

ULTRAVIOLET ABSORPTION BANDS OF CRYSTALS OF ORTHO- AND PARADICHLORO BENZENE AND PARADIBROMOBENZENE AT LOW TEMPERATURES*

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(Received for publication, September 2, 1952)

Plates V A-C

ABSTRACT. The ultraviolet absorption spectra of thin films of *o*-dichlorobenzene in the liquid state at 30°C and in the solid state at -50°C and -180°C and of *p*-dichlorobenzene and *p*-dibromobenzene in the liquid state and in the solid state at 30°C and -180°C have been investigated. In the latter two cases the solid films were also once cooled to -180°C and after bringing them to 30°C their absorption spectra were photographed. In the case of *o*-dichlorobenzene in the liquid state only three bands are observed with intervals of about 1030 cm⁻¹. Each of these is split up into two when the liquid is solidified at -50°C, and at -180°C each of the three bands for the liquid is split up into three bands. The intervals between the principal band and the satellites do not agree with any of the vibrational frequencies observed in the case of the vapour. It is suggested that formation of virtual bonds between neighbouring molecules may be responsible for such splitting of the electronic energy level.

In the case of *p*-dichlorobenzene, the liquid as well as the crystal at 30°C yield three broad bands at intervals of about 1030 cm⁻¹. When the crystal is cooled to -180°C and again brought to room temperature three more new bands corresponding to the vibration frequency 764 cm⁻¹ are observed. At -180°C, the number of bands increases owing to the appearance of other new bands corresponding to vibrational frequency 569 cm⁻¹. In the case of *p*-dibromobenzene, the solid at 30°C either before or after once being cooled to -180°C exhibits bands similar to those observed in the case of the liquid. When the solid is cooled to -180°C the bands become sharp and extra bands corresponding to vibrational frequencies 329, 537, 693, 1004, 1202 and 1431 cm⁻¹ appear. The appearance of these extra bands in both the cases is assumed to be due to sharpening of the broad bands caused by the cessation of angular oscillations at -180°C. It is suggested that formation of virtual bonds may be responsible for the damping of angular oscillations at low temperatures.

INTRODUCTION

The ultraviolet absorption spectra of several substituted benzene compounds in the liquid state above their melting points and in the solid state at low temperatures were studied previously (Swamy, 1951, 1952 *a*, 1952 *b*) and it was observed that in some cases changes take place in the number and position of the bands with solidification of the liquid and subsequent lowering of the temperature, while in other cases only the bands observed in the case of the liquid shift slightly with solidification of the liquid. Besides these changes, the solidification and cooling down to -180°C

* Communicated by Prof. S. C. Sirkar.

of *o*-dichlorobenzene and *m*-chlorotoluene were observed to bring about a splitting of the electronic energy levels of these molecules (Sirkar and Swamy 1952, Swamy 1952 *c*). In *o*-chlorotoluene the two new components were on the two sides of the principal band while in *m*-chlorotoluene both the new components were on the longer wavelength side. Also, the absence of such splitting of the energy level in the case of *p*-chlorotoluene led to the conclusion that splitting of the electronic energy level depends on the relative positions of the substituent groups and does not take place when the permanent electric moment is small. Kronenberger (1930), however, had previously observed that in the case of benzene, the *o-o* transition, which is forbidden in the vapour state, appears at -180°C . It was pointed out (Sirkar and Swamy, 1932) that this might be due to the distortion of the molecule and absence of the centre of symmetry in the solid state at -180°C .

Ortho- and para-dichlorobenzene are other examples of disubstituted benzene molecules, one having a strong permanent electric moment and the other having no such moment. The para compound is interesting for the reason that in the solid state just below its melting point the substance yields new Raman lines in the low frequency region, the positions of these lines depending on whether the substance has once been cooled in ice or not (Vuks 1936, Sirkar and Gupta, 1936, Sirkar and Ray, 1951). It was thought worthwhile to investigate whether the electronic energy level of the molecule undergoes any change with such cooling in ice and whether the changes observed in these absorption bands with lowering of temperature upto -180°C throw any light on the changes in the positions of the Raman lines in the low-frequency region which take place with the lowering of temperature upto -180°C . The absorption spectra of *p*-dichlorobenzene in different states and at different temperatures have therefore been investigated and the results have been discussed in the present paper. The absorption spectra of *p*-dibromobenzene in different states and at different temperatures have also been studied to find out whether these are similar to the spectra observed in the case of *p*-dichlorobenzene. The results for *o*-dichlorobenzene briefly reported earlier (Sirkar and Swamy, 1952) have also been discussed in detail in this paper.

EXPERIMENTAL

The experimental arrangement is that employed in earlier investigations by the author (Swamy, 1951, 1952). A hydrogen discharge tube running at 3 K. V. served as the source of continuous spectrum. Spectrograms were taken on Ilford HP 3 films with a Hilger E. J spectrograph having a dispersion of 3 A. U. per mm in the region, 2600 \AA . Chemically pure substances distilled under vacuum were used in this investigation.

Paradibromobenzene was obtained from Merck's original packing and the other two substances were obtained from U. S. A. In each case a film

of thickness about 0.2 mm was found to produce absorption bands in the near ultraviolet region. For recording absorption spectra of *p*-dichlorobenzene, and *p*-dibromobenzene in the liquid state the two quartz plates between which the film was produced were held in a brass frame which was suspended at the centre of a heater, the current through the heating coil being adjusted so that the temperature at the centre of the heater was just above the melting point of the substance under study. Absorption spectra in the solid state at -180°C were photographed with the technique described previously (Swamy 1951, 1952). An exposure of about 12 minutes was required to record the spectrum for the liquid state and for the solid state at room temperature, while the exposure required to record the spectra for the solid at -180°C was about 40 minutes. For comparison, mercury arc spectrum was recorded with the help of Hartmann diaphragm on each spectrogram.

TABLE I

 Absorption bands of *o*-dichlorobenzene; ν in cm^{-1} .

Vapour (Prominent bands) Spomer, 1949.		Present author					
		Liquid at 30°C	Assign- ment	Solid at -50°C		Solid at -180°C	Assign- ment
36230 vs	ν_0	35848 (vs) broad	ν_0	35933 (s)	A ₀	35587 (m) 35939 (vs)	C ₀ A ₀
36545 ms	$\nu_0 + 315$						
36615 ms	$\nu_0 + 385$			36368 (w)	B ₀	36399 (m) 36636 (m)	B ₀ C ₁
36670 vs	$\nu_0 + 440$	36876 (vs) broad	$\nu_0 + 1028$				
36840 ms	$\nu_0 + 610$						
36954 m	$\nu_0 + 724$			36971 (s)	A ₁	36983 (vs)	A ₁ (A ₀ + 1044)
37062 ms	$\nu_0 + 832$						
37110 ms	$\nu_0 + 880$						
37187 ms	$\nu_0 + 957$						
37250 s	$\nu_0 + 1020$						
37319 vs	$\nu_0 + 1089$						
37420 w	$\nu_0 + 880 + 315$			37403 (w)	B ₁	37450 (m)	B ₁
37504 w	$\nu_0 + 832 + 440$						
37563 w	$\nu_0 + 1020 + 315$						
37631 m	$\nu_0 + 957 + 440$					37690 (vw)	C ₂
37719 m	$\nu_0 + 880 + 610$						
37759 w	$\nu_0 + 1089 + 440$	37910 (m)	$\nu_0 + 2 \times$ 1031	38000 (m)	A ₂	38036 (s)	A ₂
38159 m	$\nu_0 + 2 \times 957$						
38215 s	$\nu_0 + 1020 + 957$						
38275 vs	$\nu_0 + 2 \times 1020$			38447 (vw)	B ₂	38494 (m)	B ₂
38395 ms	$\nu_0 + 2 \times 1089$			39030 (w)	A ₃	39081 (s)	A ₃

TABLE II
Absorption bands of *p*-dichlorobenzene; ν in cm^{-1} .

	Present Author							
	Liquid 60°C	Assignment	Solid, 30°C	Assignment	Solid, 30°C after cooling to -180°C.	Assignment	Solid, -180°C	Assignment
(Vapour Prominent bands) Spomer (1952)								
35783 vs	35342 (vs, b)	ν_0	35558 (vs)	ν_0	35577 (s)	ν_0	35593 (vs)	ν_0
36070 m							36162 (m)	$\nu_0 + 569$
36274 ms	36387 (vs, b)	$\nu_0 + 1045$					36330 (m)	$\nu_0 + 737$
36438 m								
36471 s								
36544 w								
36808 vs			36584 (vs)	$\nu_0 + 1026$			36645 (vs)	$\nu_0 + 1051$
36998 m							36842 (m)	$\nu_0 + 1249$
37069 w								
37136 w								
37205 vw								
37340 vw								
37546 m	37430 (m)	$\nu_0 + 2 \times 1044$	37611 (m)	$\nu_0 + 2 \times 1026$	36608 (s)	$\nu_0 + 1031$	37066 (m)	$\nu_0 + 2 \times 737$
37856 vs							37216 (m)	$\nu_0 + 1052 + 569$
38040 w							37382 (m)	$\nu_0 + 1052 + 337$
							37696 (s)	$\nu_0 + 2 \times 1052$
38195 w							37896 (m)	$\nu_0 + 1249 + 1052$
								$\nu_0 + 1052 + 2$
38274 ms							38118 (w)	$\times 737$
								$\nu_0 + 2 \times 1052$
38602 w							38435 (w)	+ 737
							38608 (vw)	$\nu_0 + 1052 + 737$
								+ 1249
38937 s							38748 (s)	$\nu_0 + 3 \times 1052$
39261 m							38950 (vw)	$\nu_0 + 1249 + 2$
								$\times 1052$
							39180 (vw)	$\nu_0 + 2 \times 1052$
								+ 2 \times 737

TABLE III

Absorption bands of *p*-dibromobenzene ; ν in cm^{-1} .

Vapour, (Sreerama murthy 1951), Prominent bands	Assignment	Present author			
		Liquid, 9°C	Solid, 30°C	Assignment	Solid, -180°C
35643 s	ν_0	35368 (sb)	35362 (vsb)	ν_0	35439 vs
36113 ms	$\nu_0 + 470$				35768 w
36320 ms	$\nu_0 + 677$	36268 (sb)	36380 (S)	$\nu_0 + 1018$	35976 m
36657 m	$\nu_0 + 1014$				36132 m
36787 w	$\nu_0 + 677 + 470$				36443 s
37071 m	$\nu_0 + 1449 - 21$				36641 m
					36773 vw
					36870 m
					36979 w
37092 m	$\nu_0 + 1449$				37140 w
37660 w	$\nu_0 + 2 \times 1014$				37450 s
37761 vw	$\nu_0 + 1449 + 677$				37646 m
38106 w	$\nu_0 + 1449 + 1014$				37880 m
38299 vw	$\nu_0 + 1449 + 1014 + 200$				38133 w
		37290 (m)	37400 (s)	$\nu_0 + 2 \times 1019$	38450 s
					38647 w
					38878 m
		38392 (m)			39138 w
					39345 m
			38420 (m)	$\nu_0 + 3 \times 1019$	

Assignment

ν_0

$\nu_0 + 329$

$\nu_0 + 537$

$\nu_0 + 693$

$\nu_0 + 1004$

$\nu_0 + 1202$

$\nu_0 + 1004 + 329$

$\nu_0 + 1431$

$\nu_0 + 1004 + 537$

$\nu_0 + 1004 + 693$

$\nu_0 + 2 \times 1005$

$\nu_0 + 1202 + 1004$

$\nu_0 + 1431 + 1004$

$\nu_0 + 2 \times 1004 + 693$

$\nu_0 + 3 \times 1004$

$\nu_0 + 2 \times 1004 + 1202$

$\nu_0 + 2 \times 1004 + 1432$

$\nu_0 + 3 \times 1004 + 693$

$\nu_0 + 2 \times 1202 + 1004 + 693$

RESULTS

Spectrograms for *o*-dichlorobenzene in the liquid state at 30°C and solid state at -50°C and -180°C are reproduced in figures 1-3, Plate VA. Spectrograms for *p*-dichlorobenzene in the liquid state at 60°C and in the solid state at 30°C and -180°C as well as for the sample at 30°C after it had been once cooled to -180°C are also included in Plate VA (figures, 4-7). Microphotometer records of the absorption spectra of *p*-dibromobenzene in the liquid state at 90°C as well as in the solid state at 30°C and -180°C are reproduced in figure 8 (Plate VB), and those for *o*- and *p*-dichlorobenzene in figures 9 and 10 (Plate VC). Measurements were made for the centre of the absorption peak, as the bands are broad. The wave numbers of the principal bands observed by previous workers for the vapour state are included in Tables I, II and III in which the wave numbers of the bands observed in the present investigation are given. Assignments for the absorption bands of *o*-dichlorobenzene in the solid state at -180°C have been made on the assumption that the electronic energy level is split up into three components.

DISCUSSION

(a) *Orthodichlorobenzene.*

The spectrograms published by Spomer (1942) for the absorption spectra of *o*-dichlorobenzene in the vapour state show that the ν_0 band is at 36230 cm^{-1} . The band is very strong in agreement with the fact that the $o \rightarrow o$ transition is allowed in this case. There are also prominent bands at 36670, 37250 and 37319 cm^{-1} which can be assigned as $\nu_0 + 440$, $\nu_0 + 1020$ and $\nu_0 + 1089$ cm^{-1} . There are, however, companions on the red side of all the main bands at least two of which are probably due to $v \rightarrow v$ transitions, their separations from the principal ones being only 25 and 60 cm^{-1} respectively.

In the present investigation the substance produces only three broad bands in the liquid state, the ν_0 band being at 35848 cm^{-1} . The fine structure found in the vapour state is absent. The centres of the bands are separated by intervals of 1030 cm^{-1} . In the solid state at -180°C the substance produces four intense bands marked A_0 , A_1 , A_2 and A_3 . Each of the first three of the above bands is accompanied by two fainter bands, one on each side marked C_0 , B_0 ; C_1 , B_1 and C_2 , B_2 respectively. The fainter band on the longer wavelength side of the first principal band at 35587 cm^{-1} cannot be due to a $v \rightarrow o$ transition, as the distance between the two bands is about 352 cm^{-1} , and at -180°C the number of molecules present in the excited state in this mode of vibration is negligible. It is to be concluded that the electronic energy level is split up into three components in the case of the substance in the solid state at -180°C. The assignments made on the basis of this assumption are given in Table I. The companions of

Fig. 1

.. 3

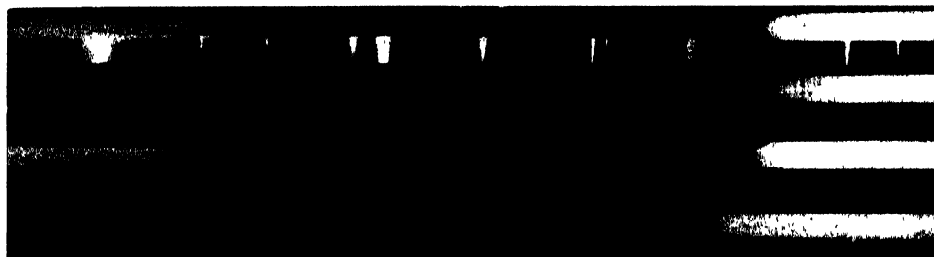


Fig. 4

.. 5

.. 6

.. 7



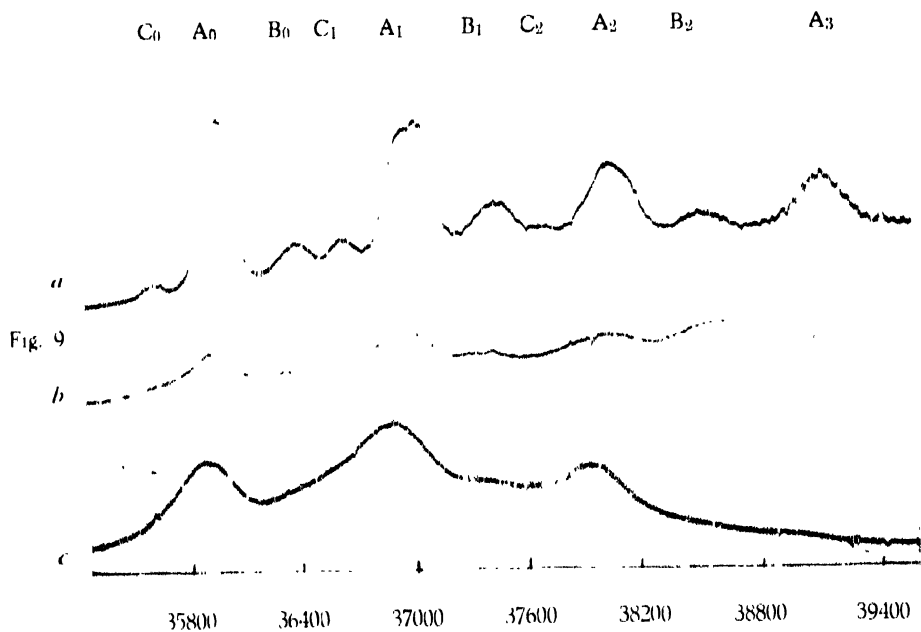
Hg 2537 $\overset{\overset{|}{\lambda}}{\text{Å}}$

Hg 2652 $\overset{\overset{|}{\lambda}}{\text{Å}}$

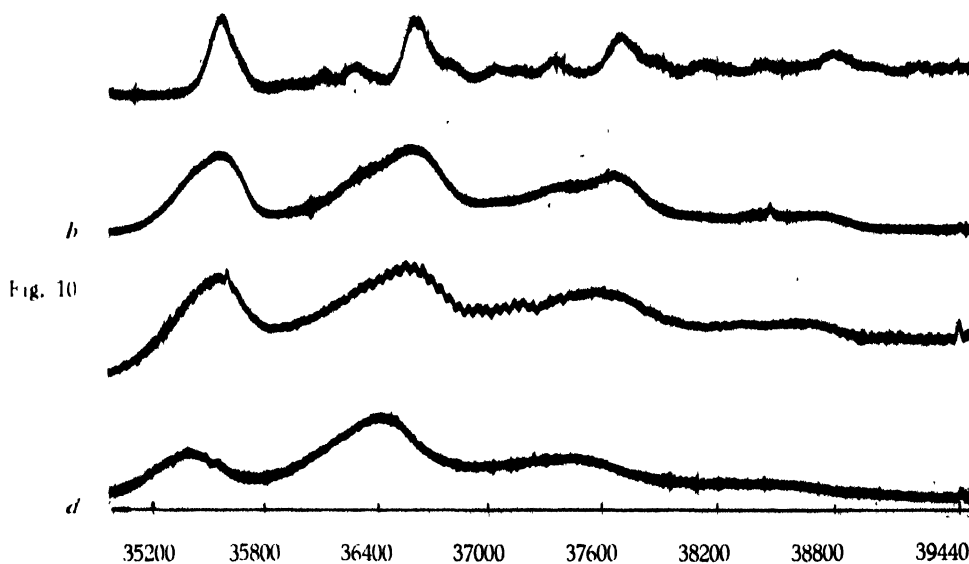
Hg 2752.9 $\overset{\overset{|}{\lambda}}{\text{Å}}$

Ultraviolet absorption spectra

1. Ortho dichlorobenzene - liquid at 30°C
2. " " solid .. -50°C
3. " " solid .. -180°C
4. Para dichlorobenzene - liquid .. 60°C
5. " " solid .. 30°C
6. " " " " 30°C after cooling to -180°C
7. " " " " -180°C



(a) *o*-Dichlorobenzene, solid at - 180°C
 (b) " " " " about - 50°C
 (c) " " liquid at - 30°C



(a) *p*-Dichlorobenzene, solid at - 180°C
 (b) " " " " 30°C after cooling to - 180°C
 (c) " " " " 30°C
 (d) " " liquid at 60°C

the principal absorption bands are much feebler than the main bands. Similar phenomenon has been observed in the case of benzene in the solid state at -259°C by Kronenberger (1930). The $0,0$ band of benzene which is forbidden in the vapour state appears strongly at -180°C , and at -259°C owing to the interaction of neighbouring molecules, the energy level is split up. The splitting of the energy level and the destruction of the symmetry of the electronic configuration in the benzene ring cannot be due to Van der Waals' forces in the lattice. This phenomenon may be due to the formation of virtual bonds between neighbouring molecules in the lattice as concluded from the results of study of the Raman spectra of benzene by Sirkar and Ray (1950). Such virtual bonds are more likely to be formed in the case of *o*-dichlorobenzene, as the molecule is strongly polar and the splitting of the energy level in this case also may be due to formation of such virtual linkages. The large shift of the ν_0 band towards longer wavelengths, which takes place with solidification of the substance, probably indicates that such an association of the molecules takes place in the lattice.

The absorption spectrum of the solid at -50°C indicates that besides the bands corresponding to those for the liquid state, there are four extra feeble bands, as shown in Table I and these can be accounted for by assuming that the energy level is split up into two components giving bands of unequal intensities. As the temperature of the solid is lowered, probably besides the close neighbours, the distant neighbours also exert influence on the energy level of each molecule, producing thereby a third component of the level.

The intermolecular field in the liquid state also is expected to have some influence on the electronic energy level. The molecules, however, have greater freedom for rotational oscillation in the liquid state and this oscillation is likely to broaden the level. The large width of the absorption bands observed in the case of the liquid actually corroborates this view. The splitting of the level in the solid state at -180°C , however, shows that some fundamental change takes place in the intermolecular field with solidification and this may be due to formation of virtual bonds among neighbouring molecules as stated above. The frequency-difference between successive bands for the liquid state is about 1030 cm^{-1} and for the solid state it is about 1044 cm^{-1} . This discrepancy may be due to the large width of the bands in the former case. The value 1044 cm^{-1} for the solid state, however, is about the mean of the two frequencies 1020 cm^{-1} and 1089 cm^{-1} observed in the case of the vapour. The results of this investigation confirm the view mentioned in an earlier paper (Swamy, 1952c) that the splitting of the electronic energy level depends on the position of the substitution group and takes place in this isomer since the dipole moment has a large value *viz.*, $2.4 - 2.5\text{D}$ (Spomer, 1942).

(b) *Paradichlorobenzene.*

The data given in Table II show that in the case of *p*-dichlorobenzene the new absorption bands which appear when the solid is cooled down to -180°C can be explained satisfactorily on the assumption that these are due to transitions to upper vibrational levels in the excited state. In this case there is no band on the longer wavelength side of the ν_0 band, and therefore, it is concluded that no splitting of the energy level with lowering of temperature occurs in this particular case. This may be due to the absence of permanent electric moment in the molecule. In the case of benzene also the splitting of electronic energy level occurs only at -259°C and no such splitting is observed at -180°C (Kronenberger, 1930). The vibrational frequencies derived from the absorption spectrum in the solid state at -180°C are slightly different from those derived from the absorption spectrum of the vapour (Sponer, 1942).

It is observed from a comparison of the data in Table II and the microphotometric records reproduced in figure 10, that the absorption spectra of *p*-dichlorobenzene in the liquid state and in the solid state at 30°C are similar, but in the case of the solid the bands shift by about 210 cm^{-1} towards shorter wavelengths from their respective positions in the case of the liquid. The bands are broad and diffuse in both the cases. When, however, the solid is once cooled in liquid air and brought to 30°C , extra bands corresponding to the transitions $\nu_0 + 764$ and $\nu_0 + 1031 + 764$ are observed. On further cooling down the solid to -180°C , the bands become narrower and additional feeble bands corresponding to the vibrational frequency 569 cm^{-1} appear. On comparing the position of the ν_0 band observed in the case of the liquid with that observed for the vapour (Sponer, 1942), it is found that the band shifts by about 400 cm^{-1} towards longer wavelengths with the liquefaction of the vapour. This shows that the intermolecular field has much influence on the electronic energy level. The molecules are expected to execute angular oscillation in the liquid and the intermolecular field acting on each molecule may fluctuate resulting in the broadening of the electronic energy level of the molecule in the liquid state. As all the bands become broad due to such a cause, the feeble bands are not resolved and only the intense bands appear as broad bands. In the case of the solid at 30°C also the bands are observed to be broad and therefore it is to be concluded that such angular oscillations of about the same amplitude are present also in the case of the solid at 30°C . When, however, the solid is once cooled in liquid oxygen and brought to 30°C again, the bands become a little sharper owing probably to cessation of such angular oscillation about one of the axes. Consequently, the bands become slightly narrower, so that the bands corresponding to the vibration frequency 764 cm^{-1} are resolved from those due to the vibration frequency 1031 cm^{-1} . When the solid is cooled down to -180°C the amplitude of the angular oscillations diminishes to a very small value, and therefore, the fluctuation of the intermolecular field is negligible. Conse-

quently, the bands become very narrow and the feeble bands are observed in this case owing to their sharpness. This sharpness of the bands of *p*-dichlorobenzene in the solid state at -180°C thus indicates almost complete cessation of angular oscillations of the molecules in the lattice at this low temperature.

It would be interesting to compare these changes observed in the absorption bands with lowering of temperature of the solid with those observed in the positions and intensities of the Raman lines in the low frequency region (Sirkar and Gupta, 1936 ; Ray, 1952). It is observed that the number of these lines increases and the frequency-shifts and intensities of some of them increase with the cooling down of the solid to -180°C . These changes as well as the large diminution of the amplitude of angular oscillation indicated by the changes observed in the absorption spectra definitely contradict the hypothesis that the Raman lines are due to angular oscillation of the molecules in the lattice. The diminution of the amplitude of angular oscillation may be due to linking up of neighbouring molecules through virtual bonds and the results obtained in the present investigation corroborate the hypothesis put forward by Sirkar (1937) that the new Raman lines in the low frequency region may be due to vibrations in associated groups of molecules.

(c) *p*-dibromobenzene.

The data reported by Sree Ramamurthy (1951) for the absorption spectra of *p*-dibromobenzene in the vapour state show that the ν_0 band which is allowed in the present case is at 35643 cm^{-1} . There are other strong bands at 36113 , 36657 , 37092 cm^{-1} which have been assigned as $\nu_0 + 470$, $\nu_0 + 1014$ and $\nu_0 + 1449\text{ cm}^{-1}$. There are of course close lying bands on the longer wavelength side of all the strong bands.

In the present investigation, the substance is observed to produce four broad bands in the liquid state. The ν_0 band is at 35260 cm^{-1} , being shifted by about 400 cm^{-1} towards longer wavelength side from the position in the vapour state. The centres of the bands are separated by 1008 cm^{-1} . In the solid state at 30°C again, the same four bands are observed, but their positions are shifted by about 100 cm^{-1} towards shorter wavelengths. The absorption spectrum of the sample brought to room temperature after once being cooled to -180°C , is exactly identical with that for the solid at room temperature which has not been cooled down below 0°C . This behaviour of the substance is different from that observed in the case of *p*-dichlorobenzene, because in the latter case new bands appear if the crystal is once cooled to -180°C and again brought to room temperature. In the solid state at -180°C , *p*-dibromobenzene produces a large number of bands. The position of the ν_0 band shifts by about 80 cm^{-1} from its position in the solid state at 30°C . The first four bands just on the higher frequency side of the ν_0 band can be assigned as $\nu_0 + 320$, $\nu_0 + 537$, $\nu_0 + 693$ and $\nu_0 + 1004\text{ cm}^{-1}$. After this we get new frequencies giving bands at $\nu_0 + 1202$ and $\nu_0 + 1431\text{ cm}^{-1}$.

The band at $\nu_0 + 1004 + 329 \text{ cm}^{-1}$ is very feeble and the band $\nu_0 + 1004 + 537 \text{ cm}^{-1}$ is just separated from the band at $\nu_0 + 1431 \text{ cm}^{-1}$. The bands $\nu_0 + 2 \times 1004 + 537 \text{ cm}^{-1}$ and $\nu_0 + 3 \times 1004 + 537 \text{ cm}^{-1}$ are not separated from the adjacent bands corresponding to the vibrational frequency 1431 cm^{-1} probably because the frequency 537 cm^{-1} becomes a little lower in these cases. The large width of the bands in the case of the solid at 30° C may be due to angular oscillations, as in the case of *p*-dichlorobenzene. The appearance of new sharp bands at -180° C may also be due to cessation of such angular oscillation at the low temperature.

The difference between the behaviour of the crystals of *p*-dichlorobenzene and *p*-dibromobenzene once cooled to -180° C and brought to 30° C may be due to the difference in the chemical affinity of the two halogen atoms, the bromine atom being less reactive than chlorine atom. It may also be due to difference in their crystal structure. The absorption bands are equally broad both in the liquid and the solid states, but in the latter case the ν_0 band has its position shifted by 100 cm^{-1} towards shorter wavelengths from its position in the former case. So this indicates a change in the intermolecular field with solidification. It is also known that new Raman lines appear with solidification. Their absence in the liquid state and appearance in the solid state are thus connected with this change in the intermolecular field with solidification. It is not unlikely that formation of virtual bonds is responsible for the apparent change in the intermolecular field and the appearance of new Raman lines in the low frequency region. The fluctuation of the intermolecular field due to angular oscillation of the molecules is probably responsible for broadening of the absorption bands as well as of the new Raman lines and cessation of such fluctuation at low temperatures probably causes sharpening of the bands and the Raman lines. This view is corroborated by the fact that in the absence of intermolecular field the absorption bands are sharp, as in the case of vapour,

The investigations are being continued with other substances and the results will be reported shortly.

ACKNOWLEDGMENTS

The author is indebted to Prof. S. C. Sirkar, D. Sc., F. N. I., for his kind interest and helpful guidance throughout the progress of the work and to the Govt. of India, for the award of a scholarship.

REFERENCES

- Kronenberger, A., 1930, *Z. f. Phys*, **63**, 494.
 Ray, A. K., 1952, *Ind. J. Phys.*, **26**, 226.
 Sirkar, S. C., 1936, *Ind. J. Phys.*, **10**, 110.
 Sirkar, S. C., 1937, *Ind. J. Phys.*, **11**, 343.
 Sirkar, S. C., and Gupta, J., 1936, *Ind. J. Phys.*, **10**, 473.
 Sirkar, S. C., and Ray, A. K., 1950, *Ind. J. Phys.*, **24**, 189.

- Sirkar, S. C., and Ray, A. K. 1951, *Ind J Phys* , **28**, 489
Sirkar, S. C., and Swamy, H. N., 1952, *J Chem. Phys* , **20**, 1177
Sponer, H , 1942, *Rev. Mod Phys* , **14**, 229.
Sreeramamurthy, C. 1951, *Current Science*, **20**, 176.
Swamy, H. N., 1951, *Ind J Phys.*, **28**, 262.
Swamy, H. N., 1952a, *Ind J. Phys.* **28**, 119.
Swamy, H. N., 1952b, *Ind. J Phys* , **28**, 223.
Swamy, H N , 1952c, *Ind J. Phys.*, **28**, (in press)
Vuks, M , 1986, *Comptes Rendus. (De Klady)* **1**, 73.