THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: II. BENZOPHENONE

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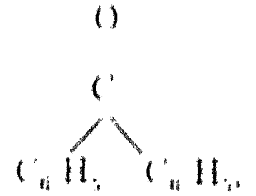
1. *Introduction*

IN the first paper of this series, it was shown that the dynamic or Raman X-ray reflections from the 001 plane of naphthalene almost completely disappear as a necessary consequence of the fact that the plane of oscillating molecules in the lattice is nearly normal to this crystal plane. An exactly opposite effect is noticed in benzophenone crystal in which the intensity of the dynamic reflection is abnormally high for the 001 plane. As in the case of naphthalene, the intensity of such reflections as compared with the static ones, is also observed to depend on the orientations of the crystal and the molecular planes in the lattice.

2. *Crystal Structure and Lattice Spectrum of Benzophenone*

Benzophenone,



$$\overset{O}{C}(C_6H_5)(C_6H_5)$$

belongs to the ortho-rhombic bisphenoidal class (Groth[1]), having a space group $D_2^4\ P2_1\ 2_1\ 2_1$ (Banerji and Haque[2], 1938). The dimensions of the unit cell are $a = 10·3$, $b = 12·11$ and $c = 8·04$ A.U. There are four molecules in the unit cell. The X-ray analysis of the crystal structure is incomplete; but Banerji and Haque[2] have observed that most of the important crystal planes yield very strong Bragg reflections, the absent reflections being from *hoo*, *oko* and *ool* where *h*, *k* and *l* are odd. Krishnan, Guha and Banerji[3] (1933) have given the magnetic susceptibilities along the *a*, *b* and *c* axes as $\psi_a = 88 \times 10^{-6}$, $\psi_b = 88·6 \times 10^{-6}$ and $\psi_c = 149·3 \times 10^{-6}$ e.m.u. The refractive indices along the three directions γ, β and α (parallel to the crystal axes *a*, *b* and *c* respectively) are $\gamma = 1·67$, $\beta = 1·68$ and $\alpha = 1·52$ (Nedungadi[4], 1941). It has been concluded from the above data of magnetic and optical anisotropies that the two benzene rings linked through the carbonyl group $C = O$ are inclined to each other at an angle of 22°·35′, the plane bisecting the two benzene rings being *normal* to the ' *c* ' axis. The line of intersection of the two benzene planes is inclined to the ' *a* ' and ' *b* ' axes, the angle made with the ' *b* ' axis being 22°·35′. Thus the biplanes of the molecule are nearly *parallel* to the 001 plane of the crystal, which is just the opposite of the condition prevailing in naphthalene.

The benzophenone molecule $(C_6H_5)_2$ CO has sixty-three possible internal vibrations. Twenty-seven of these have been observed in the Raman spectrum of the melt, of which twelve are depolarised (Nedungadi, 1941). In the crystal, in addition to these intra-molecular vibrations for each of the four molecules in the unit cell, which do not show any significant changes from the liquid, there are *twenty-four* degrees of rotational and translational freedom for the molecules, of which *twenty-one* contribute to lattice vibrations and *three* only to the Debye elastic spectrum. In the Raman spectrum of the crystal, it has been observed that the intense " wing " of the liquid on either side of the Rayleigh line is replaced by three discrete lines* at 67, 102 and 122 cm.$^{-1}$ (Venkateswaran, 1938; Gupta, 1938; and Nedungadi, 1941). It has been shown by the present author that the line at 122 has to be assigned to the deformational oscillation of the two benzene rings against each other and the other two to the lattice vibrations. Nedungadi (1941) has studied the variations of intensity of the *Raman lines* in a single crystal of benzophenone with different crystal orientations and concluded that his observations are in good agreement with the above conclusions regarding the orientation of molecules in the unit lattice.

3: *The Dynamic Reflection of X-rays by Benzophenone*

X-rays from a copper target are employed. A small crystal of benzo-phenone measuring approximately 2 mm. × 2 mm × 1 mm. is mounted with the 110 plane lying in a vertical plane. Three sets of Laue patterns are obtained, the first set with X-rays nearly grazing the 110 plane, the crystal being rotated about a vertical axis; the second set with X-rays incident nearly normally on the 110 plane, the crystal being rotated about a vertical axis and the third set of pictures being taken in the same way as the second set but with the crystal rotated about a horizontal axis: Figs. 2 and 3 in the accompanying Plate are the Laue patterns obtained for the first set with X-rays making glancing angles of 4°·19′ and 8°·24′ respectively with the 110 plane. Figs. 4 and 5 are the patterns for the second set, the X-rays making glancing angles of nearly 8° and 2° with $1\bar{1}0$ plane. Figs. 6 to 9 are the photographs obtained for the third set,

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* See Fig. 1 in the accompanying Plate.

TABLE I

No.	Ref. to Fig.	Indices of Plane	$2\theta_i$	$\theta_i + \phi$ for Kα	Lattice Spacing in A.U.		Angle* made with 001	Intensity (Dynamic)	Intensity (Static) (Banerji)
					Exp.	Theo.			
1	6	002	12°·10′	21°·12′	4·18	4·02	0°	v.v.str.	v.str.
	7	,,	19°·54′	22°· 4′	4·02	,,	,,	,,	,,
	8	,,	29°·38′	21°·12′	4·18	,,	,,	,,	,,
2	2	$01\bar{2}$	24°·59′	22°·29′	3·94	3·82	+166°	med.	. .
	6	,,	21°·12′	23°·13′	3·82	,,	+162°	str.	. .
	5	012	20°·20′	22°·29′	3·94	,,	− 15°	,,	. .
3	1	$10\bar{2}$	19°·28′	22°·29′	3·94	3·75	−159°	med.	. .
	4	,,	21°·12′	22°·54′	3·87	,,	−160°	,,	. .
4	4	$12\bar{1}$	24°· 9′	20°·47′	4·26	4·38	−160°	med.	. .
5	1	022	31°·28′	27°·18′	3·26	3·35	+ 34°	med.	. .
	4	,,	28°·22′	26°·59′	3·3	,,	,,	,,	. .
	1	$0\bar{2}2$	22°·54′	26°·58′	,,	,,	+144°	str.	. .
	2	,,	27°·21′	26°·34′	3·35	,,	+146°	,,	. .
	4	,,	20°·47′	26°·58′	3·3	,,	,,	,,	. .
6	1	202	22°· 3′	β 23°·19′	3·4	3·2	− 38°	str.	v.str.
	3	,,	19°·28′	26°·59′	3·3	,,	,,	,,	,,
	7	,,	22°· 4′	27°·44′	3·21	,,	− 36°	med.	,,
7	4	122	24°· 9′	28°· 8′	3·2	3·19	−41°	w.	. .
8	3	$1\bar{1}1$	18°· 9′	15°·53′	5·56	5·62	45°	w.	v.str.
	5	,,	19°·28′	15°·25′	5·73	,,	,,	med.	,,
	,,	111	,,	,,	,,	,,	135°	,,	,,
9	6	132	29°·38′	32°·11′	2·76	2·75	− 48°	med.	. .
	7	,,	34°·15′	32°·53′	2·72	,,	− 47°	,,	. .
10	6	021	9°·47′	14°·57′	5·91	5·86	+130°	med.	. .
11	2	201	17°·42′	20°·47′	4·3	4·34	− 60°	med.	. .
	3	,,	22°· 4′	19°·54′	4·45	,,	− 58°	,,	. .
	6	,,	15°·53′	19°·54′	,,	,,	− 69°	,,	. .
12	5	131	24°·58′	26°·10′	3·4	3·41	− 65°	v.w.	. .
13	1	110	8°·38′	11°·13′	7·87	7·85	90°	med.	v.str.
14	2	210	16°·48′	18°· 9′	4·87	4·74	90°	w.	. .
	3	$2\bar{1}0$	16°·47′	,,	,,	,,	,,	,,	. .
15	5	$2\bar{2}0$	28°· 8′	22°· 4′	4·017	3·93	90°	v.w.	v.str.
	6	,,	26°·34′	22°·29′	3·94	,,	,,	,,	,,
16	5	130	27°·44′	23°·44′	3·74	3·76	− 90°	v.w.	v.str.
17	5	$1\bar{4}0$	28°· 8′	30°·45′	2·89	2·9	90°	v.w.	v.str.

* + sign means clockwise and − sign, anti-clockwise.

Note.—v.v.str. = very very strong, v.str. = very strong, str. = strong, med. = medium, w. = weak, v.w. = very weak.

the glancing angles made with 001 plane being nearly 0°, 6°, 10° and 15° respectively. The prominent streak appearing in all the patterns is due to the 001 plane and serves as a guide for the identification of different crystal planes giving rise to Raman reflections. In Table I the visual estimates of intensities of the dynamic and static reflections are given along with the indices of the corresponding planes, the angle they make with the 001 plane at the Bragg setting, and their lattice spacings obtained from the position of the Raman spot by making use of the formula $2\,d \sin \frac{(\theta_i + \phi)}{2} = \lambda$, and the spacing calculated from a knowledge of the crystal structure. Only the Raman spots seen in the neighbourhood of the Bragg setting are included in the table, though many of them are present in the other photographs as well.

The outstanding result of the present investigation is the enormous intensity of the dynamic reflections from the 002 plane of the crystal. The intensity of the Bragg reflection from this plane is only as much as that of several other crystal planes; but on a rough estimate its dynamic reflection is at least ten times more intense than the most prominent spot from any other plane. The data given in Table I and the photographs reproduced in Figs. 2 to 9 further show that the following planes making an angle between 0—40° on either side of 001 and $00\bar{1}$ planes also yield Raman spots with fair intensity: $01\bar{2}$, $10\bar{2}$, $12\bar{1}$, 022, $02\bar{2}$ and 202. On the other hand, the Raman reflections from the planes making an angle of nearly 90° with it, namely 110, $2\bar{2}0$, 210, $2\bar{1}0$, 130, $1\bar{4}0$ and 131, are comparatively weak. Banerji and Haque have given estimates of intensities of the Bragg reflections for only a few of the planes given in the above table. A comparison of the relative intensities of the static and dynamic reflections for these planes, however, reveals that there is no direct relationship between the intensities of both cases.

4. *Significance of Experimental Results*

From the above observations of the intensities of the Raman reflections from several crystal planes of benzophenone, it is clear that the intensity is a maximum when the plane is nearly parallel to the plane of the molecule and a minimum when it is nearly perpendicular to it. The results are thus analogous to those obtained for naphthalene in the earlier paper and are readily explained on the same basis as the latter. Since the unit cell of benzophenone contains four molecules, there are twenty-one possible modes of lattice oscillations ; but as the exact position and orientation of the molecules in the lattice are not known, it is not possible to analyse these vibrations and ascertain the degeneracies involved. However, it is obvious from the known disposition of the molecules in the lattice that most of the lattice vibrations will contribute components normal to the 001 plane, thus causing a large variation of the structure amplitude of the plane. On the other hand the motions of the molecules during these vibrations being nearly parallel to the family of planes situated normal to 001 plane, their contribution to the dynamic structure factor of these planes will be a minimum. The results of the present investigation are thus in good accord with the proposed crystal structure of benzophenone.

As only three out of twenty-four degrees of rotational and translational freedom of the molecule in the unit lattice contribute to the Debye spectrum, the fraction of the total thermal energy carried by the elastic waves in the crystal is almost negligible. The diffuse scattering of X-rays by these waves should therefore be relatively very feeble, and cannot account for the great intensity of the new spots observed in the Laue photographs. Secondly, it is also evident from the habit of the crystal and its physical properties that benzophenone is much more nearly isotropic than naphthalene. This would lead us to expect the intensity of the diffuse scattering of the X-rays by the elastic vibrations by the different crystal planes to have intensities nearly in proportion to the ordinary X-ray reflections by those planes. The striking disparity actually observed in the relative intensities of the dynamic and static reflections from different planes recorded in the present investigation therefore precludes the possibility of any connection between the observed phenomena and the theory of diffuse X-ray scattering by the elastic waves in the crystal.

In conclusion the author wishes to express his respectful homage to Sir C. V. Raman, F.R.S., for his sustained interest in the work.

5. *Summary*

The dynamic reflections of X-rays from several crystal planes of benzophenone are recorded. The striking observation made in the investigation is that the intensity of the reflection from 002 plane is enormously great. Other planes on either side of the latter making angles of 0° – 40°, also give rise to Raman spots of fair intensity. On the other hand such reflections from planes making an angle of nearly 90° with the 001 plane are comparatively weak, in spite of the fact that they give very intense Bragg reflections. These experimental results are thus in striking contrast with those obtained for naphthalene in which the dynamic reflection from the 001 plane is almost completely absent. These facts are readily

explained on the basis of the theory due to Raman and Nilakantan that they arise from the vibrations of the crystal lattice. The difference in the behaviour of these reflections for naphthalene and benzophenone is due to the fact that while in the former the plane of the molecule is normal to the 001 plane, in the latter it is parallel to the 001 plane.

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