

LOW-FREQUENCY RAMAN LINES IN PARA-DICHLORO-BENZENE

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Plates IV A, B.

ABSTRACT. The low frequency lines of para-dichlorobenzene have been studied in different orientations of the crystal which was in the form of a cylinder with the symmetry axis along the length of the cylinder. Raman spectra of the liquid and of a different specimen of solid para-dichlorobenzene have also been studied. The Raman spectrum shows six polarised frequencies 330, 747, 1071-1084, 1106, 1169, 3072 and seven depolarised frequencies 299, 628, 675, 1248, 1376, 1485, 1573. In the directional excitation of the solid in the form of a single crystal it is found that if the crystal be illuminated with its symmetry axis along the direction of observation and the electric vector be along the direction of, observation or perpendicular to it along *OZ*, it is noticed that the frequencies 747, 1071 1106, 3072 are very much increased in intensity in the latter case than in the former while 308, 630, 1376 remain nearly of the same intensity in the two cases and 330, and 1576 are reduced in intensity. Similarly the low frequency line 94 is much weaker than 27 when the electric vector is along *OY* and stronger when the electric vector is along *OZ*. The frequency 54 remains strong in all the cases. The tensors have been derived for these frequencies, which indicate that each frequency represents a symmetric and an asymmetric oscillation. The tensor for 94 also indicates that the asymmetric component is much weaker than the component of symmetric oscillation. This frequency, therefore, behaves like the frequencies 747, 1106, etc.

The frequencies 299 and 330 also show variations in intensity. The frequency 299 in liquid is increased to 308 in solid. In the liquid 299 is weaker than 330 but in the solid 308 is comparable to and even greater than 330.

In the solid pictures we find two different low frequency spectra. In our picture we get the frequencies 27, 54 and 94 while in the other we get 45, 57 and 84 although the liquid spectrum is the same in the two cases. As 27 does not vanish in any orientation, it follows that the disappearance of frequency 27 in the second case is not an orientation effect. The latter frequencies were obtained by Venkateswaran by rapid cooling from the melt and it is likely that the second solid was obtained in that way. It is suggested that the results reveal a change of structure of para-dichlorobenzene in the way the crystal is grown.

INTRODUCTION

The low frequency Raman spectrum of para-dichlorobenzene has been investigated by Vuks (1936, 1937), Sirkar and Gupta (1936, 1937), Sirkar and Bishui (1937) and Venkateswaran (1938). Vuks found that the low frequency spectrum changes with temperature and from this he concludes that there are two modifications of the substance—the α -modification being stable below 32°C and the β -modification is stable above 32°C. The transformation according to Vuks does not involve any change of volume. Vuks has called these low frequencies as lattice oscillations. Sirkar and Gupta and also Sirkar and Bishui find that there is no change in the Raman spectra at 32°C and 45°C.

They, however, report a change when the mass is cooled in ice and brought to the room temperature. The former authors also report that there is no change in Laue patterns with the hot and the cold crystal. Venkateswaran is also unable to confirm the change in the spectra of para-dichlorobenzene at less than 25°C and greater than 33°C as reported by Vuks attributing it to a change of crystal form, although the substance was kept for well over a week at ice-cold temperature. Sirkar and his co-workers aver that these oscillations are not of the lattice but arise from intermolecular oscillations of polymerised groups in the solid. The results of these authors are given in the Table I.

It may be seen from Table I that the frequency 27 has been obtained only by Vuks and that he has distinguished between the α - and β -modifications by the appearance or disappearance of this frequency. It is now well known that the intensity of Raman lines in a crystal varies with directional excitation. It is therefore important to study whether its disappearance is an orientation effect or due to crystal modification as suggested by Vuks. It may be stated that the pictures reproduced by Sirkar and co-workers and also by Venkateswaran are not good enough to clearly bring out the frequency 27. Both these authors have not worked with single crystals with the result that the Rayleigh line has become much over-exposed due to extraneous light. By working with single crystals we have been able to get very good pictures and the low frequency lines have come out very distinctly without being masked by the halation due to Rayleigh line.

CRYSTAL STRUCTURE

According to Hendricks (1933) para-dichlorobenzene belongs to the mono-

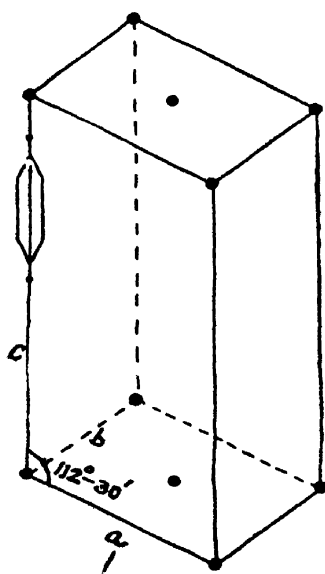


FIG. 1

clinic prismatic class having the point group C_{2h} , and the unit cell contains two molecules. The dimensions of the unit cell are $a=5.88\text{\AA}$, $b=4.1\text{\AA}$ and $c=14.88\text{\AA}$, $\angle \theta=112^{\circ} 30'$. The unit cell is shown in figure 1. The centre of inversion is located at the centre of each molecule and the orientation of other molecules can be obtained by the glide plane of reflection in (010) planes, the gliding being parallel to the a -axis. The elements of symmetry are

- C_2 Screw axis (1, 2)
- i Centre of symmetry (1) (2)
- σ_h Glide plane (1, 2)

The b -axis in the crystal is the axis of two fold symmetry while the c -axis is easily identified as the crystal is elongated along this axis. The crystal

TABLE I

Liquid	Vaks Solid		Sirkar and Gupta Solid		Sirkar and Bishui Solid		Venkateswaran Solid	
	<25°C α-mod.	>32°C β-mod.	45°C (melted and cooled)	32°C mass once cooled in ice	80°C Liquid	31°C Solid	25°C	45°C
	27.5							
	46.5	43.3	40(1)	46(2)		40(25)		43(6)
	54	54.5	50(2)	50(2)		50(25)	48(6)	55(5)
	93	82	82(2)	93(2)		82(2)	93(6)	88(5)
299.7 (5)	307.6 (5)	304.1 (5)			309(2)	305(1)	308(1)	
329.5(10)	328 (10)	329.5(10)			330(3)	330.2	327(1)	
748.1(10)	745 (10)	745.2(10)			745(4)	745(3)	745(2)	
1108.4(10)	1104.5(10)	1103.9(10)			1106(3)	1102(4)	1102(3)	
3071.3(10)	3071.3(10)	3072.2(10)			3072(5)	3070(4)	3070(3)	

being monoclinic, one of the optic axes β coincides with the symmetry axis b of the crystal, the other two optic axes namely α and γ lie in the plane (010). Their exact orientation is not known but as $\angle \theta = 112^\circ 30'$ they will be making small angles with the a - and c -axes. Bragg (1939) has shown that for aromatic crystal of the naphthalene class the length of the molecule lies along the elongated axis. In the case of para-dichlorobenzene, since c is very large in the unit cell, the length of the molecule should be nearly parallel to the c -axis along which the optical polarisation should be maximum. According to Hendricks, the molecules are almost parallel to the c -axis in the projection of the unit cell on the ac plane. We may therefore consider the molecules as roughly lying in the bc plane, the breadth of the molecule being along the b -axis and the length along the c -axis. We may therefore roughly regard b -axis as the axis of intermediate polarisability and the a -axis as the axis of minimum polarisability. We have assumed for the sake of simplicity that γ -axis of polarisability lies along the c -axis and the α -axis along the a -axis although these will in general be slightly inclined to these directions.

LATTICE OSCILLATIONS IN PARADICHLOROBENZENE

It is now well known that all crystals give low frequencies. Placzek (1934) has shown that the modes of vibration of a crystal lattice may be analysed by considering the unit cell as the basis. Bhagavantam (1939) has in this way considered the modes of vibration of a number of crystals such as calcite, NaN_3 , gypsum and Saksena of quartz. Experimental work on the directional excitation in crystals by Bhagavantam (1940) in calcite, Nedungadi (1939) in NaN_3 and Saksena (1940) in quartz agree completely with the theoretical predictions which shows that all frequencies shown by a crystal are lattice frequencies. In a molecular crystal the low frequency region appears well separated from the regions of high frequencies which represent the molecular frequencies, but this is not so in the case of a linked crystal like quartz where such a distinction cannot be made. The low frequencies in a crystal are particularly sensitive to temperature.

In para-dichlorobenzene the low frequency spectrum is well separated from the high frequency region which represents molecular frequencies. The molecule $\text{C}_6\text{H}_4\text{Cl}_2$ has a symmetry D_{2h} and possesses a centre of symmetry. The thirty internal modes are therefore equally divided in the Raman active and infra-red active classes, the Raman active modes being infrared inactive. Out of the 15 Raman active modes 6 are polarised and 9 depolarised.

The crystal of para-dichlorobenzene has a symmetry C_{2h} and has a centre of symmetry at each molecule. The Raman active modes will therefore be infra-red inactive. As there are two molecules in the unit cell, there are now 24 atoms and 72 degrees of freedom. For the two molecules we will

have 60 internal and 12 external degrees of freedom. The 30 internal modes and the six degrees of translation and rotation of each molecule, can be coupled in the same or opposite phase to give 60 internal modes and 12 external modes. As regards the internal modes, we may not expect any appreciable change of frequency of molecular vibrations by coupling them because the bindings in a molecule are very much stronger than those between the two molecules. Each of the 30 internal modes will therefore be merely doubly degenerate without showing any appreciable change of frequency.

The external modes will be of two types namely translational and rotational produced by coupling of translations and rotations of the two molecules. As the centre of symmetry is preserved in rotation, the rotational modes will be Raman active and translational modes Raman inactive. Mathematically these results may be expressed in the following Table II.

TABLE II

C_{2h}	E	C_2	σ_h	i	n_i	T	External modes		n_i'	Selection rules		Surviving tensor components
							T'	R'		R	IR	
A_g	1	1	1	1	18	0	0	3	15	p	f	$\epsilon_{\alpha\alpha}, \epsilon_{\beta\beta}, \epsilon_{\gamma\gamma}, \epsilon_{\alpha\gamma}$
A_u	1	1	-1	-1	18	T_x	2	0	15	f	a	
B_u	1	-1	1	-1	18	T_x, T_y	1	0	15	f	a	
B_g	1	-1	-1	1	18	...	0	3	15	p	f	$\epsilon_{\alpha\beta}, \epsilon_{\beta\gamma}$
U_R	24	0	0	0								
ϵ_R	72	0	0	0								

n_i is the total number of modes, n_i' the number of internal modes, T' , R' the modes of translational and rotational type and T pure translations. The Raman active modes in the crystal may be divided into two classes, namely, totally symmetric A_g and asymmetric B_g . As the centre of symmetry lies at each molecule in the crystal, each of the Raman active modes of the molecule will be Raman active in the crystal and will belong to both the symmetric and anti-symmetric class. Similarly the three rotations of the molecule will give rise to three totally symmetric and three anti-symmetric Raman active rotational modes in the crystal.

The three symmetric modes are those in which the rotations are in the opposite sense in the two molecules. As the lattice modes involve intramolecular forces, we may not expect the same frequency for the two modes, but as these frequencies are small it may not be possible to resolve the differences and the lines will therefore appear as broad bands. According to Bhagavantam (1941) oscillations coming under the translatory type have

small frequencies and the Raman lines are weak while those coming under the rotatory type will be characterised by relatively large frequencies and will give rise to strong lines if the rotating group has large anisotropy.

The tensor components of the Raman active modes in the crystal can be determined by their behaviour in directional excitation. If OX be the direction of illumination, OY the direction of observation and OZ at right angles to both, then the depolarisation ratio ρ , for the electric vector along

OY is $\rho_{o\mu} = \frac{\epsilon_{\mu\mu}^{\omega}}{\epsilon_{\mu\mu}^{\omega}}$ and for the electric vector along OZ , $\rho_{\omega} = \frac{\epsilon_{\omega\omega}^{\omega}}{\epsilon_{\omega\omega}^{\omega}}$. If α, β, γ

be the directions of the optic axes of the crystal then since β axis is the axis of symmetry a totally symmetric vibration has four surviving tensor components $\epsilon_{\alpha\alpha}, \epsilon_{\beta\beta}, \epsilon_{\gamma\gamma}, \epsilon_{\gamma}$ and an anti symmetric vibration only two components $\epsilon_{\alpha\beta}, \epsilon_{\beta\gamma}$. The method of deriving the behaviour of these vibrations for directional excitation has been discussed by Saksena (1940). These are given in Table III.

TABLE III

Symmetry axis	OZ			OY			OX		
	OZ	OY	un-pol	OZ	OY	un-pol	OZ	OY	un pol
Symmetric $\epsilon_{\alpha\alpha}=a, \epsilon_{\beta\beta}=b, \epsilon_{\gamma\gamma}=c,$ $\epsilon_{\alpha\gamma}=d, \epsilon_{\alpha\beta}=0, \epsilon_{\beta\gamma}=0.$	$\frac{0}{b^2}$	$\frac{d^2}{0}$	$\frac{d^2}{b^2}$	$\frac{d^2}{c^2}$	$\frac{0}{0}$	$\frac{d^2}{c^2}$	$\frac{0}{a^2}$	$\frac{0}{d^2}$	$\frac{0}{a^2+d^2}$
Antisymmetric $\epsilon_{\alpha\alpha}=\epsilon_{\beta\beta}=\epsilon_{\gamma\gamma}=\epsilon_{\alpha\gamma}=0,$ $\epsilon_{\alpha\beta}=e \quad \epsilon_{\beta\gamma}=f.$	$\frac{f^2}{0}$	$\frac{0}{e^2}$	$\frac{f^2}{e^2}$	$\frac{0}{0}$	$\frac{e^2}{f^2}$	$\frac{e^2}{f^2}$	$\frac{e^2}{0}$	$\frac{f^2}{0}$	$\frac{e^2+f^2}{0}$
Both type symmetric and antisymmetric	$\frac{f^2}{b^2}$	$\frac{d^2}{e^2}$	$\frac{d^2+f^2}{b^2+e^2}$	$\frac{d^2}{c^2}$	$\frac{e^2}{f^2}$	$\frac{d^2+e^2}{c^2+f^2}$	$\frac{e^2}{a^2}$	$\frac{f^2}{d^2}$	$\frac{e^2+f^2}{a^2+d^2}$

We thus see that with the symmetry axis along the direction of observation, the symmetric vibrations will be absent when the electric vector is along the direction of observation while the anti-symmetric vibrations will be absent when the electric vector is along the perpendicular direction OZ . If a vibration is both symmetric and anti-symmetric the depolarisation ratios are as shown in the third row.

Bhagavantam has considered the lattice modes of para-dichloro-benzene but he has omitted the frequency 27 observed by Vuks. According to him only three oscillations are observed and each is a symmetric and anti-symmetric mode.

EXPERIMENTAL

The crystal was supplied to us by late Shrimati S. Bai. It was grown from melt by the process of slow cooling and was free from impurities as it was grown after several crystallizations. The crystal was in the form of

a cylinder with its symmetry axis along the length of the cylinder. As the crystal evaporates rapidly and internal cracks develop easily, it was not cut in the form of a cube whose axes are along the axes of polarisability ellipsoid, but was worked as such. The crystal was quite clear in a fairly large region and free from internal strains. The light from a horizontal arc was focused on the crystal contained in a glass tube and was polarised with the help of a polaroid with an efficiency of 90% in the 4358 Å region. A double image prism of calcite was used to split the scattered light into horizontal and vertical components. The pictures were taken on a Hilger two prism glass spectrograph and measured on a Hilger comparator. These results are shown in Tables V and VI. One picture (Fig. *e*, Plate IV A) of the liquid spectrum and one picture (Fig. *c* and Fig. *d*) of the solid taken on a Fuess glass spectrograph were also given to us by late Shrimati S. Bai and their results are also included here.

The low-frequency spectrum of the solid picture (Fig. *b*) taken by Shrimati S. Bai differs materially from that of our crystal although the molecular frequencies are identically the same. This crystal must have grown under different conditions. The results of measurements of the low frequency lines on the solid pictures taken by S. Bai support the results of Sirkar and co-workers and of Venkateswaran while the results of measurements of the spectra taken by us with the other crystal support the results of Vuks. The results of measurements on the two solid pictures and the liquid picture are given in Table IV and the results of directional excitation in Table V.

TABLE IV

Low frequencies	Molecular frequencies								Spectrograms	
Solid I (15) (30) (8)	308 (10)	330 (10)	630 (8)	747 (10)	1071 (2)	1106 (10)	1160 (0)		(a) & (f)	
Solid II (12) (8) (5)	308 (8)	330 (8)	630 (6)	747 (6)	1071 (0)	1106 (6)			(b) & (c)	
Solid II (8) (6) (6)	308 (2)	330 (8)	630 (5)	747 (8)	1071 (2)	1106 (8)	1160 (1)		<i>d</i> .	
Liquid Polarisation	299 (5) D	330 (8) P	628 (4) D	675 (0)	747 (8) P	1071 (3) P	1084 (3) P	1106 (8) P	1160 (2) P	(e)
Solid I			1376 (1)	1485 (1)	1573 (8)	3072 (15)				(a) & (f)
Solid II			1376 (1)	1485 (1)	1573 (4)	3072 (10)				(b) & (c)
Solid II			1376 (1)	1485 (1)	1573 (6)	3072 (12)				(d)
Liquid Polarisation	1248? (0)	1376 (1) D	1485 (1)	1573 (6) D	3072 (10) P					(e)

The liquid spectrum has been reported earlier by Kohlrausch and co-workers who report 11 frequencies (for reference vide Hibben, 1939). The liquid picture (*c*) reported here is a very overexposed one and it shows the presence of weak frequencies 675, 1248, 1485. The *f*-excitation of strong frequencies 747 and 1573 should fall at 690 and 1516 which are far removed from the observed values. The frequency 1485 also occurs in several solid pictures. The polarisation picture shows that there are 7 well polarised lines in the liquid while there should be only 6 according to theory. The frequencies 1071 and 1084 form a close doublet both being polarised. It is interesting to note that the sum of two strong frequencies 331 and 747 is 1078 which lies in between the observed frequencies 1072 and 1084. It is possible therefore that the frequency at 1078 has split as a result of Fermi resonance. A comparison of the solid and liquid picture shows a definite frequency shift for the frequency 299 in the liquid to 308 in the solid [Figs. (*c*) and (*d*)]. A comparison of the pictures of the two solids (I) and (II) shows remarkable differences. The frequency 27 of solid (I), Fig. (*a*) is absent in solid (II), Fig. (*b*) where a new frequency at 45 is present. There is also a shift in the frequency 94 reported for solid (I). Also in solid (I) 54 is the strongest frequency while in solid (II) it is 45. The spectrum of solid (I) is the same as that of Vuks and the spectrum of solid (II) the same as that of Sirkar and Venkateswaran. By a comparison of the two spectra (*c*) and (*d*) for solid (II) we find that while the spectrum (*d*) is stronger, the lattice lines and frequency 308 in (*d*) are weaker than in (*c*) and the remaining molecular frequencies, excepting 308, are stronger. The frequency 308 shows a much larger diminution of intensity than the lattice frequencies.

The low frequency Raman lines are very strong compared to molecular frequencies. The visual intensities recorded for them are of the anti-Stokes lines in 4046 excitation while the intensity recorded for the molecular frequencies are of the Stokes lines in the 4358 excitation.

The following points may be noted :

(1) A comparison of the spectrograms (*f*) and (*g*) (Plate IV B) of total intensity taken with symmetry axis along *OY* but with the electric vectors along *OY* in one and *OZ* in the other shows that the frequencies 747, 1071, 1106, 3072—particularly the first three, are very much increased in intensity in the latter case when the electric vector is along *OZ*, while the frequencies 308, 630, 1376 remain nearly of the same intensity in the two cases and the frequencies 330, 1573 are reduced in intensity in the latter case. The frequencies 747, 1071, 1106 and 3072 are almost of the same intensity as 630 and 1573 when excited by the electric vector along *OY*.

(2) Among the low frequencies 54 remains the strongest in all the spectrograms. With the symmetry axis along *OY*, the frequency 27 is stronger than 94 when the electric vector is along *OY* in (*f*), while it is much weaker than 94 when the electric vector is along *OZ* in (*g*). The frequency

TABLE V

Directional excitation of Raman lines

Illumination along OX			Observation along OY													Spectrogram.			
Symm. axis along	Electric vector along	Scattered component.	Low frequencies.			Molecular frequencies													
			27	54	94	308	330	300	747	1072	1106	1376	1485	1573	3072				
OY	OY	S_x	6	20	4	6	5	4	5	2	6	1	$\frac{1}{2}$	1	10	} \leftarrow (i) \odot			
OY	OY	S_z	8	12	6	5	8	5	8	3	8	2	$\frac{1}{2}$	6	12				
OY	OY	S_x, S_z	15s	30	6br	10	10	6	6	2	5	1	1	5	12	(l) \odot			
OY	OZ	S_x	4	6	5	1	0	0	1	1	1				2	} \odot (k) \leftarrow			
OY	OZ	S_z	3	5	3	1	1	1	2	1	2				4				
OY	OZ	S_x, S_z	15	30	25	10	6	6	12	6	12	2		2	15	(g) \leftarrow			
OZ	OY	S_x	1	2	3											} \leftarrow (f) \odot			
OZ	OY	S_z	1	8	0														
OZ	OY, OZ	S_x	5	12	3	2	2		2	0	2			$\frac{1}{2}$	3	} \leftarrow (l) \odot			
OZ	OY, OZ	S_z	5	12	1	1	3		2	$\frac{1}{2}$	2			1	3				
OX	OY, OZ	S_x	5	8	1	0	2		1		1			1	2	} \leftarrow (h) \odot			
OX	OY, OZ	S_z	6	6	2	0	2		1		1			$\frac{1}{2}$	2				

94 also appears weakest when the symmetry axis is along OX in (h). The behaviour of 94 is thus similar to the behaviour of frequencies 747, 1071, 1106, 3072, which get stronger when the electric vector is along OZ and symmetry axis along OY.

(3) The frequency 27 does not disappear in any picture.

DISCUSSION OF SPECTRA OF SOLID (II).

(a) Molecular frequencies :

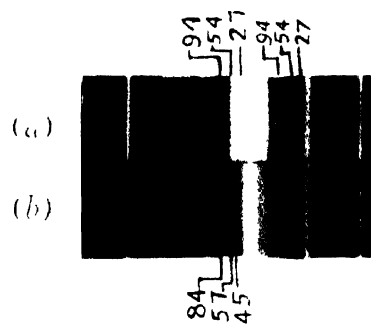
We shall first consider the liquid spectrum. According to theory we should get 15 Raman lines of which 6 should be polarised and 9 depolarised. The six polarised frequencies are 330, 747, 1071-1084, 1106, 1169, 3072 and seven depolarised lines are 299, 628, 675, 1248, 1376, 1485, 1573. The six polarised frequencies naturally represent the planar vibrations of the molecule ; of these 330 is a C-Cl oscillation, 3072 is a C-H oscillation and the others are C-C oscillations. Among the depolarised oscillations 299 and 630 represent vibrations perpendicular to the plane of the benzene ring.

All the lines in the liquid spectrum appear in the solid with the same frequency. Each of these lines is both a symmetric and anti-symmetric

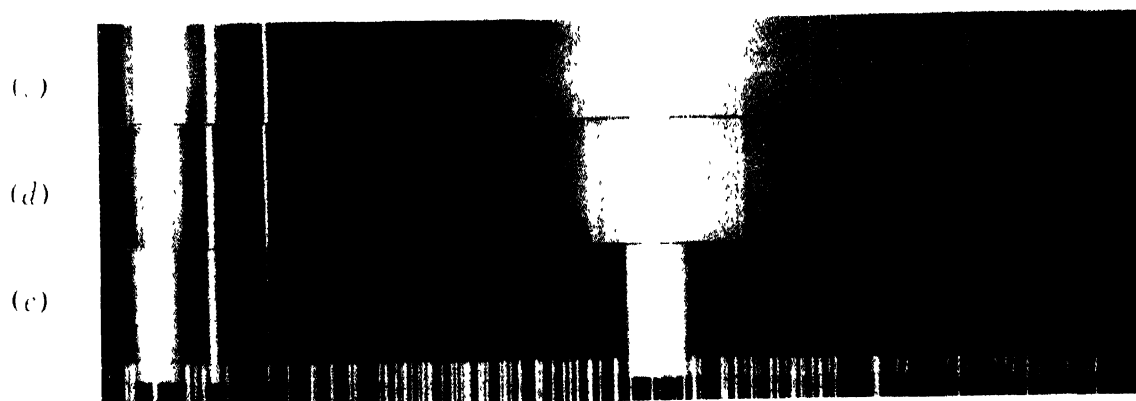
oscillation with respect to the crystal and the behaviour of these lines in directional excitation is dependent upon the fact as to which of the two is stronger. From Table III we see that if the symmetry axis of the crystal is along the direction of observation, the symmetric oscillations are absent and the anti-symmetric oscillations appear with great intensity if the electric vector is along the direction of observation but the reverse happens if the electric vector is along the perpendicular direction OZ . Now since the molecular frequencies appear in both the cases they are both symmetric and anti-symmetric. The total intensity of a symmetric oscillation when the electric vector as well as the symmetry axis are both in the direction of observation is 0, while that of an anti-symmetric oscillation is $e^2 + f^2$. If a vibration is both symmetric and anti-symmetric its intensity will be $e^2 + f^2$ where e and f are component tensors of the anti-symmetric type. If, however, the electric vector is along OZ the intensity of both together will be $d^2 + c^2$ where d and c are component tensors of the symmetric type of oscillation. If, therefore, greater intensity occurs for a particular oscillation in the second case, the symmetric tensor components must be greater than the anti-symmetric ones. In this way it has been possible to write the tensor components and analyse the vibrations.

It has been stated in the previous section that when the symmetry axis is along OY and the exciting electric vector along OZ or OY . [spectrograms (g) and (f)], the frequencies 747, 1071, 1106, 3072 are stronger in the former case than in the latter while 330 and 1576 are stronger in the latter case than in the former and the frequencies 308, 630, 1376 remain nearly of the same intensity in the two cases. It follows from what has been stated above that the sum of the tensor components $d^2 + c^2$ of symmetric oscillation of the frequencies 747, 1071, 1106, 3072 is much greater than the sum of tensor components $e^2 + f^2$ of the anti-symmetric oscillation of these frequencies, while for 330 and 1573 the sum $d^2 + c^2$ is smaller than $e^2 + f^2$ and for frequencies 308, 630, 1376 the two are almost the same.

The frequencies 747, 1071, 1106, 3072 are the polarised frequencies in the liquid spectrum, and therefore represent the totally symmetric planar vibrations of the molecule. It has been shown by Nedungadi (1941, 42) in naphthalene that when the electric vector is in the plane of the molecule, the planar vibrations are excited more strongly than when it is perpendicular to the molecular plane. In the case of a para-dichlorobenzene the molecule lies roughly in the bc plane where b is the symmetry axis and c the length of the molecule. If the symmetry axis b is along the direction of observation OY , and the c -axis vertical along OZ then whether the electric vector is along OZ or OY it remains in the plane of the molecule. But the electric vector will excite more strongly in the direction OZ because this direction is along the length of the molecule which is the direction of maximum optical polarisation (*vide* Plate IVB, Fig. g). If the electric vector is along OY the



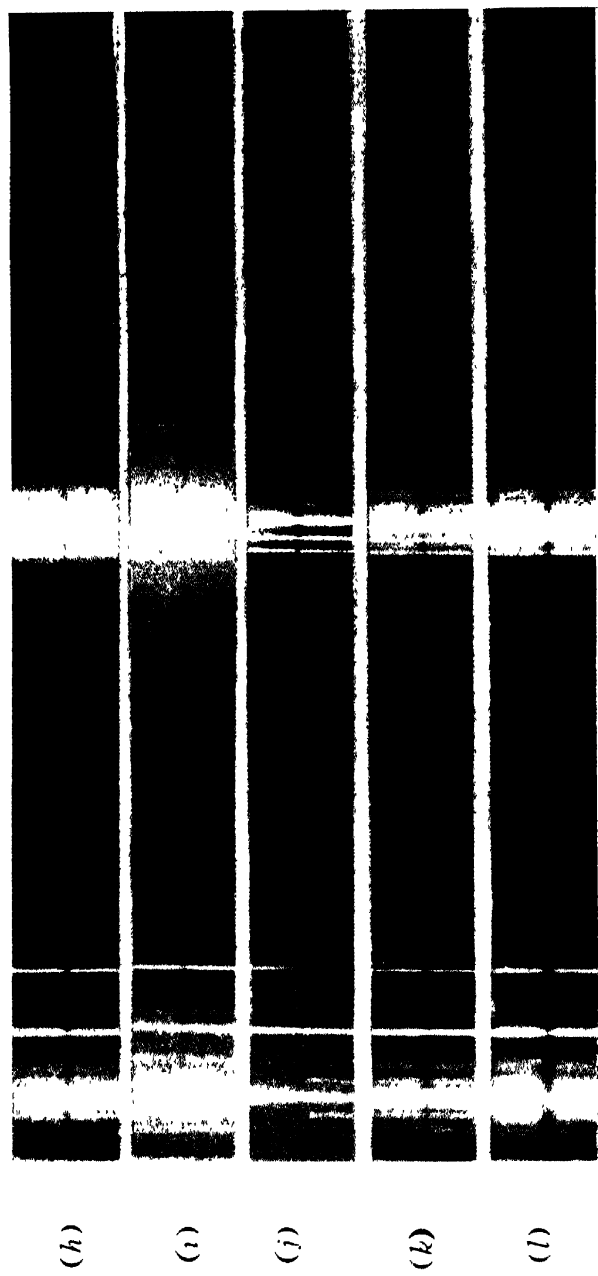
Low frequency lines of solid (I) and (II).



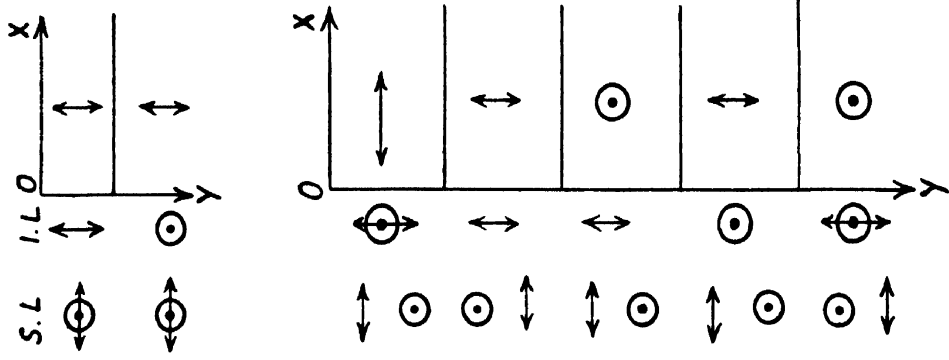
Raman spectra of solid (II) and liquid.



Two different Raman Spectra of solid(I).



Polarisation of Raman lines of solid (I) in different orientations.



direction of observation, it lies along the breadth of the molecule, and these frequencies will be weaker for two reasons, firstly because the breadth of the molecule is in a direction of intermediate polarisation and secondly because the totally symmetric vibrations will scatter weakly when the electric vector is along the direction of observation. From Fig. (k) Plate IV B we see that the molecular frequencies have come out very weak when the electric vector is along OZ and the symmetry axis along OY . This is easily explained if we imagine the c -axis to lie along the direction of illumination OX so that the electric vector OZ is now perpendicular to the plane bc of the molecule. In this case the electric vector OZ shall excite very weakly.

The behaviour of the frequency 330 appears to be different from those of the other lines 747, 1071, 1106, 3072 in the liquid. The former decreases in intensity when the electric vector is along OZ and symmetry axis along OY while the latter increases in intensity. As all these frequencies represent the totally symmetric vibrations of the molecule, they should be expected to behave alike. It is possible that the difference in behaviour may be related to the nature of the vibration.

The frequency 299 also shows large variation in intensity and frequency in passing from solid to liquid. In the liquid the frequency 299 is weaker than 330 but in the solid it becomes comparable in intensity to 330 and even stronger and its frequency also increases to 308, [Plate IVA, Figs. (e), (d) and (c)]. This frequency, like 628, is an anti-symmetric oscillation perpendicular to the plane of the ring, and so the anti-symmetric tensor components would be larger than the components of the symmetric tensor. It is possible that 308 represents the anti-symmetric oscillation and 300 the symmetric one but the latter may be too weak to appear. No such variation of frequency has been noticed in other lines. But the frequency 330 in the solid behaves differently from other polarised vibrations like 747, 1106, etc. and more like the depolarised frequency 1573. This may be explained by supposing that it is also an anti-symmetric oscillation, in the crystal.

(b) Lattice frequencies :

The behaviour of the low frequency Raman lines in the crystal in directional excitation can be explained if we represent the frequencies by the three tensors :

27			51			91		
6	5	3	12	12	5	4	2	4
6	5	6	12	5	8	2	2	3
3	6	4	5	8	9	7	8	7

The figures which are only relative and give the squares of tensor components, have been arrived at by a careful study of all the spectrograms taken with crystal and in different orientations with the help of Table III by following the method described in the preceding paragraphs. It may be

seen that each frequency consists of a symmetric and an anti-symmetric part but in the frequency 94 we find that the components e and f representing the anti-symmetric oscillation are smaller than the remaining tensor components a, b, c, d which represent a symmetric oscillation. Thus 94 behaves in the same way as the polarised molecular frequencies 747, 1106 etc. When the symmetry axis is along OY and electric vector along OZ , the intensities of the three frequencies 27, 54, 94 being given by the value of $d^2 + c^2$ are as 7 : 14 : 11 while if the electric vector be along OY they will be given by the value of $e^2 + f^2$ and are as 11 : 20 : 5. Thus in the first case 94 is stronger than 27 and in the second case weaker while 54 is always the strongest. Using these tensors the polarisation of the lattice frequencies have also been written down and compared with the observed values :

Symmetry axis Electric Vector	OZ	OZ	OY	OY	OX
	OY	OY & OZ	OZ	OY	OY & OZ
27 Calculated	3/5	9/10	3/4	3/6	11/15
	1/1	5/5	3/4	6/8	5/6
54 Calculated	5/12	13/17	5/9	12/8	20/17
	2/8	12/12	5/6	20/12	8/6
94 Calculated	4/2	7/4	4/7	2/3	5/8
	3/10	3/1	3/6	4/6	1/2

It has been stated earlier that the low frequency Raman lines represent rotational oscillations. The frequency of a rotational oscillation will depend upon the moment of inertia involved in a given oscillation while its intensity will depend upon the molecular anisotropy produced in a given vibration. The frequency 94 may therefore be regarded as due to oscillations about the length of the molecule or the c -axis as the moment of inertia about this axis is minimum, while the frequency 27 will represent an oscillation about an axis perpendicular to the plane of the molecule or roughly the a -axis as the moment of inertia involved in this case will be the largest. The moment of inertia will have an intermediate value about the breadth of the molecule and the intermediate frequency 54 may reasonably be assigned to oscillations about this axis. As the intensity depends upon the optical anisotropy coming into play during a vibration, we may expect the frequency 54 to be the strongest as the oscillations about the breadth of the molecule will involve the largest anisotropy.

It is to be remarked that the lattice frequencies are very much more intense than the molecular frequencies. If we take three soft crystals—gypsum, naphthalene and para-dichlorobenzene, we find that the lattice lines are much weaker than the molecular Raman lines in gypsum, of comparable intensity in naphthalene and of large intensity in para-dichlorobenzene. As

the lattice Raman lines are rotational oscillations, it is likely that this difference is due to the anisotropy of the rotating group. In gypsum the rotating group SO_4 is tetrahedral and has the smallest anisotropy and so the lattice lines will be weak. In para-dichlorobenzene, however, the anisotropy of the rotating group is the largest, firstly, because the molecule is plane and secondly because it is very much elongated along one of the axes, and so the lattice lines may be expected to be very intense.

Comparison of the spectra of the solids (I) and (II).

Several spectrograms of solid (I) reveal clearly the three low frequency lines 27, 54 and 94 cm^{-1} both in the 4046 and 4358 excitations, but the two pictures (c) and (d) taken with Buss glass spectrograph by S. Bai reveal three different frequencies 45, 57 and 84 although the liquid spectrum is the same in the two cases. The frequency 27 does not appear in that picture. The spectrograms taken with crystal in different orientations also reveal the fact that the frequency 27 does not vanish in any orientation. Hence its disappearance in one picture is not due to an orientation effect.

The difference in behaviour between solids (I) and (II) is also indicated by the behaviour of the molecular frequencies 308 and 330. In the two pictures (c) and (d) of solid (II) we find that in one picture (d) which is stronger of the two, the molecular frequencies have come out stronger than in the other but all the lattice frequencies and the frequency 308 are weaker. This is different from the behaviour of solid (I) in which the lattice frequency 94 behaves differently from other lattice frequencies and more like the symmetrical oscillations. Further, when the symmetrical vibrations are stronger, the frequency 330 is weaker than 308 in solid (I) (Fig. g) but 308 is weaker than 330 in solid (II) (Fig. d) Also 54 is the strongest frequency in solid (I) and 45 in solid (II).

Venkateswaran, while working with para-dichlorobenzene cooled from melt also gets the same frequencies as those of solid (II) namely 45, 57, 84. In this case the substance cooled was not a single crystal, while in our case it is a single crystal since it was grown from melt by slow cooling. It is possible that a change of structure may occur in rapid cooling and in fact Sirkar and Bishui and also Vuks report change of frequencies by sudden cooling in ice. We therefore feel inclined to think that a change of structure does occur in sudden cooling.

Bech (1906) and Vuks have discussed the transformations of para-dichlorobenzene. Bech points out that when this liquid is cooled below 39°C a sudden contraction of volume takes place, and this is considered as a modification of the lattice. Vuks has discussed a transformation in which the molecules rotate in their position so that the projection on the *ac* plane is now inclined to the *c*-axis. This transformation would require no change of volume as the lattice is unaltered and it takes place at 32°C . But according to Sirkar and Gupta this transformation would involve a change of X-ray

intensities in Laue spots which has not been noticed by them. Venkateswaran and also Sirkar and co-workers fail to report any change of spectra by change of temperature. It however, appears definite to us that some change of structure does take place in the way the crystal is grown and the point requires further investigation.

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