

RAMAN SPECTRA OF ORTHO AND META DICHLOROBENZENE IN DIFFERENT STATES AND AT DIFFERENT TEMPERATURES*

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Plates IV A, B

ABSTRACT. The Raman spectra of ortho and meta dichlorobenzene in different states and at different temperatures have been photographed and compared with each other and with that due to *p*-dichlorobenzene. In the case of the ortho compound two lines at 468 and 487 cm^{-1} due to the mode ϵ''_g coalesce to form one intense line at 478 cm^{-1} and the line at 433 cm^{-1} becomes weaker when the substance is solidified and cooled down to -180°C . These changes have been explained by attributing the line at 487 cm^{-1} to a carbon ring vibration in a single molecule while the line at 468 cm^{-1} to the same vibration in a dimer. In the case of the meta compound some of the lines disappear with solidification and these results have been also explained by assuming the presence of dimers as well as monomers in the liquid state and only dimers in the solid state of the substance. The Raman lines due to C—H valence oscillation become sharper with solidification so that the lines 3062 and 3080 cm^{-1} are resolved from each other.

The new lines in the low-frequency region are different for the two substances. At a temperature of -60°C , the crystal of ortho dichlorobenzene produces a single new line at 25 cm^{-1} while the crystal of *m*-dichlorobenzene produces two broad bands at 56 and 81 cm^{-1} respectively. When the temperature is lowered to -180°C , the line at 25 cm^{-1} of *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ crystal disappears but three new lines appear at 68, 81 and 92 cm^{-1} respectively. For similar change of temperature of the meta compound a new line appears at 35 cm^{-1} , the band at 56 cm^{-1} splits up into two lines at 50 and 61 cm^{-1} and the line 81 cm^{-1} shifts to 89 cm^{-1} . It is pointed out that although these two molecules have smaller number of symmetry elements than the *p*-dichlorobenzene molecule, the number of the new lines in the low frequency region is much larger in the latter case. The significance of these results has been discussed.

I N T R O D U C T I O N

The Raman spectra of paradichlorobenzene in the solid state have engaged the attention of a large number of workers (Vuks, 1936; Sirkar and Gupta, 1936; Venkateswaran, 1938; Rousset, 1948; Korshunov, 1950; Narain and Saksena, 1951 and Ray, 1951). Rousset (1948) assigned the new lines in the low-frequency

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region to the different modes of angular oscillation of the molecules about three axes in the crystal lattice. Korshunov (1950) attributed the origin of three of the nine such lines observed by him to the translational oscillations which are ordinarily forbidden at room temperature but appear at low temperature, while Narain and Saksena (1951) postulated the existence of two different crystal modifications to explain the origin of two different sets of low-frequency lines observed by them in the case of two specimens. In one of these modifications they assumed the existence of free rotation of the molecules about an axis. Ray (1951) observed that the Raman spectrum in low-frequency region of *p*-dichlorobenzene crystal is identical for an approximately single crystal and a polycrystalline mass of the substance, but the spectrum is altered if the crystal is once cooled down to a few degrees below 0°C and then brought back to room temperature again. On analysing the data given by different authors, Ray (1951) concluded that these low-frequency lines of *p*-C₆H₄Cl₂ crystal cannot be attributed to the angular oscillations of molecules in the field of simple Van der Waals' force of crystal lattice. The results of ultraviolet absorption spectra of this compound obtained by Sirkar and Swamy (1953) lend further support to the conclusion arrived at by Ray (1951). The absorption bands of crystals of *p*-C₆H₄Cl₂ become extremely sharp at low temperatures. They concluded from these results that angular oscillations of the molecules cease at low temperature. The intensity of the low-frequency lines does not diminish, however, with lowering of temperature. From a comparison of the results of the investigations on the Raman spectra with those on ultraviolet absorption spectra, Swamy (1953) concluded that the low-frequency lines in the case of *p*-C₆H₄Cl₂ cannot be due to the angular oscillations of the molecules in the crystal lattice.

The suggestion put forward by Korshunov (1950) can be tested by studying the Raman spectra in the low-frequency region of a few suitably chosen substituted benzene compounds. If his interpretation for the origin of three low-frequency lines be correct, we would expect the number of low-frequency lines to be larger in the Raman spectra of crystals of ortho and meta dichlorobenzene than in the case of *p*-dichlorobenzene in the solid state, because in the former two cases the unit cell has no centre of symmetry and the translational oscillations of the lattice are allowed. On the other hand, Sirkar and Swamy (1952) observed, while studying the ultraviolet absorption spectra of *o*-dichlorobenzene at low temperatures, that the influence of intermolecular field on the molecules of this substance is strong enough to split up the electronic energy levels into three components. In the case of *m*-dichlorobenzene also similar results are expected. Further, the Raman spectra of these two substances in the vapour state have been studied by Spomer and Kirby-Smith (1941). The data published by them indicate that some of the strong lines due to molecular vibrations of these two compounds are absent in the Raman spectra of the substances in the vapour state.

Microphotometric records of Raman spectra

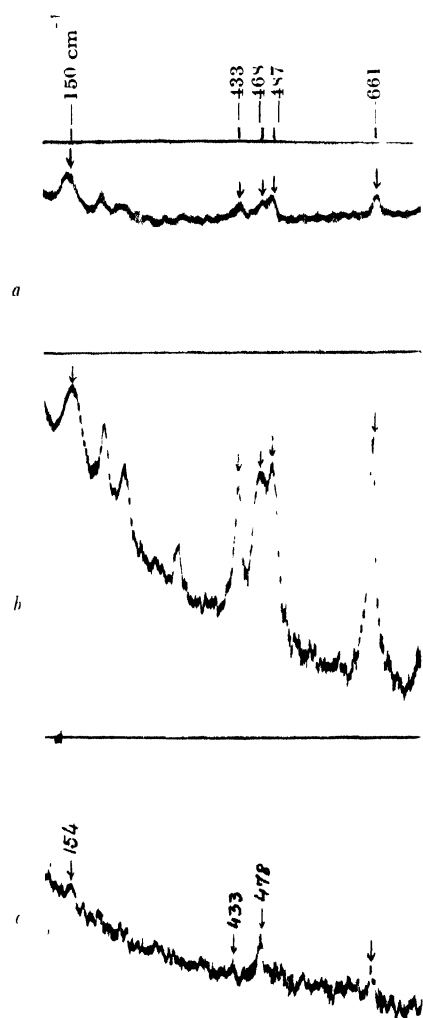


Fig. 1
Ortho dichlorobenzene
(a) Liquid at 110°C
(b) Liquid at 28°C
(c) Solid at -180°C

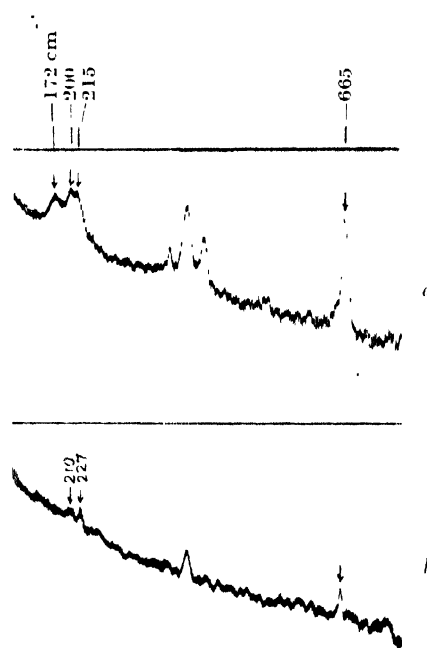


Fig. 2
Meta dichlorobenzene
(a) Liquid at 28°C
(b) Solid at -180°C

Microphotometric records of Raman spectra

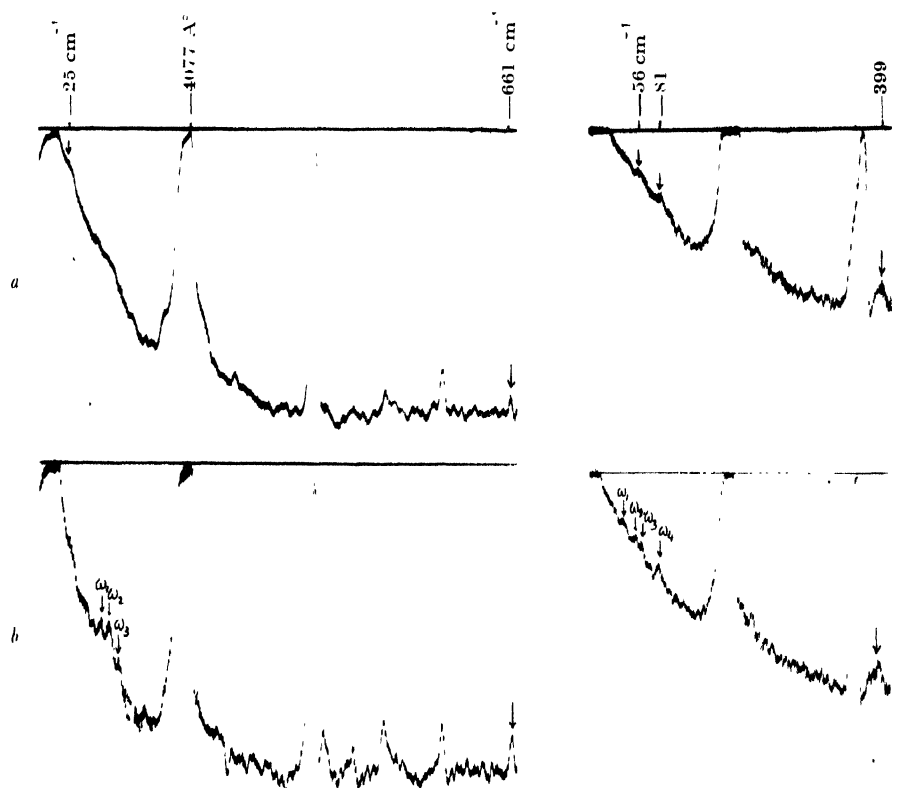


Fig. 3

Ortho dichlorobenzene

(a) Solid at about -60°C

(b) Solid at -180°C

 $w_1 = 68 \text{ cm}^{-1}$, $w_2 = 81 \text{ cm}^{-1}$, $w_3 = 92 \text{ cm}^{-1}$

Fig. 4

Meta dichlorobenzene

(a) Solid at about -60°C

(b) Solid at -180°C

 $w_1 = 35 \text{ cm}^{-1}$, $w_2 = 50 \text{ cm}^{-1}$ $w_3 = 61 \text{ cm}^{-1}$, $w_4 = 89 \text{ cm}^{-1}$

The object of the present investigation was to find out whether similar changes take place in the Raman spectra of the two substances with the change from liquid to solid phase and whether the relative positions of the two halogen atoms in the molecule have any influence on the number and intensity of the new lines which appear in the low-frequency region with the solidification of these substances.

EXPERIMENTAL

The liquids ortho and meta dichlorobenzene were supplied by B. D. H. Laboratory and Schuchardt Co. Ltd. respectively and they were of chemically pure variety. They were again distilled in vacuum before every exposure. The Raman lines of these liquids were, as usual, compared with those obtained by previous workers in order to test the purity of the samples. The Raman spectra of the substances in the solid state at different low temperatures were recorded in the same way as described in previous papers (Biswas, 1954*a*, 1954*b*). In all cases the spectra were photographed on Ilford Zenith plates with the help of a Fuess glass spectrograph having dispersion of about 11 \AA° in the 4047 \AA° region. The microphotometer records were taken with a Kipp and Zonen type self-recording Moll microphotometer.

RESULTS AND DISCUSSION

Tables I and II contain the calculated Raman shifts of the substances both in the liquid state and in the solid state at different low temperatures. The tables also include for comparison the Raman shifts of the substances in the liquid phase as observed by Swaine and Murray (1933). Microphotometric records showing the intensities of the low-frequency lines in relation to that due to some molecular vibration and also showing the relative intensities of some of the molecular vibrations in different states have been reproduced in figures 1, 2, 3 and 4 (Plates IVA, IVB).

(a) *Intramolecular oscillations:*

From Table I it is found that the lines at 698 (0), 780 (1), 934(0), 1070 (0) and 1460 (0) cm^{-1} observed in the present investigation for the liquid state of ortho dichlorobenzene have not been reported by the previous workers. Similarly Table II shows that meta dichlorobenzene in the liquid state yields a few extra Raman lines at 744 (0), 773 (3), 872 (0), 891 (1) 934 (1) and 2983 (1) cm^{-1} . The spectrograms of the present investigation have been probably exposed for a longer period and hence some feeble lines have appeared in them. The extra line at 773 cm^{-1} is, however, quite intense and it is difficult to understand why it was not reported earlier. On the other hand, a few feeble lines reported by earlier workers in the case of meta dichlorobenzene cannot be traced in the spectrograms obtained in the present investigation. These lines are at 1018 (0), 1456 (0), 1544 (0) and 1625 (0) cm^{-1} respectively.

TABLE I
Orthodichlorobenzene, $o\text{-C}_6\text{H}_4\text{Cl}_2$
 $\Delta\bar{\nu}$ in cm^{-1}

Vapour Spomer & Smith (1941)	Liquid		Solid (Present author)	
	Swaine & Murray (1933)	Present author	At about -60°C 25 (3) k	At -180°C
				68 (2) k 81 (3) e,k 92 (1b) k
	154 (10)	150 (10b) \perp e,k	154 (3) e,k	157 (4) e,k
194 (w)	203 (3)	204 (4) \pm e,k	200 (1) e	200 (1) e
	239 (1b)	243 (3b) \pm e, \pm k	251 (1b) e,k	251 (1b) e,k
300 (m)	330 (0b)	333 (3) \perp e,k	335 (0) e,k	335 (0) e,k
434 (vw)	430 (1)	433 (6) \perp e,k,i	433 (2) e,k	433 (1) e,k
	469 (1)	468 (5b) \perp e,k	478 (3b) e,k	478 (4) e,k
487 (m)	483 (2)	487 (7b) e,k		
664 (m)	658 (5)	661 (8) \perp e,k,i 698 (0) e	661 (3) e,k	661 (3) e,k
760 (w)	756 (0b)	750 (2b) e,k 780 (1) e,k 855 (0) e 934 (0) e	750 (0) e,k 780 (0) e	750 (0) e,k 780 (0) e
	1020 (1)	1021 (3b) e,k	1021 (0) e,k	1021 (0) e,k
1035 (st)	1041 (10)	1041 (10) e,k 1070 (0) e	1041 (4) e,k	1041 (6) e,k,i
1133 (st)	1129 (5)	1134 (8) e,k,i	1134 (3b) e,k	1134 (4b) e,k
	1160 (1b)	1159 (3) e,k	1159 (0b) e,k	1159 (1b) e,k
1271 (w)	1274 (1b)	1276 (3) e,k 1382 (1) e,k 1460 (0) e	1276 (0) e,k	1276 (0) e,k
=				
1598 (w)	1577 (4)	1574 (8) e,k	1574 (3) e,k	1574 (4) e,k
	1607 (0b)	1601 (0) e		
	2994 (1)	3004 (0) e,k	3004 (0) e,k	3004 (1) e,k
3082 (st)	3073 (10)	3067 (8) e,k,i	3070 (6) e,k,i	3070 (8b) e,k,i
3150 (w)	3146 (3)	3145 (1) e,k	3145 (0) e,k	3145 (0) e,k

(The letters w, m, st, vw within brackets indicate weak, medium, strong and very weak intensity respectively.)

TABLE II
m-Dichlorobenzene, $m\text{-C}_6\text{H}_4\text{Cl}_2$
 $\Delta\bar{\nu}$ in cm^{-1}

Vapour	Liquid		Solid (present author)	
	Sponer & Smith (1941)	Swaine & Murray (1933)	Present author	At about -60°C At -180°C
				35 (1)e,k
			56 (4b)e,k	50 (3)e,k
				61 (4)e,k
			81 (4b)e,k	89 (4)e,k
205 (wb)	202 (3)	172 (5) ± e, i k	210 (1)e	210 (1b)e
	216 (2)	215 (6) ± e, i k	227 (3)e,k	227 (4)e,k
356 (w)	366 (1)	367 (2)e,k	367 (0)e	367 (0)e
399 (m)	399 (4b)	399 (11) † e,k,i	399 (5)e,k	399 (6)e,k
	428 (2)	430 (4) † e,k,i	430 (1)e,k	430 (1)e,k
613 (vw)	530 (0)	531 (2)e,k		
665 (m)	666 (4)	665 (9)e,k,i 744 (0)e 773 (3)e,k 872 (0)e 891 (1)e,k 934 (1)e	665 (4)e,k	665 (5)e,k
998 (st)	999 (10) 1018 (0)	990 (15)e,k,i	990 (7)e,k,i	990 (8)e,k,i
1056 (m, vb)	1070 (3b) 1109 (2)	1067 (5)e,k,i 1108 (3)e,k	1067 (1)e,k 1108 (0)e,k	1067 (2)e,k 1108 (0)e,k
1129 (m)	1126 (4) 1240 (0) 1425 (0) 1456 (0) 1544 (0)	1130 (9)e,k,i 1159 (3)e,k 1253 (2)e,k 1415 (2)e,k	1130 (2)e,k 1159 (0)e 1253 (0)e 1415 (0)e	1130 (4)e,k 1159 (0)e 1253 (0)e 1415 (0)e
1590 (m)	1579 (5b) 1625 (0)	1582 (10)e,k 2983 (1)k	1583 (4)e,k	1583 (6)e,k
3090 (st)	3076 (10)	3068 (12b)e,k,i	3065 (8)e,k,i 3080 (0)e	3062 (9)e,k,i 3080 (3)e,k
3169 (w)	3152 (2)	3150 (2)e,k	3150 (0)e	3150 (0)e,k

(The letters w, m, st, vw, etc., within brackets indicate weak, medium, strong and very weak intensity respectively; and letter b indicates broad).

When liquid $o\text{-C}_6\text{H}_4\text{Cl}_2$ is solidified and cooled down to a temperature of -60°C , the Raman lines at 150, 204, 243 and at 3067 cm^{-1} are found to shift respectively to 154, 200, 251 and 3070 cm^{-1} . The microphotometric records reproduced in figure 1 show that the intensities of these lines also undergo changes when the liquid is solidified and cooled down to different low temperatures. The intensity of the line at 150 cm^{-1} increases while the line at 433 cm^{-1} becomes weaker at -180°C . The most remarkable change, however, takes place in the pair at 468 and 487 cm^{-1} . Both these lines are fairly strong in the case of the liquid, but with solidification and cooling down of the solid to -60°C , these two lines are replaced by a single line at 478 cm^{-1} . This line is much stronger than any individual member of the pair (vide fig. 1) and has a frequency-shift intermediate between those of the two lines mentioned above. We can, therefore, conclude that the two lines merge into one another in the case of the crystal at low temperatures. The Raman spectra of ortho and meta dichlorobenzene in the vapour state were studied previously by Sponer and Kirby-Smith (1941). They observed only the line at 487 cm^{-1} while the line 468 cm^{-1} was absent in the case of the vapour. In order to find out whether the change in this doublet takes place gradually with rise of temperature of the liquid, the Raman spectrum of liquid $o\text{-C}_6\text{H}_4\text{Cl}_2$ at 110°C was also studied. The microphotometric records reproduced in figure 1 show that the line at 468 cm^{-1} becomes weaker when the liquid is heated to 110°C . These results can be explained on the assumption that the line at 468 cm^{-1} is due to dimers and the line 487 cm^{-1} is due to the monomers present in the liquid and that the number of dimers diminishes with rise of temperature and the dimers disappear in the vapour state. In the case of the solid state, however, the dimeric molecules are under uniform intermolecular field and this may change the frequency a little so that a line at 478 cm^{-1} is produced.

The line 487 cm^{-1} was assigned to the carbon ring vibration of symmetry e_g^+ (Nordheim and Sponer, 1943). It has been concluded now that the line 468 cm^{-1} is also due to such a mode in the dimer formed by the association of molecules in the liquid. The presence of permanent electric moment seems to be responsible for this type of influence, because in the case of para dichlorobenzene no such change is observed in the corresponding line at 330 cm^{-1} . In the liquid the molecules can orient freely and it appears that strongly associated pairs can be formed in the liquid. In the case of the solid state of $o\text{-C}_6\text{H}_4\text{Cl}_2$ the influence of regularly arranged dipoles around each dipole acts in opposition and the resultant influence is less than that in the case of an isolated associated pair of dipoles.

One of the strong lines at 150 cm^{-1} of $o\text{-C}_6\text{H}_4\text{Cl}_2$ in the liquid state has not been detected by Sponer and Kirby-Smith (1941) on the spectrogram for the vapour state of the substance. In the solid state, this line becomes more

intense and shows an increase in the frequency-shift. Hence the origin of this line should also be attributed to dimers formed by the polar molecules of $o\text{-C}_6\text{H}_4\text{Cl}_2$ in the liquid state. This line due to deformation oscillation in the dimer is totally depolarised probably due to the presence of a symmetry element.

In the case of m -dichlorobenzene, the line at 215 cm^{-1} shifts to 227 cm^{-1} and becomes relatively stronger when the substance is solidified and cooled down to different low temperatures. The first line at 172 cm^{-1} of the liquid $m\text{-C}_6\text{H}_4\text{Cl}_2$ seems to disappear completely in the solid state while the line at 200 cm^{-1} shifts to 210 cm^{-1} and becomes diffuse and weaker with solidification of the substance. The photometric records of these lines due to molecular vibration of the substance in different states have been reproduced in figure 2. The line at 172 cm^{-1} which disappears with solidification and the line at 200 cm^{-1} which has a very small intensity in the solid state may be both due to some deformation vibration in the single molecule and the line 215 cm^{-1} may be due to similar vibration in the associated group or a dimer. In the solid state most of the molecules form associated groups and the line at 215 cm^{-1} due to this mode in the associated group becomes stronger while the other two become weaker. Further, in the case of m -dichlorobenzene we get a broad line at 3068 cm^{-1} due to the C-H valence oscillation of the molecules in the liquid phase, while in the solid state at -180°C we get, instead, a pair of relatively sharp lines at 3062 and 3080 cm^{-1} respectively. These two lines are broad in the liquid phase and appear as a single broad band, while in the solid state they are sharp and are resolved into two distinct lines.

The substances studied in the present investigation are both polar and the principal changes in the vibrations take place at a temperature not much below their freezing points. This result is in agreement with that obtained by Swamy (1953), who noticed that some changes occur in the absorption bands of o -dichloro-benzene even at a temperature of -50°C of the solidified mass.

(b) *Low-frequency lines :*

The microphotometric records reproduced in figure 3 show that o -dichlorobenzene in the solid state at -60°C gives rise to a single and intense new line at 25 cm^{-1} in the low-frequency region. With lowering of temperature of the solidified mass to -180°C , this line at 25 cm^{-1} disappears while three other new lines appear at 68 , 81 and 92 cm^{-1} respectively. The line at 81 cm^{-1} has intensity comparable to that of some of the intense lines due to molecular vibrations. The microphotometric records given in figure 4, show the low-frequency lines exhibited by the meta compound in the solid state at -60°C and

-180°C . At -60°C the crystal produces broad and intense Raman lines at 56 and 81 cm^{-1} respectively. When the polycrystalline mass is gradually cooled down to -180°C , the broad band at 56 cm^{-1} splits up into two intense and sharp lines at 50 and 61 cm^{-1} , while the band at 81 cm^{-1} shifts to 89 cm^{-1} and becomes more intense and sharper. Also a new line at 35 cm^{-1} appears with the lowering of temperature to -180°C .

It would be interesting to compare these results with those observed in the case of *p*-dichlorobenzene, because such a comparison would reveal the influence of relative positions of the same substituent atoms in the molecule on the nature of the Raman spectrum in the low-frequency region. The low-frequency lines exhibited by the crystals of these three isomers at different temperatures are given in Table III. The frequencies for *p*-dichlorobenzene crystal are taken from the results reported by Ray (1951).

TABLE III

 $\Delta\nu$ in cm^{-1}

<i>o</i> - $\text{C}_6\text{H}_4\text{Cl}_2$ crystal		<i>m</i> - $\text{C}_6\text{H}_4\text{Cl}_2$ crystal		<i>p</i> - $\text{C}_6\text{H}_4\text{Cl}_2$ crystal	
at about 60°C	at -180°C	at about 60°C	at -180°C	at about 28°C	at -180°C
25 (3)			35 (1)	17 (3)	11 (3)
				40 (2)	30 (4)
		56 (4b)	50 (3)	50 (2)	55 (3)
68 (2)			61 (4)		61 (4s)
81 (3)		81 (4b)	89 (4)	83 (2b)	106 (3s)
92 (1b)					127 (0)

The results given in Table III can be used to test the correctness of the suggestion put forward by Korshunov (1950). According to the explanation offered by him some of the faint lines observed in the low-frequency region in the case of *p*-dichlorobenzene are due to translational oscillations which are forbidden in the case of centro-symmetrical crystals. In the Raman spectra of the asymmetric molecules of *o*- and *m*- $\text{C}_6\text{H}_4\text{Cl}_2$ these lines are expected to be much stronger than in the case of symmetric molecules of the para compound, but contrary to this expectation the number of new lines in the low-frequency region in the crystals

of para compound is much greater than those yielded by the ortho or the meta compound. Hence, the explanation for the origin of three faint Raman lines at low temperature due to $p\text{-C}_6\text{H}_4\text{Cl}_2$ offered by Korshunov (1950) does not seem to be correct. The data given in Table III further show that the lowering of temperature of the crystals of these isomeric compounds always increases the number of new lines in the low-frequency region and that the maximum number of such lines is exhibited by the crystal of $p\text{-C}_6\text{H}_4\text{Cl}_2$ at -180°C . The ultraviolet absorption spectra of ortho and para dichlorobenzene have already been studied by Sirkar and Swamy (1952) and by Swamy (1953). The results indicate that the angular oscillations of the molecules of these dichlorobenzenes cease at low temperatures. The increase in the number, and sometimes in the intensity of the low-frequency Raman lines, therefore, definitely contradicts the hypothesis that most of these new lines should originate from the angular oscillations of the molecule in the crystal lattice. On the other hand, a consistent explanation for the changes in these new Raman lines in the low-frequency region can be found by attributing them to the vibrations of groups of molecules formed by association in the solid state. In such a group of molecules the number of low-frequency lines can increase at lower temperatures due to association with next neighbours. Such association with next neighbours at lower temperatures disturbs the symmetry of the associated group and brings about a change in the polarisability of the group during any of its resulting vibrations. This can satisfactorily account for the change in intensity of some of the low-frequency lines with lowering of temperature of the crystal. Further, the appearance of larger number of new Raman lines in the low-frequency region in the case of the crystals of the para compound may be due to the fact that the Cl-atoms are at the two extreme ends of the benzene ring and this probably helps in the formation of larger intermolecular complexes in the case of the para compound. The enhancement in the frequency-shifts of some of these new Raman lines in the low-frequency region with lowering of temperature is evidently due to the increase in the strength of some of these virtual bonds at lower temperature. The above discussion on the low-frequency Raman spectra of these three isomeric molecules clearly shows that the new Raman lines in the low-frequency region in these crystals primarily originate from the vibrations in associated groups of molecules formed through virtual bonds in the solid state and that no other hypothesis can satisfactorily explain all the observed facts regarding the Raman spectra of these substances.

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