

THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: III. HEXAMETHYL-TETRAMINE

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1. Introduction

THE two earlier papers of this series dealt with crystals of aromatic compounds, *viz.*, naphthalene and benzophenone. The molecules of these crystals being highly anisotropic in shape, the effect of their translatory and rotational oscillations would be very different on crystal planes respectively parallel and perpendicular to the plane of the aromatic rings. As a result, a striking disparity in the relative intensities of the dynamic and static reflections from the different planes was observed. For the sake of comparison it is of great interest to consider the phenomena observed with hexamethyl-tetramine which is one of the few well-studied organic substances crystallising in the cubic system. On the basis of the ideas already indicated we should expect to find in this case a closer parallelism between the intensities of the Raman and Bragg reflections by the planes of the crystal. This conclusion is strikingly supported by the experimental results.

2. Crystal Structure and Lattice Spectrum of Hexamethyl-tetramine

The crystal structure of hexamethyl-tetramine—urotropin—has been investigated by Gönell and Mark (1923), and Dickinson and Raymond (1923), and with especial thoroughness by Wycoff and Corey (1934). The unit cell is a body-centred cube having an edge-length of $a = 7.02$ A.U. and contains two molecules of $C_6H_{12}N_4$. The only planes giving first order reflections are those having two odd and one even indices.

The molecule $C_6H_{12}N_4$ possesses a symmetry T_d . Due to the high order of symmetry, many of the molecular vibrations are degenerate. There are ten modes of vibrations characteristic of the ring, of which eight are Raman active and four are infra-red active. Kohlrausch and co-workers (1938) have observed all these eight lines below 1500 cm.^{-1} , besides the C-H vibrations. In the crystal the two molecules of the unit cell which give in general, all the internal frequencies observed in aqueous solutions, possess

in addition twelve degrees of rotational and translatory freedom which yield the lattice and the acoustic spectra. Since the crystal has an O_h symmetry and the molecule is isotropic, it is easily seen that these will yield only one inter-molecular vibration (or hindered translation) along the diagonal of the unit cube, which is triply degenerate, and two hindered rotations which are also triply degenerate. A group-theoretical analysis of the crystal vibrations shows that the translatory vibration comes under the symmetry class F_{2u}^* which is inactive in the Raman and the infra-red. One of the rotatory vibrations belongs to the class F_{1g} and is inactive in both Raman and infra-red. The other appears in the class F_{2g} and is active only in the Raman. A preliminary investigation made to record the lattice spectrum of the crystal yielded only a weak picture which indicated a faint line below 100 cm.^{-1} . A detailed investigation of this region with single crystals is now in progress.

3. *The Dynamic Reflections of X-rays by Hexamethyl-tetramine*

A tiny crystal of urotropin prepared from a solution of a mixture of water and alcohol was used in the investigation. The experimental arrangement was the same as that described in the previous communications. The X-rays were first made incident normally to the 110 plane of the crystal, which is one of its natural faces. A series of twenty-eight Laue photographs were taken with the crystal rotated about the vertical cube-edge from 0° to 45° . Figs. 1 to 8 in the accompanying Plate reproduce some of the typical photographs obtained. Fig. 1 gives the pattern when the X-rays are exactly normal to 110. The two strong dynamic reflections from 110 and $1\bar{1}0$ and four weak reflections from 011 and $0\bar{1}1$ and 101 and $10\bar{1}$ forming an irregular hexagonal pattern may be clearly observed. Besides, the four Raman spots due to (211) planes are also recorded in the neighbourhood of the corresponding Laue spots. Figs. 2 to 8 are for the positions of the crystal for which the goniometer readings are nearly 2° , 7° , 26° , 30° , 33° , $37^\circ 30'$ and 45° respectively. The only crystal planes which give Bragg reflections within the range included in the present investigation are (110), (200), (211), (220) and (222). All these reflections may be easily identified from the patterns illustrated in the Plate. Measurements of the positions of the spots were, however, made from all the twenty-eight photographs taken and the representative data are given later in Tables II to IV.

* The notations are those used by Placzek in *Handbuch der Radiology*, Vol. 2, page 297.

4. *Experimental Results and their Discussion*

1. *Relative intensities of the dynamic and static reflections.*—Table I gives the estimated intensities of the Raman spots of the different planes and the intensities of the Bragg reflections given by Wyckoff and Corey (W. and C.) and Gönell and Mark (G. and M.)

TABLE I

Indices of planes	Intensity (Dynamic)	INTENSITY (STATIC)	
		W. & C.	G. & M.
110	v.str.	1281	v.str.
200	med.	447	m.str.
211	str.	..	str.
220	v.w.	300	w.
222	str.	..	str.

It will be seen that the intensities of the dynamic and the static reflections are proportionate for the five planes which represent four totally different directions in the crystal. Of the three lattice vibrations of the crystal, the two hindered rotations do not change the structure amplitude of the principal planes. Hence the only vibration which is active in the Raman X-ray reflections is the hindered translation which is triply degenerate. This affects the structure amplitudes of various planes to a similar extent.†

2. *The sharpness and orientation of the Raman spots.*—One of the significant observations made on the Raman spots from the (100), (110) and (211) planes of the crystal is that they are fairly sharp and well-defined if not too far removed from the Laue reflections. This is in striking contrast to the 'diffuse' spots that are usually recorded in crystals, *e.g.*, rock-salt or benzophenone or highly complicated structures like sorbic acid (Lonsdale, *etc.*, 1941). This is no doubt connected with the fact that there is only one lattice oscillation which modulates the incident X-rays and the dynamic reflections in each case arise from a single set of phase-waves. When there are more than one lattice vibration involved, the observed Raman spot is the result of the superposition of a series of reflections from several phase-waves which make different angles with each other. This is presumably one of the reasons why most of the organic and inorganic crystals yield only diffuse spots at angles even slightly different from the Bragg setting.

† Theoretical calculation shows that the (100) and (111) reflections which do not appear in the Bragg are weakly active in the Raman X-Ray effect.

It may further be noticed from the illustrations that for oblique incidence, the orientation of the Raman spots is different from the corresponding Laue spots. Pisharoty (1941) has shown in a recent paper that while the Laue spots are elliptical, the Raman spots are round in shape as a consequence of the fact that the total deviation of the ray from the incident beam remains nearly constant for small changes in the angle of incidence. When the cross-section of the incident X-ray beam is not circular, but elongated as in the present investigation, the Raman spots should for the same reason, have the same shape as the direct spot and be parallel to its length. This is what is observed in the case of spots from (110) and (211) planes. It may also be observed from Figs. 2 and 6 that as the static reflection by (211) planes recedes away from the dynamic reflection, the latter deviates slightly from the line joining the central and the Laue spots. This indicates that the phase-wave responsible for the (211) dynamic reflection is not normal but inclined to the plane containing the incident beam and the normal to the crystal plane.

3. *The geometry of the dynamic reflections.*—Tables II to IV give the lattice spacing d calculated for the different planes at different crystal orientations by making use of the Raman-Nath formula (1940),

$$2 d \sin \frac{\theta + \phi}{2} \sin \left(\vartheta + \frac{\phi - \theta}{2} \right) = \lambda \sin \vartheta,$$

where θ is the glancing angle of incidence and $(\theta + \phi)$, the angle made by the spot-maximum with the central ray and ϑ , the inclination of the phase-waves to the crystal planes. It may be seen that in the case of (200) and (110) planes, the spacing d remains nearly constant and equal to the theoretical value over a wide range of angles, if we take $\vartheta = 90^\circ$. When the

TABLE II

(200) Reflections: Phase Wave-angle $\vartheta = 90^\circ$. Crystal Spacing = 3.501 Å

No.	X-ray Wave-length	2θ	$\theta + \phi$	$\phi - \theta$	Calculated Spacing in Å
1	CuK α	15°·52'	25°·12'	9°·20'	3·455
2	"	19°·27'	"	5°·45'	3·448
3	"	23°·48'	"	1°·24'	3·443
4	"	30°·53'	25°·26'	— 5°·27'	3·415
5	"	34°·50'	"	— 9°·24'	3·426
6	"	36°·42'	"	—11°·16'	3·429

TABLE III

(110) Reflections: Phase-wave Angle $\vartheta = 90^\circ$. Crystal Spacing = 4.964 \AA

No.	X-ray Wave-length	2θ	$\theta + \phi$	$\phi - \theta$	Calculated Spacing in \AA
1	CuK $_{\alpha}$ and CuK $_{\beta}$	0°	$16^\circ.40'$	$16^\circ.40'$	5.102
2	„	$7^\circ.49'$	$16^\circ.54'$	$9^\circ.5'$	4.995
3	CuK $_{\alpha}$	$11^\circ.6'$	$17^\circ.25'$	$6^\circ.19'$	5.089
4	„	$12^\circ.42'$	$17^\circ.40'$	$4^\circ.58'$	5.023
5	„	$13^\circ.30'$	$17^\circ.55'$	$4^\circ.25'$	4.940
6	„	$16^\circ.54'$	$17^\circ.40'$	$0^\circ.46'$	5.007
7	„	$20^\circ.26'$	$17^\circ.55'$	$-2^\circ.31'$	4.940
8	„	$24^\circ.17'$	$17^\circ.40'$	$-6^\circ.37'$	5.014
9	„	$28^\circ.20'$	$17^\circ.50'$	$-10^\circ.30'$	4.942
10	„	$29^\circ.12'$	$17^\circ.55'$	$-11^\circ.17'$	4.96

TABLE IV

(211) Reflections: X-Ray Wave-length = 1.537 A.U. Crystal Spacing = 2.865 \AA

No.	2θ	$\theta + \phi$	$\phi - \theta$	CALCULATED SPACING IN \AA	
				$\vartheta = 90^\circ$	$\vartheta = 65^\circ.54'$
1	$26^\circ.34'$	$30^\circ.53'$	$4^\circ.19'$	2.889	2.84
2	$29^\circ.12'$	$31^\circ.5'$	$1^\circ.53'$	2.876	2.83
3	$31^\circ.18'$	$31^\circ.42'$	$0^\circ.14'$	2.886	2.885
4	$31^\circ.42'$	$31^\circ.42'$	0°	2.887	2.887
5	$34^\circ.6'$	$31^\circ.42'$	$-2^\circ.34'$	2.815	2.924
6	$36^\circ.42'$	$31^\circ.54'$	$-5^\circ.0'$	2.799	2.855
7	$38^\circ.48'$	$32^\circ.6'$	$-6^\circ.42'$	2.784	2.860
8	$40^\circ.47'$	$32^\circ.6'$	$-8^\circ.41'$	2.787	2.885

glancing angle is less than the Bragg angle, the apparent shift of the Raman spot due to K $_{\beta}$ reflections merging with those of K $_{\alpha}$ is taken into account in making the calculations. This shows that the phase-waves for the lattice vibration considered are perpendicular to the (100) and (110) planes. On the other hand, for the prismatic plane (211) which makes an angle of

$65^{\circ} \cdot 54'$ with 010 plane, the lattice spacing calculated using $\vartheta = 90^{\circ}$ shows a progressive diminution as the angle of incidence is increased. It remains fairly constant if we put $\vartheta = 65^{\circ} \cdot 54'$, as is only to be expected from the above-mentioned direction for the phase-waves. The lateral shift of the (211) Raman spot from the line joining the central and the Laue spots is also evidently connected with the azimuthal inclination of the phase-wave. The observations of the reflections from the (111) planes are neither sufficiently extensive nor sufficiently accurate to draw any conclusion regarding the phase-wave angle for those planes.

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Summary

The X-ray reflections from the (110), (200), (211) and (111) planes of hexamethyl-tetramine shows that the intensities of the dynamic reflections follow the same order as the intensities of the corresponding static reflections. The Raman spots of the crystal are relatively sharp compared to those from organic and inorganic crystals of complicated structure. These observations are readily explained by the fact that the molecular and the crystal structures of the substance have a high order of symmetry and that for the principal planes there is only one Raman X-ray active lattice vibration which corresponds to a movement of the two molecules against each other along the cube diagonal. The geometry and orientation of the spots are also found to depend on the direction of the phase-waves connected with the above vibration.

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