

THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: I. NAPHTHALENE

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1. Introduction

ONE of the most remarkable and significant facts in crystal physics brought to light by recent investigations is the appearance of monochromatic vibrations of very low frequency as a very general feature in the lattice spectra of crystalline solids. The Raman spectra of practically all crystals, both of the inorganic and the organic class, and of the most varied type, *e.g.*, elements, ionic and molecular lattices, exhibit lines with low frequency shifts. These lines (of which there may be several) appear with the solid, often with notable intensity and sharpness, but disappear or else are replaced by a continuous spectrum when the substance melts or passes into solution. The literature of the subject has been reviewed by the author¹ in a paper in the Raman Jubilee Volume (1938) where studies of the phenomenon in several organic crystals are also described. The origin of these low frequency lines is now well understood to be due to the oscillations of the atoms, ions, or molecules in the lattice with respect to one another, such oscillation being either hindered translations or hindered rotations according to circumstances. Such vibrations being of low frequency, they are strongly excited by thermal agitation and appear with both diminished and increased frequency in the spectra. Simple considerations indicate that a large proportion of the thermal energy of the solid, especially in organic crystals where there are several molecules in the unit cell, must be taken up by such low frequency monochromatic vibrations. It is also evident that such vibrations would powerfully influence the structure amplitudes of the lattice planes and hence must play a notable part in determining the effects resulting from the passage of X-rays through the crystal.

Considering the experimental facts stated above and also the theoretical ideas developed by Sir C. V. Raman in a paper appearing earlier in these

Proceedings; it follows that the passage of X-rays through an organic crystal should result in the excitation of the specific modes of vibration having these low frequencies and hence also in a dynamic reflection of the X-rays by the lattice planes whose structure amplitudes are varied by such vibrations. Further, the character of these reflections, *viz.*, their intensity, geometric direction, sharpness and their temperature variations should exhibit the closest correlation with the geometry, frequency and amplitude of these modes of vibration. As the frequencies of these modes are usually low (30 to 100 cm.^{-1} in spectroscopic units), their intensity should show a strong temperature dependence, diminishing rapidly with a fall of temperature, but reaching a limiting value at the lowest temperatures. A study of the typical case of pentaerythrytol from this point of view has already appeared in an earlier paper by the present writer in these *Proceedings*. In order to illustrate other aspects of the subject, a detailed study has been made of three cases, *viz.*, naphthalene, benzophenone and urotropin, in which we have a detailed knowledge both of the crystal structure and also of the low frequency infrared vibrations from the studies of their Raman spectra.

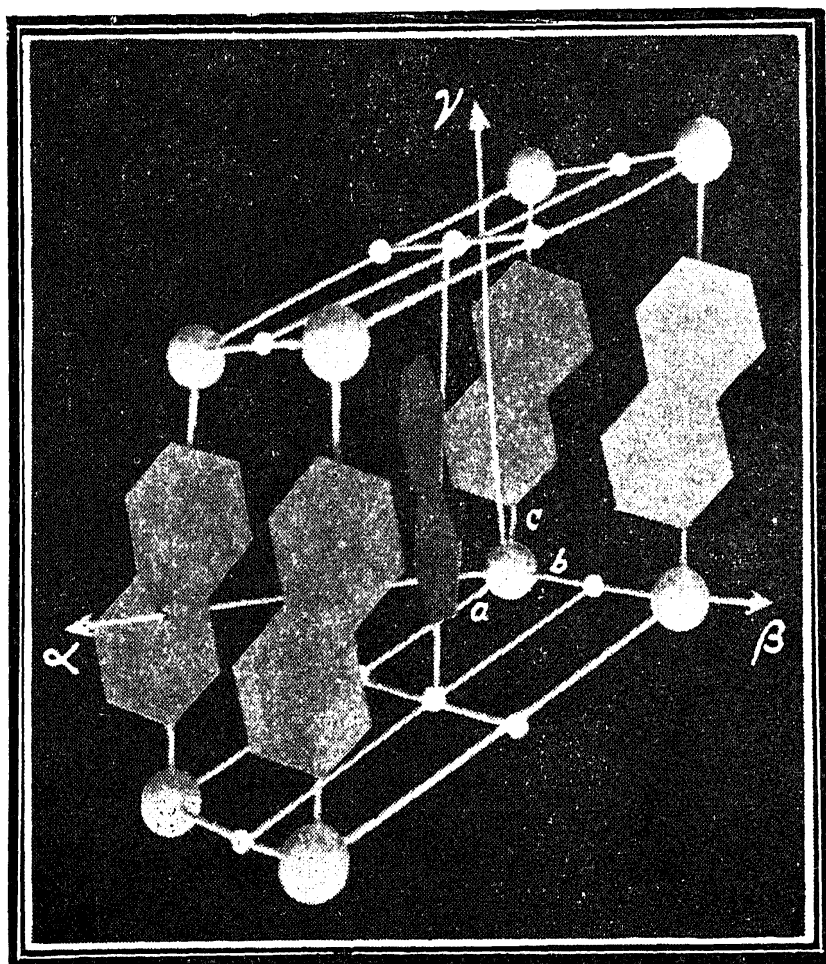


FIG. 7. Crystal Model of Naphthalene

2. Crystal Structure and Lattice Spectrum of Naphthalene

Naphthalene $C_{10}H_8$ belongs to the monoclinic prismatic class in the space group C_{2h}^5 . The unit cell has the dimensions $a = 8.29$, $b = 5.95$ and $c = 8.68$ Å and $\beta = 122^\circ 42'$ (Bragg,² 1921; Banerji,³ 1930; and Robertson,⁴ 1933) and contains 2 molecules of $C_{10}H_8$. The molecule consists of two fused benzene rings lying in a plane. The orientation of the molecules in the crystal is illustrated in Fig. 7* taken from a paper recently published by Nedungadi. The long axis of the molecule makes angles of $\phi = 115^\circ.3$, $\psi = 102^\circ.6$ and $\omega = 28^\circ.7$ and the short axis $\phi' = 71^\circ.2$, $\psi' = 28^\circ.8$, $\omega' = 69^\circ.1$ respectively with a , b and c' axes (c' is perpendicular to a and b) of the crystal. The orientation of the second molecule in the centre of unit cell is given by the glide plane reflection of the corner molecule in the 010 plane, the glide plane being parallel to the 'a' axis. The above crystal structure of naphthalene is in agreement with the magnetic and optical anisotropies observed in the crystal.

The molecule of naphthalene belongs to the symmetry class D_{2h} (Kohlrausch,⁵ 1935; Bonino,⁶ 1936; Saxena,⁷ 1938) and has 48 normal modes of internal vibration, 24 of which are active in the Raman effect and 20 in the infra-red. In the crystal these internal vibrations of the two molecules in the unit cell presumably remain the same, as is shown by the identity of the Raman spectrum of the substance in the liquid and in the crystalline state (Nedungadi,⁸ 1941). The total of twelve degrees of rotational and translational freedom of the two molecules together, give rise to the lattice oscillations and the Debye elastic waves in the crystal, *nine* of them being assigned to the former and *three* to the latter. Thus it is clear that the elastic vibrations would contribute only a relatively small part of the thermal energy of the crystal at the room temperature. Since the crystal possesses a low order of symmetry, the nine lattice oscillations are most probably all non-degenerate. In the Raman spectrum of naphthalene crystal, four lines have been observed (Gross and Vuks,⁹ 1935, 1936; Venkateswaran,¹ 1938; and Nedungadi,⁸ 1941) which have to be definitely attributed to the lattice vibrations. Fig. 8 in the accompanying Plate reproduces the spectrum of a single crystal of naphthalene photographed by Nedungadi. As the frequencies are low, they are thermally excited at the room temperature as is shown by the almost equal intensities for the Stokes and anti-Stokes Raman lines in the spectrum.

3. Dynamic X-Ray Reflections in Naphthalene

The X-ray analogue of the Raman effect in naphthalene was studied by Bhagavantam and Bhimasenachar¹⁰ (1941). They observed the dynamic

* In Fig. 7, a , β and γ are the axes of the optical polarisability ellipsoid.

X-ray reflections by 001, 002 and $20\bar{1}$ planes of naphthalene, but these were recorded only when the crystal orientations were nearly the same as those required for the static reflections. For other orientations and other planes they were unable to observe the spots presumably because the source of X-rays used by them was not sufficiently strong. The more powerful equipment available at this Institute has made a thorough investigation possible. A thin plate of naphthalene crystal, prepared from a solution of a mixture of alcohol and water, is mounted on a goniometer with the 001 (cleavage) plane lying in a vertical plane. The source of X-rays was a demountable self-rectifying filament X-ray tube with copper anti-cathode and run at 25 mA and 45 kilo-volts. As the crystal sublimates rapidly, a series of twelve Laue photographs were taken in succession with an exposure time of half an hour in each case. Figs. 1 and 2 in the accompanying Plate are the patterns obtained with the incident beam making a glancing angle of $6^{\circ} \cdot 45'$ and $11^{\circ} \cdot 42'$ with the 001 plane, being thus very near the Bragg angles for the first order ($6^{\circ} \cdot 5'$) and for the second order ($12^{\circ} \cdot 7'$) reflections from that plane for the copper K_{α} radiations. It may be noticed that the static reflections are recorded with great intensity in both the photographs. But there is only a faint indication of the dynamic reflection of the first order in either case. In Fig. 1, the second order dynamic reflection is recorded weakly as a diffuse spot in the same line as the central spot and the 001 Laue spot. At the same time the *weak* Laue spot in a direction making an angle of nearly 120° with the 001 Bragg reflection, is accompanied by a *strong* dynamic reflection. In Fig. 2, the latter is very close to the Laue spot showing that the crystal is very near the Bragg setting for the corresponding crystal plane. From the distance of this spot from the centre and the intensity of the Bragg reflection and the setting of the crystal, the plane is identified as $0\bar{1}1$ plane. Figs. 3-6 are taken with the crystal rotated both about the vertical and horizontal axes. It may be observed that several crystal planes give rise to Raman reflections. For the normal incidence on the 001 plane of naphthalene, the X-rays are making a glancing angle of $4^{\circ} \cdot 15'$ with the $20\bar{1}$ plane, which varies only slightly as the crystal is rotated about a vertical axis. Thus in Figs. 3 and 4, for which the 001 plane lies in a vertical plane, the angles of incidence of the Laue spot due to $20\bar{1}$ plane, which may be observed vertically above the central spot, are $4^{\circ} \cdot 59'$ and $4^{\circ} \cdot 44'$. The crystal planes corresponding to the other dynamic reflections could be identified from their position on the plate, the angle they make with $20\bar{1}$ reflection and with each other and the known orientation of the crystal.

Table I gives the indices of these planes, the glancing angles* of incidence θ_i and the angle of reflection ($\theta_i + \phi$), the spacing d calculated from the relation, $2d \sin \frac{(\theta_i + \phi)}{2} = n\lambda$ for the Raman reflection, the estimated intensity

TABLE I

No.	Indices of Plane	Ref. to Fig.	θ_i	$\frac{1}{2}(\theta_i + \phi)$ for $K\alpha$	Lattice Spacing in A.U.		Intensity (Dynamic)	Intensity (Static)	
					Experimental	Calculated		Bragg	Robertson F'
1	001	1	6°·45'	5°·55'	7·476	7·3	w.	v.st.	27·5
		2	11°·42'	v.w.	"	"
2	002	1	6°·45'	12°·9'	3·65	3·65	"	..	15·5
		2	11°·42'	w.	..	"
3	0 $\bar{1}$ 1	1	12°·50'	9°·33'	4·63	4·66	v.st.	0	6
		2	11°·0'	9°·33'	"	"	"	..	"
4	110	3	6°·54'	9°·40'	4·52	4·58	st.	st.	37
5	11 $\bar{1}$	4	11°·12'	9°·27'	4·68	4·63	med.	med.	..
6	120	3	17°·42'	16°·30'	2·7	2·77	w.	..	12·5
7	20 $\bar{1}$	3	4°·59'	10°·46'	4·115	4·12	med.	st.	40
		4	4°·44'	10°·33'	4·2	"	"	"	"
		5	8°·32'	"	"	"	"	"	"
		6	14°·51'	"	"	"	"	"	"
8	21 $\bar{1}$	3	13°·56'	12°·52'	3·45	3·39	"	"	..
		4	7°·22'	v.w.
		5	7°·56'	12°·48'	3·47	3·39	med.	st.	..
9	20 $\bar{2}$	5	6°·11'	12°·28'	3·56	3·72	"	..	21·5
		6	11°·18'	"	"	"	"	..	"
10	200	6	12°·52'	β 11°·18'	3·546	3·46	"	st.	40
11	$\bar{2}$ 1 $\bar{1}$	3	5°·56'	β 10°·47'	3·645	..	"
12	22 $\bar{2}$	4	16°·30'	17°·52'	2·5	2·32	"	..	14
13	2 $\bar{2}$ $\bar{2}$	5	16°·11'	17°·42'	2·53	..	w.

Note.—v.st.=very strong, st.=strong, med.=medium intensity, w.=weak and v.w.=very weak; F'=structure factor.

of the latter and the intensities of the corresponding static reflections given by Sir William Bragg (1921) and Robertson (1933). It is clear from the data given in the above table that the intensity of the dynamic reflections from the

* The plate distance for Figs. 1 and 2 is 5·2 cm. and for Figs. 3-6 is 5·7 cm.

crystal planes is by no means proportional to the intensity of the corresponding Bragg reflection. The most intense modified spot is given by the $0\bar{1}1$ plane which has a low structure factor. The planes 110 , $20\bar{1}$, $21\bar{1}$ and 200 which have the highest structure factors also give rise to modified spots with medium intensity. On the other hand, in spite of the fact that the 001 plane, according to Sir William Bragg, gives the strongest reflection and has a large structure factor, the first and second order dynamic reflections by it appear only extremely weakly. The experimental results thus clearly demonstrate that the intensity of the dynamic reflections are determined by considerations very different from those controlling the intensity of the static reflections by the same planes.

4. *Significance of the Experimental Results*

The basic idea in the quantum theory of X-ray reflection in crystals is that the frequency of the incident radiation is modulated by the monochromatic infra-red vibrations of the crystal. In an earlier paper appearing in this issue it has been shown that the frequencies lying in the region of $30-100 \text{ cm.}^{-1}$ are alone effective in the modified X-ray reflections by organic crystals. Therefore for the purpose of the present discussion, we may ignore the internal vibrations of the naphthalene molecule. Since the plane of the molecules in the crystal is nearly *normal to the* 001 plane, five rotations and two translations out of the nine possible lattice vibrations involve movements *parallel to the* 001 plane. Therefore, these vibrations do not affect the structure amplitude of the latter. As the displacements of the molecules due to the remaining two lattice vibrations normal to 001 planes are also relatively small, the dynamic reflections of the X-rays from this plane resulting from those lattice vibrations should be expected to be relatively weak. The opposite situation prevails for the planes $0\bar{1}1$, 110 , $20\bar{2}$ and $21\bar{1}$. The plane of the molecule is nearly parallel to them and all the lattice vibrations make their maximum contribution to the variation of the structure amplitude. Thus, even when the static structure factor is low as for $0\bar{1}1$, the Raman reflection will be very strong. The crystal planes 200 , $20\bar{1}$, 120 and $11\bar{1}$ lie between these two extremes with respect to the lattice vibrations and the dynamic reflections from them will, therefore, be of medium intensity as compared with the corresponding Bragg reflection. The experimental facts observed in the present investigation are in good agreement with these conclusions.

The observations include a wide range of crystal planes making angles between 55° and 125° with the cleavage plane. It is obvious that the almost total disappearance of the reflection from the 001 plane which gives one of the strongest Bragg reflections and the great intensity of the reflection from

the $0\bar{1}1$ plane which has a very low structure factor cannot be accounted for on the basis of the Faxén-Waller theory (Zachariasen, 1940) that the observed spots are the maxima due to the diffuse scattering of X-rays by the elastic waves in the crystal.

In conclusion I express my sincere gratitude to Sir C. V. Raman, F.R.S., N.L., for his suggestions and interest in the work.

5. Summary

The Raman X-ray reflections from 001 , $0\bar{1}1$, 110 , $11\bar{1}$, $20\bar{1}$, 200 , $20\bar{2}$, 120 , $2\bar{1}\bar{1}$, $2\bar{2}\bar{2}$ and $2\bar{2}\bar{2}$ planes of a naphthalene crystal are obtained. It is observed that the first and second orders of the dynamic reflections from 001 (cleavage) plane are extremely weak, in spite of the fact that its static structure factor is high. On the other hand, these reflections from $0\bar{1}1$ plane which has a very low structure factor, are very strong. The 110 , $20\bar{1}$, $21\bar{1}$ and 200 planes which give the strongest Bragg reflections also yield the Raman spots with medium intensity. These experimental facts are readily explained in relation to the known crystal structure and the lattice vibrations of naphthalene, if we assume the basic idea in the quantum theory of X-ray reflection in crystals put forward by Raman and Nilakantan that the frequency of the incident radiation is modulated by the monochromatic infra-red vibrations of the crystal lattice. A study of the relative intensities of the dynamic reflections from the different crystal planes clearly demonstrates that the character of these reflections is determined by the geometry and amplitude of the lattice vibrations.

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