

ON THE RAMAN SPECTRA AND FLUORESCENCE OF ORTHO AND PARACHLOROTOLUENE IN THE SOLID STATE *

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Plate XVIII

ABSTRACT The Raman spectra of ortho and parachlorotoluene in the solid state at -180°C have been photographed and compared with those for the liquids at room temperature. Four new lines in the low-frequency region have been observed in each case, two of them having almost the same frequencies in the two cases. The intensities of these new lines are much smaller than those of the prominent lines due to the liquids. It is further observed that in the case of *o*-chlorotoluene some of the prominent Raman lines observed for the liquid state undergo large changes in intensity and position and the line 2928 cm^{-1} splits up into three lines when the liquid is solidified and cooled to -180°C . It is suggested that the line 163 cm^{-1} of liquid *o*-chlorotoluene which shifts to 185 cm^{-1} in the case of the solid might be due to a dimer. It is observed that these substances exhibit broad intense fluorescence bands in the visible region in the solid state at -180°C , and in the liquid state there is no fluorescence in the case of *p*-chlorotoluene, but *o*-chlorotoluene shows a continuous fluorescence in the whole visible region.

INTRODUCTION

The Raman spectra of many substituted benzene compounds in the solid state at low temperatures were studied previously by Sirkar and Bishui (1946) and Ray (1950, 1951, 1952). It was observed by the latter author that in almost all the substituted benzene compounds several new lines appear in the low frequency region when the substances are solidified, and when they are further cooled down, some of the lines shift away from the Rayleigh line. The positions of the lines observed in the different substitution compounds, however, do not depend essentially on the moments of inertia of the molecules, and from this fact it was concluded by Ray (1951) that the lines are not produced by rotational oscillations of the molecules pivoted in the lattice as postulated by some previous workers (Kastler and Rousset, 1941). In order to find out whether in a di-substituted benzene compound the relative positions of the two substitution groups have an influence on the number and positions of the new lines in the low frequency region which may appear in the Raman spectra of these substances in the solid state, the Raman spectra of ortho- and parachlorotoluene in the solid state have been studied in the present investigation, and the results have been discussed in the light of the various theories put forward regarding the origin of the new lines in the low frequency region.

* Communicated by Prof. S. C. Sirkar

EXPERIMENTAL

Ortho and parachlorotoluene supplied by May and Baker of U. S. A. were distilled in vacuum, as usual. A preliminary investigation showed that the Raman spectrum of the second liquid does not exhibit any appreciable fluorescence although the first one shows a continuous fluorescence spectrum. The number of lines in each case, however, agreed with those published by previous workers. This proved the purity of the substances. The method used for studying the Raman spectra of these substances in the solid state at the temperature of liquid oxygen was the same as that used by previous workers in this laboratory (Bishui, 1948). Ilford Special Rapid plates were used to photograph the spectra for the solid state and a Fuess spectrograph with a dispersion of about 10.8 \AA per mm. in the 4046 \AA region was employed. The Raman spectra for the liquids at room temperature were also photographed with the same spectrograph in order to compare these with the Raman spectra for the solid state. The experimental tubes containing the solid was at -180°C . No attempt was made to record very weak lines which might be present in the Raman spectra of the two substances in the liquid state.

RESULTS AND DISCUSSION

(a) *Raman spectra.* The spectrograms for the two substances in the liquid state and in the solid state at -180°C are reproduced in Plate XVIII. The frequency-shifts are given in Tables I and II. The frequencies of the Raman lines of the two substances reported by previous workers and given by Magat (1936) are also included in the tables for comparison.

A comparison of the data given in Tables I and II shows that both the substances yield four new Raman lines in the low frequency region in the solid state at -180°C and two of these lines have the same frequencies in both the cases. The other two lines are at 78 and 102 cm^{-1} in the case of *o*-chlorotoluene and at 85 and 129 cm^{-1} in the case of *p*-chlorotoluene. These lines are, however, much feebler than similar lines observed in other disubstituted benzene compounds, such as *p*-dichlorobenzene or *p*-dibromobenzene. It was pointed out by Ray (1951) that all the monosubstituted benzenes studied by him yield in the solid state at -180°C five new Raman lines in the low frequency region and that the positions of these lines cannot be correlated with the moments of inertia of the molecules about their three axes. The lines are also quite sharp and intense in all these cases. In the present case the two chlorotoluenes do not yield any such intense Raman lines and the lines are rather broad. Had these lines been due to rotational oscillations of the molecules pivoted in the lattice, as postulated by Kastler and Rousset (1941) they would be as intense as in the case of other similar

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TABLE I
Orthochlorotoluene
 $\Delta \nu$ in cm^{-1}

Liquid, Magat (1936)	Liquid at 25°C Present author	Solid at -180°C
163 (8)	163 (5) e, k	36 (0) e, k 50 (1) e, k 78 (0) e, k 102 (2) e, k 186 (5) e, k 243 (0b) c, k 363 (0) e 448 (1) e, k 550 (3) e, k 673 (5) e, k
247 (5)	24 (4) e, k	802 (3) e, k
361 (3)	361 (1) e	
447 (4)	443 (3) e, k	
552 (7)	550 (3) e, k	
675 (6)	673 (5) e, k	
745 (1)		
803 (4)	800 (4) e, k	
852 (00)		
989 (1)		
1016 (0)		
1043 (8)	1040 (8) e, k	1034 (5) e, k
1132 (2)		
1156 (2)	1155 (2) e, k	1156 (1) e, k
1204 (5)	1205 (5) e, k	1210 (2) e, k
1270 (0)		
1378 (2)	1376 (2) e, k	1378 (1) e, k
1426 (0)		
1574 (3)	1572 (3) e, k	1572 (1) e, k
1592 (3)	1593 (3) e, k	1596 (1) e, k
2859 (0)		2905 (2) k
2926 (5)	2928 (5) e, k	2930 (2) k
3013 (0)		2956 (1b) k
3062 (7)	3062 (7) e, k	3066 (5) e, k

TABLE II
Parachlorotoluene, $\Delta \nu$ in cm^{-1}

Liquid, Magat (1936)	Liquid at 25°C, Present author	Solide at -180°C
307 (8)	306 (3) e, k	38 (2) e, k 50 (1b) e, k 85 (1b) e, k 129 (2) e, k
376 (12)	374 (5) e, k	390 (1b) e, k
634 (5)	636 (3) e, k	372 (3) e, k 630 (1) e, k
692 (1)		
796 (12)	796 (8) e, k	792 (5) e, k
822 (2)	818 (1) e, k	
1090 (12)	1092 (10) e, k	1090 (5) e, k
1177 (1)		
1208 (7)	1210 (5) e, k	1210 (3) e, k
1303 (0)		
1379 (4)	1383 (2) e, k	
1454 (0)		
1596 (8)	1598 (8) e, k	1590 (2) e, k
2924 (8 I)	2930 (5) e, k	2920 (2) e, k
3031 (4)	3040 (3b)	
3064 (10 I)	3062 (10) e, k	3062 (5) e, k

molecules. Hence these lines may be due to intermolecular oscillations in groups of associated molecules as pointed out by Sirkar (1937) and also recently by Ray (1950, 1951).

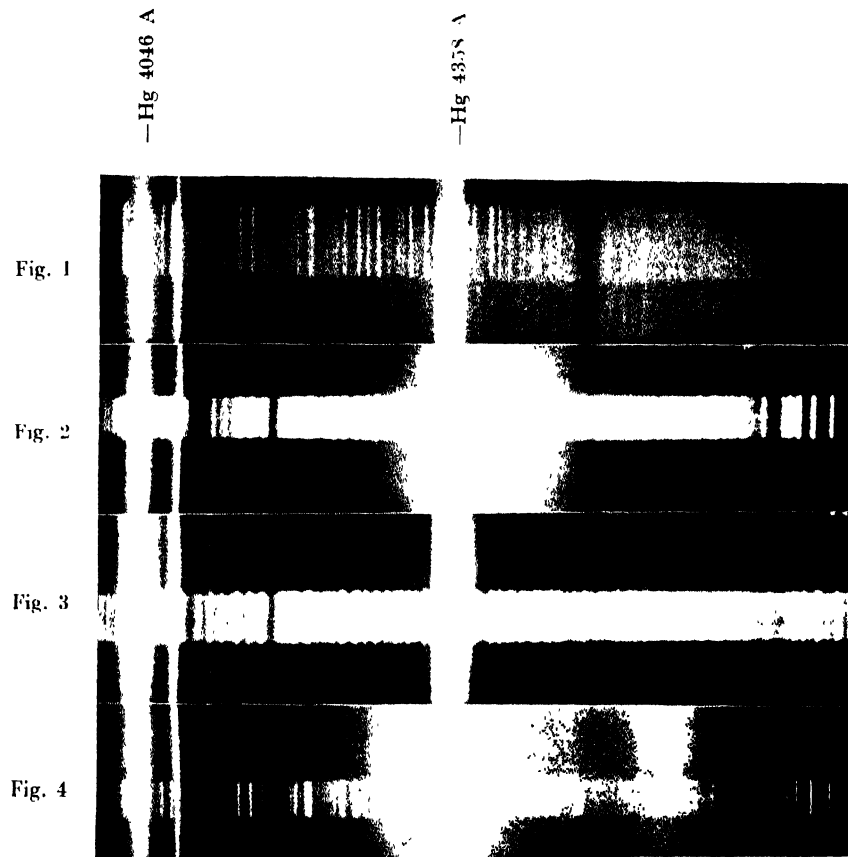
Some of the other Raman lines undergo changes in intensity and position with the solidification of these two substances. For instance, in the case of orthochlorotoluene the line 163 cm^{-1} shifts to 186 cm^{-1} the line 246 cm^{-1} becomes much weaker and broader and the line 2928 cm^{-1} splits up into three lines at 2905 , 2930 and 2956 cm^{-1} when the liquid is solidified and cooled down to -180°C . In the case of parachlorotoluene the line 306 cm^{-1} shifts to 320 cm^{-1} and becomes broader while the lines 1598 and 2930 cm^{-1} shift to 1590 and 2920 cm^{-1} respectively with the solidification. Further, the lines 1572 and 1503 cm^{-1} of *o*-chlorotoluene and the line 1598 cm^{-1} of *p*-chlorotoluene become much weaker when the liquids are solidified. Since these lines are due to $\text{C}=\text{C}$ oscillation, this diminution of intensity may indicate a diminution in the number of such double bonds in the molecule with the solidification. All these facts clearly indicate a strong influence of intermolecular field on the frequencies of oscillation of certain modes and this influence may be due to association of the molecules in the solid state which may be responsible also for the origin of the new lines in the low-frequency region.

(b) *Fluorescence spectra.* It can be seen from Plate XVII that the both the substances in the solid state at -180°C exhibit fluorescence bands in the visible region. The positions of centres and width of the intense bands are given in Table III.

TABLE III
Fluorescence bands

<i>o</i> -Chlorotoluene			<i>p</i> -Chlorotoluene		
Position of band in A. U.	Intensity	Width in A. U.	Position of band in A. U.	Intensity	Width in A. U.
4400	5	100	4300	5	50
			4500	2	50
			4640	10	100
4760	2	50			

The spectrogram for *o*-chlorotoluene in the liquid state also shows a stronger continuous background extending from 4100 \AA upto about 5100 \AA . Even after distilling the liquid in vacuum repeatedly it was not possible to get rid of this fluorescence. The spectrogram for the substance in the solid state, however, shows weak continuous fluorescence over the region from about 4250 \AA upto about 4400 \AA and two bands, one strong and wide band at 4400 \AA and a feebler band at 4760 \AA . The frequency-difference is about 1565 cm^{-1} . This frequency corresponds to the $\text{C}=\text{C}$ valence oscillation.



Raman spectra

- Fig. 1. *o*-Chlorotoluene, liquid at 26° C
 Fig. 2. " " solid at -180° C
 Fig. 3. *p*-Chlorotoluene, liquid at 26° C
 Fig. 4. " " solid at -180° C

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It is also an interesting fact that although *p*-chlorotoluene does not yield any Raman line with frequency-shift below 306 cm^{-1} , *o*-chlorotoluene gives an intense line at 163 cm^{-1} . This fact may indicate a fundamental difference between the nature of the molecules in the liquid state in two cases. Probably in the case of *o*-chlorotoluene the molecules exist as dimers which give rise to this line at 163 cm^{-1} and also the continuous fluorescence mentioned above may be due to these dimers. In the case of *p*-chlorotoluene in the liquid state probably the molecules do not form such dimers and, therefore, the line 163 cm^{-1} is absent in this case and no fluorescence is exhibited by this liquid. When the liquid is solidified, probably groups of strongly associated molecules are formed in this case also and they give rise to the fluorescence bands given in Table III as well as the new Raman lines given in Table II. The frequency-difference between the first and the second and the first and the third bands are approximately 1230 and 1650 cm^{-1} respectively. It is significant that these frequencies correspond to those of the lines due to C-C and C=C oscillations of the molecule. Of course, the bands are very broad but this coincidence indicates that these valence oscillations are coupled to the electronic energy level of the ground state of the associated molecule during emission of the fluorescence radiation.

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