^{17} \\ l_y^5 + l_y^9 + l_y^{13} + l_y^{17} \end{array} \right\} & \dots\dots\dots & A_{2g} \\
 l_z^5 + l_z^9 + l_z^{13} + l_z^{17} & \dots\dots\dots & B_{1g} \\
 \left. \begin{array}{l} l_x^5 + l_x^9 + l_x^{13} + l_x^{17} \\ l_y^5 + l_y^9 - l_y^{13} - l_y^{17} \end{array} \right\} & \dots\dots\dots & B_{2g}
 \end{array}$$

Normal co-ordinates coming under A_{1g} and B_{1g} , although Raman-active, involve rotations of the CO_3 groups about the Z axis and since the XY plane is nearly a plane of optical symmetry, we can confidently conclude that these modes will not produce appreciable intensities in Raman scattering. Under A_{2g} and B_{2g} , we should expect four lines appearing as two close doublets or two broad bands covering the whole series. Their behaviour, under directional excitation, will be markedly reciprocal to that of the total symmetric internal oscillations. Besides these, we may expect a few lines arising from the translatory type of oscillations. They will be characterized by comparatively low frequencies and possibly in some cases a behaviour which is not reciprocal to that of the total symmetric oscillation.

9. Crystals Containing Linear Molecules

As a typical example of this class, we shall choose mercurous chloride. This substance crystallizes in the tetragonal system under the space group D_{4h}^{17} . The tetragonal unit cell contains two molecules of Hg_2Cl_2 and the lattice is molecular but the unit cell of the smallest possible size contains only one molecule. The formulæ given in the foregoing sections do not apply to this case as the molecule is linear and is a special type of group having only two degrees of rotational freedom. It is, however, clear that there will be no lattice oscillations of the translatory type and there will be only one doubly degenerate external oscillation of the rotatory type. The crystal structure of this substance is shown in Fig. 7. The group operations,

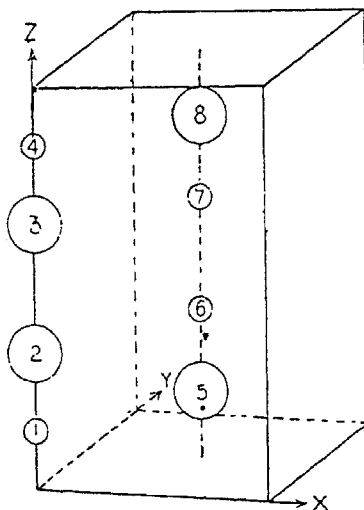


FIG. 7

Character Table, etc., are given below in full* so as to cover the internal oscillations also.

Mercury atoms are numbered 1 and 4. Chlorine atoms are numbered 2 and 3. 6 and 7 are equivalent to 1 and 4. 5 and 8 are equivalent to 2 and 3. In this case $s=1$ and $p=0$. The operations of the group are:

- E .. (Identity)
- 2 C¹ .. (1) (2) (3) (4)
- C² .. (1) (2) (3) (4)
- 2 C₂ .. (14) (23)
- 2 C₂' .. (14) (23)
- i .. (14) (23)
- 2 S¹ .. (14) (23)
- σ_h .. (14) (23)
- 2σ_v .. (1) (2) (3) (4)
- 2σ_v' .. (1) (2) (3) (4)

D _{4h} ¹⁷											External						
	E	2 C ¹	C ²	2 C ₂	2 C ₂ '	i	2 S ¹	σ _h	2σ _v	2σ _v '	n _i	T	T'	R'	n _i '	Raman	Infrared
A _{1g} ..	1	1	1	1	1	1	1	1	1	1	2	0	0	0	2	p	f
A _{2g} ..	1	1	1	-1	-1	1	1	1	-1	-1	0	0	0	0	0
B _{1g} ..	1	-1	1	1	-1	1	-1	1	1	-1	0	0	0	0	0
B _{2g} ..	1	-1	1	-1	1	1	-1	1	-1	1	0	0	0	0	0
E _{1g} ..	2	0	-2	0	0	2	0	-2	0	0	2	0	0	1	1	p	f
A _{1u} ..	1	1	1	1	1	-1	-1	-1	-1	-1	0	0	0	0	0
A _{2u} ..	1	1	1	-1	-1	-1	-1	-1	1	1	2	1	0	0	1	f	p
B _{1u} ..	1	-1	1	1	-1	-1	1	-1	-1	1	0	0	0	0	0
B _{2u} ..	1	-1	1	-1	1	-1	1	-1	1	-1	0	0	0	0	0
E _{1u} ..	2	0	-2	0	0	-2	0	2	0	0	2	1	0	0	1	f	p
ω _R ..	4	4	4	0	0	0	0	0	4	4							
ω _R (s) ..	1	1	1	1	1	1	1	1	1	1							
h _j χ _j ' (n _i)	12	8	-4	0	0	0	0	0	8	8							
h _j χ _j ' (T)	3	2	-1	-2	-2	-3	-2	1	2	2							
h _j χ _j ' (T')	0	0	0	0	0	0	0	0	0	0							

* Although, in this paper, we are mainly dealing with the lattice oscillations, this case is considered in some detail with a view to correct some of the mis-statements made in the earlier paper (Reference 1). These have arisen on account of the fact that a larger unit cell than is proper had been wrongly chosen at that time.

Corresponding to the 12 degrees of freedom of the four atoms in the unit cell, we get three translations (acoustic series), three single and three doubly degenerate limits (optical series) of which one is an external oscillation of the rotatory type and is Raman active. The normal co-ordinates are given below:

$$\left. \begin{aligned} Q_1' (i) &= m_2 (z_1 - z_4) + m_1 (z_2 - z_3) \\ Q_2' (i) &= z_1 - z_4 - z_2 + z_3 \\ Q_x (T) &= x_1 + x_2 + x_3 + x_4 \\ Q_y (T) &= y_1 + y_2 + y_3 + y_4 \\ Q_{4a}' (i) &= m_2 (x_1 + x_4) - m_1 (x_2 + x_3) \\ Q_{4b}' (i) &= m_2 (y_1 + y_4) - m_1 (y_2 + y_3) \end{aligned} \right\} \begin{array}{l} \dots \dots \dots A_{1g} \\ \dots \dots \dots E_{1g} \end{array}$$

By altering the signs of terms with suffixes 2 and 4 in the normal co-ordinates occurring under A_{1g} , we obtain Q_2 and $Q_3' (i)$ coming under A_{2g} . Similarly, we obtain $Q_{5a}' (i)$, $Q_{6a}' (L)$ and their b -components coming under E_{1g} from those given under E_{1g} .

$Q_{6a}' (L)$ and its b -component represent the rotatory type of external oscillation. This is likely to give rise to an intense Raman line but probably of a very low frequency. It has not so far been recorded. Besides this, we should expect three Raman lines of the internal type, two of which are of the total symmetric class and the third is of the degenerate class. Three strong lines at 165 (6), 273 (4) and 295 (1) have been observed in the Raman spectrum of Hg_2Cl_2 crystals. The two higher frequencies may be identified with those coming under A_{1g} whereas the one at 165 may be identified with the degenerate oscillation. An additional weak line at 320 has also been recorded and this is probably the overtone of the forbidden fundamental ν_4 whose value, by analogy with the case of acetylene and such other molecules, may be expected to lie close to 165.

10. Summary

In spite of what has occasionally been stated in the literature (Sirkar, 1937), it is believed that there are no special reasons to assume that the low frequency lines that occur in the Raman spectra of crystals have an origin that is essentially different from that ascribed to the high frequency lines. They are all regarded as representatives of the various optical series into which the normal oscillations of a crystal may be divided. Reasons have been given to show why the limiting oscillation in each series may be selected as a representative of that whole series and its characters studied. For convenience in description, these are divided into three classes, namely, the internal, the rotatory type of external and the translatory type of external

ones. Formulæ, which help us to classify the normal oscillations in the above manner, are developed and applied to some typical cases.

In interpreting the results, two guiding principles are to be borne in mind. All the oscillations coming under the translatory type, especially, in organic crystals and others of low melting point, will be characterized by low or vanishingly small frequencies and the corresponding Raman lines, if they occur at all, will be weak. On the other hand, those coming under the rotatory type will be characterized by relatively large frequencies and generally give rise to strong Raman lines if the rotating group has a marked optical anisotropy. Since the region under investigation is, however, very crowded, we should expect several complications such as overlapping, splitting, etc., to set in, and these make the interpretation of the experimental results somewhat difficult.

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