RAMAN SPECTRA AND FLUORESCENCE OF A FEW SUBSTITUTED TOLUENES IN THE SOLID STATE AT DIFFERENT LOW TEMPERATURES*

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ABSTRACT. The Raman spectra of m-$CH_3C_6H_4Cl$, m-$CH_3C_6H_4Br$ and o-, m- and p-$CH_3C_6H_4OH$ in the liquid state and in the solid state at different temperatures were studied. Each of the liquids has yielded a few now feeble lines not reported by previous workers. It is found that except in the case of p-cresol, a strong line in the neighbourhood of 200 cm^{-1} disappears in each case when the liquid is solidified. An explanation has been offered for this change. Similar to the case of other subsitituted benzenes, a few Raman lines appear in the low-frequency region when the substances are solidified. Changes in the frequency-shifts, as well as in the intensities of those new lines, are observed on lowering the temperature of the crystals to −180°C. An attempt has been made to interpret these results.

INTRODUCTION

Previous investigations on the Raman spectra of a few disubstituted benzene compounds in the solid state at different temperatures have shown that when these substances are solidified, a few new Raman lines appear in the low-frequency region in each case and the change which they undergo with change of temperature of the solidified mass is different for different compounds. Further, it has been observed previously (Sanyal, 1953; Biswas, 1954) that certain substituted toluenes exhibit two broad flourescence bands in the visible region when they are solidified and cooled to −180°C and that this appearance of fluorescence bands in the solid state is accompanied by an appreciable diminution in the intensity of a Raman line due to C = C vibration of the molecules. Sometimes it is also found that a strong Raman line observed in the case of the liquid phase of some disubstituted benzenes disappears when the substances are solidified (Biswas, 1955). One of such compounds is o-dichlorobenzene which shows a splitting in its ultraviolet absorption bands in the solid state (Sirkar and Swamy, 1952) at low temperatures. This splitting up of the absorption bands and also the disappearance of some strong Raman lines in the solid state can both be accounted for by assuming

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the existence of a strong intermolecular field in the solid state of the substance produced by the formation of virtual bonds amongst the neighbouring molecules. The data available so far are not, however, adequate to lead to a general conclusion regarding the behaviour of these Raman lines with change of temperature. It was, therefore, thought worthwhile to study a few more disubstituted benzene compounds the ultraviolet absorption spectra of which show similar splitting of the absorption bands in the solid state or show any other peculiarities. With these objects in view, the present intestigation on the Raman spectra of meta chloro- and meta bromotoluene and also of the three isomeric o-, m- and p-cresols in the solid state at low temperatures was undertaken. The ultraviolet absorption spectra of these compounds (excepting m-bromotoluene) have been studied by Swamy (Swamy, 1952a; Swamy, 1952c). The cresols were particularly chosen to find out whether the replacement of the halogen atoms of chloro- or bromo-toluenes by the hydroxyl group brings about any fundamental change in the Raman spectra of these substances in the solid state in the low-frequency region.

EXPERIMENTAL

The liquids meta chlorotoluene and meta bromotoluene were supplied by Schuchardt Co. Ltd. and City Chemical Corporation, N.Y. respectively, while ortho cresol was secured from May and Baker Ltd., England. Meta and para cresol were obtained from B. D. H. Ltd. and were of 98% pure variety. The two halogen substituted toluenes were distilled in vacuum once before every exposure, but some special care was taken to purify the cresol compounds. The cresols were fractionated under vacuum successively for five or six times, each time rejecting the first and last fractions of the distillate. The Raman spectra of all these compounds in the liquid phase were recorded and compared with the results given by previous workers. Further, for unequivocal assignment of the lines, the Raman spectra of ortho and para cresol in the liquid state were also recorded using the 4358A° line of mercury only as the exciting radiation by cutting off the 4047 A° group with a filter of rhodamine 6 GBM solution mixed with solution of p-nitrotoluene in suitable proportions. The polarisation of the Raman lines of the two halogen substituted toluenes in the liquid phase was estimated in the usual manner by photographing simultaneously both the veritical and the horizontal components of the Raman lines produced by interposing a double-image prism just in front of the slit of the spectrograph. The Raman spectra of these substances in the solid state at different low temperatures were recorded in the same way as described earlier (Biswas, 1954a; 1954b). In all cases the spectra were photographed on Ilford Zenith plates with a Fuess glass spectrograph having a dispersion of about 11A° per mm in the region of 4047A°. The microphotometer records were taken with a Kipp and Zonen type self-recording Moll microphotometer.

RESULTS AND DISCUSSION

The Raman shifts of the different substances in the liquid and solid states at different temperatures are given in Tables I-V. The data on the Raman spectra of all these substances in the liquid state as given in the Annual Tables of Constants and Numerical Data (Magat, 1936) are also included for comparison. The polarisation of these compounds were studied previously by different workers, but as the data were not available we redetermined qualitatively the polarisation of the Raman lines of the two halogen substituted toluenes in the liquid state. In Tables I and II the capital letter P or D against any particular Raman line indicates whether the line is polarised or deplorised to the extent 6/7.

(a) RAMAN LINES DUE TO INTRAMOLECULAR VIBRATIONS

(i) Metachlorotoluene.

The data given in Table I show that two extra weak lines at 884(0) and 948(0) cm^{-1} recorded in the present investigation in the liquid phase of m-chlorotoluene, are not given by previous authors. On the other hand, the lines 613(4)? and 3031(4) cm^{-1} reported by previous authors are not observed in the present investigation. The spectrogram obtained in the present investigation is a well-exposed one and the lines are definitely absent. Again, each of the lines 231 and 1216 cm^{-1} reported by previous workers is actually split up into two lines. These are at 222(5) and 247(5) cm^{-1} in the former case and at 1209(1) and 1219(4) cm^{-1} in the latter case.

A group of three intense lines at 187, 222 and 247 cm^{-1} respectively shows some remarkable change with the change from the liquid to the solid phase. The first line at 187 cm^{-1} seems to disappear while the second line shifts a little towards the Rayleigh line when the substance is solidified and cooled down to −70°C. The line at 2926 cm^{-1} due to C–H stretching vibration of the molecule in the liquid shifts to 2919 cm^{-1} in the solid state at −70°C and a new broad weak line at 2849 cm^{-1} is observed. On further lowering the temperature of the solidified mass to −180°C, two more new lies at 2910 and 2953 cm^{-1} have been observed. Moreover, the intensities of both the lines 1571 and 1601 cm^{-1} of the liquid seem to decrease with solidification of the substance as these two lines are more intense than the line 1383 cm^{-1} in the case of the liquid while they are weaker than the same line in the spectrogram due to the solid at −180°C.

(ii) Metabromotoluene:

In the case of metabromotoluene in the liquid state also we observe a few feeble extra Raman lines not reported by earlier workers (Magat, 1936). These are at 467(00), 862(1), 892(1) and 943(0) cm^{1} respectively. Further, the line at 1206(4) cm^{-1} is resolved into two lines at 1205(1) and 1211(4) cm^{-1} respectively

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TABLE I

m-Chlorotoluene (m-Cl.C$_6$H$_4$CH$_3$)

$\Delta \bar{v}$ in cm^{-1}

Liquid				Solid (Present author)	
Magat (1936)	Present author			At about − 70°C	At − 180°C
				43 (2) e,k	50 (1) o,k
				125 (1) o,k	129 (3) e,k
187 (6)	187	(5)±e,+k	D	—	—
231 (7)	222	(5)±e,±k	D	218 (1b) e,	218 (1b) e
	247	(5)±e,±k	D	247 (1) o,k	247 (1) e,k
387 (1)	394	(1) e,k	P		
417 (7)	419	(6) ±e,k	P	419 (2) e,k	419 (2) e,k
522 (6)	522	(6)±e,k	P	522 (2) o,k	522 (2) e,k˙
613 (4)?					
683 (7)	683	(7) ±e,k	P	683 (3) e,k	683 (3) o,k
771 (2)	775	(2) e,k			
855 (3)	861	(3) e,k	P		
	884	(0) e			
	948	(0) o			
996 (10)	998	(10) e,k,i	P	998 (5) o,k	998 (5) e,k
1046 (1)	1042	(1) e,k			1042 (0) o,k
1080 (3)	1077	(4) e,k	P	1077 (1) e,k	1077 (1) e,k
1097 (1)	1102	(2) e,k			1102 (0) o,k
1165 (1)	1160	(2) e,k			
1216 (4)	1209	(1) e,k			
	1219	(4) e,k	P	1219 (2) e,k	1219 (2) e,k
1379 (3)	1383	(2) e,k	P	1380 (0) o	1380 (0) e,k
1582 (3)	1574	(3) e,k	D	1574 (0) e	1574 (1) e,k
1600 (4)	1601	(4) e	D	1601 (0) o	1601 (0) e,k
2862 (2)				2849 (1b) k	2849 (1b) k
					2910 (1) k
2921 (7b)	2926	(6b) e,k	P	2919 (2b) e,k	2919 (2) e,k
3031 (4)				2953 (1) k	2953 (1) k
3060 (7b)	3062	(10b) e,k,i	P	3066 (6) e,k,i	3066 (6) e,k,i

TABLE II

m-Bromotoluene   (m-Br.$C_3H_4CH_3$)

$\Delta \bar{v}$ in cm^{-1}

| Liquid | | | Solid (Present author) | |
Magat (1936)	Present author		At about −80°C	At −180°C
			33 (2) k	33 (1) k
			120 (1) o,k	126 (3) e,k
171 (7)	173 (7b)±e, ǀ k	D	—	—
197 (5)	200 (5)±e,+ k	D	203 (5b) e	203 (5b) e
225 (6)	224 (6b)±e,+ k	D	242 (2) e,k	242 (2) o,k
306 (9)	308 (9)±o,k,i	P	314 (5) o,k	314 (5) o,k
378 (0)	381 (0) e			
	467 (00) e			
518 (6)	522 (6)±e,k	P	522 (2) e,k	522 (2) e,k
667 (7)	671 (7)±o,k,i	P	671 (4) o,k	671 (4) e,k
770 (0.5)	774 (1) o,k			
789 (0.5)				
831 (3)	835 (3) e,k	P	835 (0) e,k	835 (0) o,k
	862 (0) e			
	892 (1) o			
915 (1)				
	943 (0) o			
990 (10)	998 (11) e,k,i	P	998 (6) o,k	998 (6) e,k
1022 (2)	1029 (2) e,k	P	1029 (0) o,	1029 (0) o
1065 (5)	1070 (5) o,k	P	1070 (2) e,k	1070 (2) e,k
1162 (1)	1166 (1) e,k			
1206 (4)	1205 (1b) o			
	1211 (4) e,k	P	1211 (2) e,k	1211 (2) e,k
1365 (3)				
	1383 (4) e,k	P	1383 (1) e	1383 (1) e,k
1411 (0)				
1567 (4)	1571 (5) o	D	1571 (1) e,k	1571 (1) e,k
1593 (4)	1601 (5) e	D	1601 (0) e,k	1601 (0) e,k
2874 (1)	2865 (2) e,k	P	2865 (0) k	2865 (0) k
2923 (3)	2926 (7b) e,k	P	2915 (4b) e,k	2915 (4) e,k
				2932 (0) k
3051 (4b)	3062 (9b)	P	3065 (6b) e,k,i	3067 (6) e,k,i

TABLE III

Orthocresol. $(o\text{-}CH_3C_6H_4OH)$

$\Delta\bar{v}$ in cm^{-1}

Liquid		Solid (present author)	
Magat (1936)	Present author	At about −30°C	At −180°C
		45 (1b) k	40 (1) k
			68 (1) k
		90 (2b) k	85 (1b) k
190 (6)	190 (5)±e,k	—	—
274 (5)	275 (5)±e,k	280 (0)	280 (0)
305 (0)	316 (1) e,k		
445 (0)	445 (2) e,k		
530 (5)	531 (4) e,k	531 (0) e	531 (0) e
584 (6)	587 (7)±e,k	587 (1) e,k	587 (1) e,k
	646 (0) e		
	695 (0) e		
	711 (0) e		
749 (12)	749 (12)±e,k,i	749 (4) e,k	749 (4) e,k
847 (2)	845 (2) e,k		
989 (3)	992 (3) e,k	992 (0) e,k	992 (0) e,k
1044 (7)	1040 (10) e,k,i	1040 (3) e,k	1040 (4) e,k
	1094 (1) e		
1110 (0)	1109 (1) e		
1156 (3)	1155 (4) e,k	1155 (1) e,k	1155 (1) e,k
1238 (4)	1235 (1) e	1240 (1) e,k	1240 (1) e,k
1256 (4)	1258 (6) e,k	1258 (2) e,k	1258 (2) e,k
1380 (3)	1383 (3) e,k	1383 (1) e,k	1383 (1) e,k
1438 (1)	1444 (2) e,k		
	1471 (1) e		
	1510 (1) e		
1588 (?)	1597 (4) e,k	1597 (2) e,k	1597 (1) e,k
1614 (4)	1619 (6) e,k	1619 (1) e,k	1619 (0) e
2920 (7)	2920 (6) e,k	2920 (3) e,k	2920 (3) e,k
		2948 (2) k	2948 (2) k
3057 (7)	3063 (8b) e,k	3063 (3b) e,k	3063 (3b) e,k
3203 (1)			

TABLE IV

Metacresol (m-$CH_3.C_6H_4OH$)

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

Liquid		Solid (rpesent author)	
Magat (1936)	Present author	At about −40°C	At −180°C
			95 (1b) k
214 (6)	216 (6b)±e,k	219 (0) e	219 (0) e
239 (6)	245 (7b)±e,k	249 (0) e	249 (1) e
307 (0)	305 (1b) e		
	450 (0) e		
521 (5)	518 (6) e,k	518 (0) e,k	518 (1) e,k
541 (5)	543 (6) e,k	543 (0) e,k	543 (1) e,k
563 (0.5)	569 (2) e,k		
735 (8)	734 (12) e,k,i	734 (3) e,k	734 (4) e,k
777 (0)	779 (1) e		
833 (0)	848 (0) e		
	956 (0) e		
998 (10)	1002 (15) e,k,i	1002 (5) e,k	1002 (6) e,k
1084 (4)	1085 (5) e,k	1084 (1) e,k	1088 (1) e,k
1160 (2)	1166 (4) e,k	1166 (0) e,k	1166 (0) e,k
1277 (5)	1276 (5b) e,k	1276 (2b) e,k	1276 (2b) e,k
1378 (3)	1383 (5) e,k	1383 (1) e,k	1383 (1) e,k
1448 (0)			
	1460 (0) e,k		
1592 (3)	1593 (5) e,k	1593 (0) e	1593 (0) e
1610 (3)	1616 (4) e,k	1616 (0) e	1616 (0) e
2923 (6)	2920 (6b) e,k	2920 (2b) k	2920 (3b) k
			2949 (0) k ?
3051 (9)	3052 (7b) e,k,i	3052 (3b) e,k	3052 (4b) e,k

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TABLE V

Paracresol (p-$CH_3.C_6H_4OH$)

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

Liquid		Solid (present author)	
Magat (1936)	Present author	At about — 30°C	At — 180°C
		47 (1b) k	47 (1) k
		90 (0b) k	90 (1b) k
	282 (0b) e		
337 (6)	338 (6b)±e,k	343 (1b) o,k	343 (2) e,k
	406 (0) e		
464 (6)	462 (6)±e,k	467 (1) e,k	467 (1) e,k
507 (0)	513 (1) e		
646 (5)	644 (6)±e,k	644 (1) e,k	644 (2) e,k
700 (1)	698 (2) e,k		
736 (1)	742 (2) o,k		
	809 (0) e		
825 (4)	829 (5b) e,k,i	829 (1) e,k	829 (2) e,k
841 (9)	845 (11)±e,k,i	840 (5) e,k	840 (6) e,k
	969 (0) e		
	1032 (0) e		
1170 (3)	1167 (3) e,k	1167 (0) o	1167 (0) e,k
	1205 (2) e,k		
1213 (4)	1219 (5) e,k	1211 (1) e,k	1211 (2) e,k
	1253 (3b) e,k	1253 (1) e,k	1253 (2) e,k
1296 (0)	1295 (1) e,k		
1380 (3)	1383 (4) e,k	1383 (0) e,k	1383 (1) e,k
1450 (0)	1460 (1) e		
	1517 (0b) e		
	1597 (4) e,k	1588 (0) e,k	1588 (1) e,k
1608 (4)	1613 (6) e,k	1600 (1) o,k	1600 (2) e,k
2866 (2)	2864 (3b) e,k	2864 (0) k	2864 (0) k
2921 (5)	2920 (4b) e,k	2912 (2b) e,k	2912 (2b) e,k
3018 (0)	3012 (2) e,k	3012 (0) k	3012 (0) k
	3048 (2) e,k	3048 (0) k	3048 (0) k
3055 (7)	3063 (6) e,k,i	3058 (5) e,k	3058 (6) e,k
3189 (1)	3201 (1) k		

in the present investigation. On the other hand, the lines 789(0.5), 915(1) and 1411(0) cm^{-1} reported by previous workers are not observed in the dense spectrogram obtained in the present investigation. Corresponding to three lines below 300 cm^{-1} of *m*-chlorotoluene, this substance also yields a group of three intense lines with frequency shifts 173(7b), 200(5) and 224(6) cm^{-1} respectively. The microphotometer records showing the relative intensities of these lines observed in the liquid state as well as in the solid state at —180°C are reproduced in figure 1. It can be seen from the records that the first line at 173 cm^{-1}
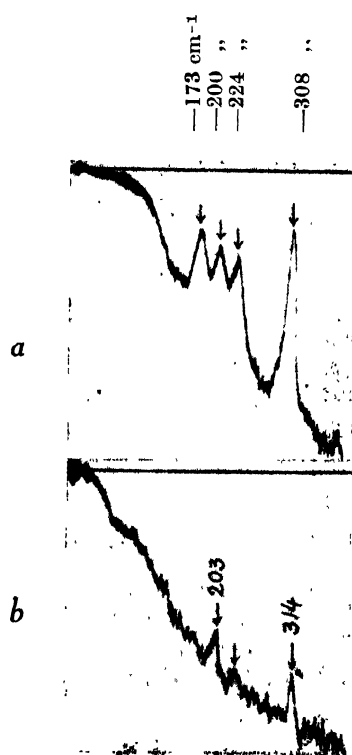
Fig. 1

Fig. 2

Microphotometric records of the Raman spectra

Fig. 1. Metabromotoluene
  (a) Liquid at room temp,
  (b) Solid at—180°C
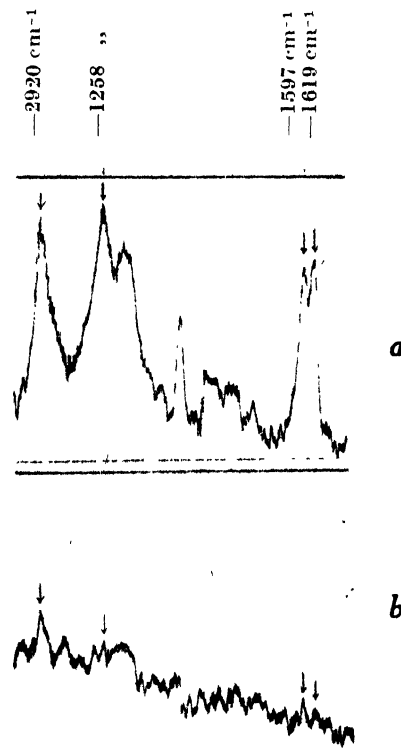
Fig. 2. Orthocresol
  (a) Liquid at room temp.
  (b) Solid at - 30°C

disappears while the line at 224 cm^{-1} becomes sharper and shifts by about 18 cm^{-1} away from the exciting line at —180°C. The line at 200 cm^{-1} which is relatively weak in the liquid phase becomes very intense in the case of the solid state. Further, the width of the line also increases considerably with the solidification of the liquid. In addition to the above changes, the line at 2926 cm^{-1} shifts to 2915, a new fainter line appears at 2932 cm^{-1} and the

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doublet at about 1600 cm⁻¹ becomes relatively weaker when the substance is solidified and cooled down to —180°C.

It is thus seen from the results discussed above that the lines 187cm⁻¹ and 173 cm⁻¹ of *m*-chlorotoluene and *m*-bromotoleuene respectively disappear almost completely with the solidification of the liquids, while the intensity of the line 200 cm⁻¹ of the latter compound increases with solidification. In order to understand the significance of these changes, it is necessary to make correct assignment, of these lines which are observed to be totally depolarised. In the molecules of *m*-chlorotoluene and *m*-bromotoluene, the vibrations involving bending of the C-Cl or C-Br and the C-(CH₃) bond in the plane of the molecule are expected to give rise to the Raman shifts in the neighbourhood of 200 cm⁻¹ if the assignment made by Sponer and Kirby-Smith (1941) in the case of some lines in this region due to ortho dichlorobenzene be assumed as correct. However, in the case of the ortho- or meta compounds studied in the present investigation, we can expect only two such modes producing only polarised Raman lines, because there is no two-fold axis of symmetry. Actually, however, three totally deplorised lines are observed in either of these liquids. So it is difficult to assign the lines to any mode involving bending of the C-CH₃ and C-Cl or C-Br bonds in the plane of the molecules. On the other hand, neglecting the hydrogen atoms in the CH₃ group, we can assume that these molecules have a plane of symmetry and these lines may be due to some displacements at right angles to the plane of the molecule. Mere bending of the C-CH₃ or C-Cl or C-Br bonds at right angles to the plane of the molecules however, gives rise to lines of much higher frequency-shifts Hence the lines are to be assigned to some mode in which both the carbon atom and the halogen atom attached to it are displaced at right angles to the plane of the molecule. Probably these are of the type $E_{2u}(\nu_{20})$, given by Herzberg (1946).

We can expect, however, two totally deploarised lines due to such modes. The third line which vanishes almost completely when the liquids are solidified cannot therefore be attributed to any mode of the single molecule. Probably one of these modes in some of the molecules in the liquid state is affected by the field of the neighbouring molecules so that the frequency diminishes a little. This can happen if due to random orientation of the molecules in the liquid some of the molecules are suitably oriented and are sufficiently close to each other to form associated groups of molecules. In the crystalline state, however, the molecules become regularly arranged and the resultant field of neighbouring molecules may counterbalance the effect of the virtual bond so that the frequency of the particular mode becomes almost the same as that of the single molecule. Actually, however, the frequency-shift of one of the two lines observed in the case of the solid is slightly smaller than that in the liquid state.

In the case of ortho-and metadichlorobenzene also some of the lines in this region are probably due to the mode E_{2u} as suggested above for the case of

chloro-and bromotoluene and if such an assumption is made, the difficulty pointed out by Sponer and Kirby-Smith (1941) does not arise.

(iii) *Orthocresol.*

From Table III it can be seen that the extra weak lines observed in the case of this liquid at 646(0), 695(0), 711(0), 1094(1), 1471(1) and 1510(1) cm^{-1} respectively were not reported by previous workers. When the substance is solidified and cooled down to different low temperatures, the strong line at 190 cm^{-1} observed in the case of the liquid disappears completely while the intensity of the line 275 cm^{-1} diminishes. Further, with solidification, a new strong line appears at 2948 cm^{-1} and the line 1240 cm^{-1} becomes almost as intense as the line 1258 cm^{-1}. Also, the relative intensities of the lines at 1597 and 1619 cm^{-1} seem to be reversed with the solidification and cooling down to lower temperature (figure. 2).

The lines at 190 and 275 cm^{-1} are probably due to some modes involving displacements at right angles to the plane of the molecule and correspond to the mode E_{2u} (ν_{20}) of the benzene molecule as pointed out earlier. Now in one of these modes all the atoms move at right angles to the plane of the molecule and probably on solidification strong virtual bonds are formed between neighbouring molecules so that the frequency becomes much smaller and the corresponding line shifts towards the region within 100 cm^{-1} from the exciting wavelength. The appearance of the new line at 2948 cm^{-1} due to the C-H valence oscillation and the increase in intensity of the line due to C-H bending vibration probably supports the view that the molecules become strongly associated in the solid state causing shift of the line at 190 cm^{-1}.

(iv) *Metacresol.*

Data given in Table IV show that the feeble lines at 450(0) and 956(0) cm^{-1} observed in the present investigation are not reported by earlier authors (Magat, 1936). The weak line at 1460(0)cm^{-1} may probably correspond to the weak line at 1448 (0) cm^{-1} reported by previous workers. When the liquid is solidified, the lines at 216 and 245 cm^{-1} shift to 219 and 249 cm^{-1} respectively, but unlike the corresponding lines of the ortho compound these lines persist in the solid state. The appearance of the new line at 2948 cm^{-1} in the case of the ortho comound is probably connected with the diminition in the intensity of the lines 190 and 275 cm^{-1}. In the case of the meta compound no change takes place in the relative intensities of the two lines 216 and 239 cm^{-1} probably because no strong hydrogen bonding takes place through the hydrogen atom of the C-H group.

(v) *Paracresol.*

In the case of paracresol (Table V) also a few extra lines are observed in the liquid phase of this substance. They are at 282(0), 406(0), 809(0), 969(0), 1032(0), 1253(3b), 1517(0) and 3048(2) cm^{-1}. respectively. Amongst these

extra lines, the lines at 1253 and 3048(2) cm⁻¹ are not very weak. The lines at
1213 and 1608 cm⁻¹ reported by earlier authors (Magat, 1936) are resolved in the
present investigation into doublets at 1205 and 1219 cm⁻¹ and at 1597 and 1613 cm⁻¹
respectively. The lines at 338, 462, 845, 1219, 1597, 1613 and 2920 cm⁻¹ shift
respectively to 343, 467, 840, 1211, 1588, 1600 and 2912 cm⁻¹ when the substance
is solidified. Moreover, excepting the line at 2920 cm⁻¹ all of the broad lines
produced in the liquid phase of this substance become sharp in the solid state at
—180°C.

The lines 1597 and 1613 cm⁻¹ are due to deformations in the benzene ring
in which the displacements take place in the plane of the molecule and we
seldom notice any decrease in the frequency-shifts of these lines with solidification
of the substance. In this particular case, therefore, such a diminution in the Raman
shifts of these lines indicates that the strength of the bond amongst the atoms of
the benzene ring is probably slightly weakened in the solid state. The slight
decrease on solidification in the frequency-shift of the strongest line at 845 cm⁻¹
which is probably due to the breathing vibration of the substituted ring also cor-
roborates this statement.

(b) New Raman lines in the low-frequency region in the solid state

The microphotometer records of figures 3 and 4 show the number and
relative intensities of the new Raman lines in the low-frequency region pro-
duced by the two halogen substituted toluenes studied in the present investigation.
Metachlorotoluene in the solid state at —70°C gives rise to two new lines at 43
and 125 cm⁻¹ respectively. With lowering of temperature to —180°C these lines
shift to 50 and 129 cm⁻¹ respectively. The change in their intensities with change
of temperature of the solidified mass is, however, more prominent than the change
in frequency. The relative intensities of these two lines change from the ratio
2:1 to 1:3 with change of temperature from —70°C to —180°C. The low-fre-
quency Raman spectrum of solidified metabromotoluene has similar appearance
for the two temperatures –80°C and —180°C, but the frequency-shifts are slight-
ly smaller. The behaviour of these lines with change of temperature is also similar
to that of *m*-chlorotoluene. In the case of cresols at least one of the new lines
in the low-frequency region is very broad even at —180.°C. The change in
the relative positions of the OH and CH₃ groups seems to alter the low-frequency
lines considerably. The meta compound in the solid state yields only one new
broad line in the low-frequency region while the para and ortho compounds yield
respectively two and three such lines at —180°C. A comparison of the changes in
the ultraviolet absorption spectra of the three cresols with similar changes in the
temperatures of the substances (Swamy, 1952) shows that in the case of the para
compound the bands become sharper at —180°C while in the case of the other two
compounds the bands do not become very sharp even when the substances are cooled
down to —180°C. The new Raman lines, however, are sharper and more intense in

the case of the para compound than in the case of the meta compound. This comparison shows that the angular oscillation of molecule in the crystal lattice cannot be mainly responsible for the origin of low-frequency lines in crystals, because
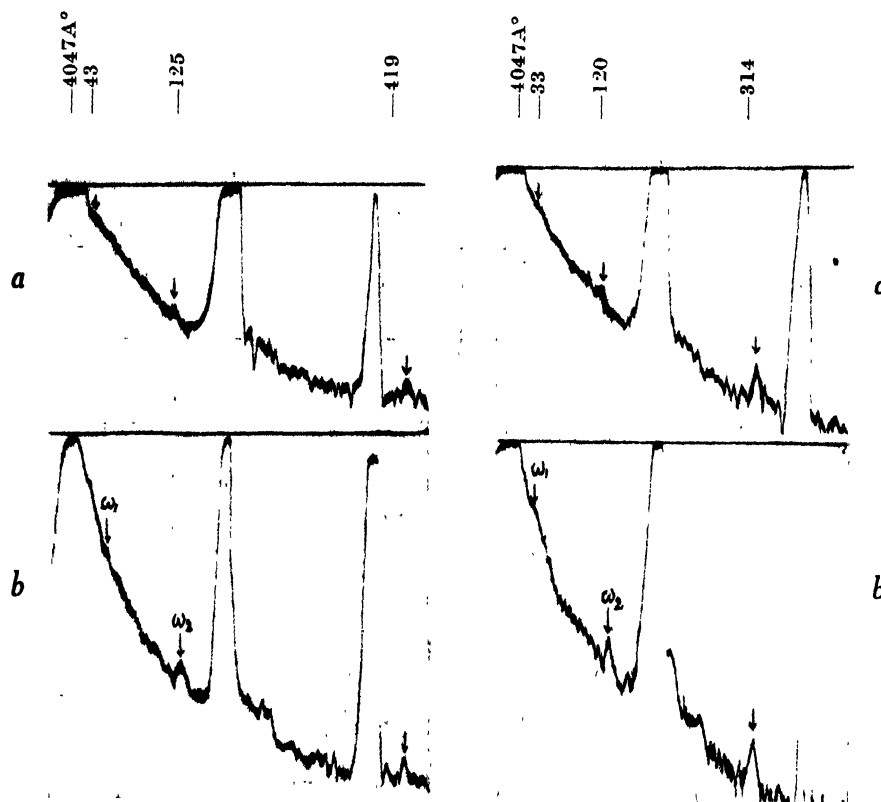

Fig. 3   Fig. 4

Microphotometric records of the Raman spectra

Fig. 3. Metachlorotoluene	Fig. 4. Metabromotoluene
(a) Solid at −70°C	(a) Solid at −80°C
(b) Solid at −180°C	(b) Solid at −180°C
($\omega_1 = 50cm^{-1}$; $\omega_2 = 129cm^{-1}$)	($\omega_1 = 33cm^{-1}$, $\omega_2 = 126cm^{-1}$)

the new lines in the low-frequency region are intense and greater in number in the case of paracresol than in the case of the meta compound while the ultraviolet absorption spectra indicates that the angular oscillation nearly ceases in the solid state at low temperature in *p*-cresol and such angular oscillations at least partially persist in the solid state at −180°C in meta cresol.

It would be interesting to compare the low-frequency Raman spectra of all the three isomers of chlorine and bromine substituted toluenes in the solid state, because such a comparison would show the influence of change in the relative positions of the substituents and of the mass of the substituents on the number and positions of the new lines. The low-frequency Raman lines of these compounds

are given in Table VI. The figures in parentheses in the table indicate the visually estimated intensities of these lines.

It appears from Table VI that there is no correlation between the frequency-shifts of the new lines and the mass of the substituent atoms in the same type of isomer, because the line 50 cm^{-1} is present in the spectra of all the chlorotoluenes

TABLE VI

Δv in cm^{-1}

Chlorotoluenes at −180°C			Bromotoluenes at −180°C		
Ortho (Sanyal, 1953)	Meta (Present author)	Para (Sanyal, 1953)	Ortho (Biswas, 1954)	Meta (Present author)	Para (Biswas 1954)
36] (0)		38 (2)	36 (2)	30 (1)	
50 (1)	50 (1)	50 (1b)			52 (1)
78 (0)		85 (1b)			
102 (2)			1C0 (4b)		94 (3b)
	129 (3)			126 (3)	
					133 (4)
					162 (1)

and parabromotoluene. Again, it is observed that the line at about 126 cm^{-1} in the case of the meta compounds is extremely weak when the substances are solidified and cooled to about —80°C, but when the temperature is lowered to —180°C the intensity of the line increases to three times its value at —80°C in the case of both metachlorotoluene and metabromotoluene. This observation precludes the possibility of attributing this line to any mode of angular oscillation about an axis of the molecule, because in that case the intensity would not increase at low temperatures . Further, the increase in the frequency-shifts of the lines with lowering of temperature cannot be explained by any other hypothesis except that of the formation of virtual bonds and strengthening of these bonds at lower temperatures.

(c) FLUORESCENCE SPECTRA

Both metachlorotoluene and metabromotoluene produce two broad fluorescence bands in the visible region in the solid state at —180°C. Amongst the cresols, only the ortho compound produces one broad fluorescence band under similar conditions. The fluorescence bands in all the above three compounds are, however, weak. The approximate position for the centres of the bands, the interval between two successive bands in any compound as well as their visually estimated intensities are given in Table VII.

TABLE VII

Fluorescence spectra

Compound (solidified & cooled to −180°C)	No. of bands	1st band		2nd band		Band interval in cm⁻¹
		Position in cm⁻¹	Intensity	Position in cm⁻¹	Intensity	
m-Chlorotoluene	2	23211	1	21611	1	1600
m-Bromotoluene	2	23195	1	21592	1	1603
o-Cresol	1	20419	2	—	—	—

The interval between the two successive fluorescence bands of the two halogen sub,tituted toluenes is about 1600 cm⁻¹ which may correspond to the frequency of C = C vibration in these molecules. It appears from such coincidence that the electronic state of the benzene ring itself is responsible for this fluorescence. Swamy (1952) observed that the v_0 band of *m*-chlorotoluene shifts from 36315 cm⁻¹ to 37015 cm⁻¹ with solidification and lowering of temperature to −180°C. Whether this band is rsponsible for the fluorescence or a new band that appears on the longer wavelength side is not known.

ACKNOWLEDGMENT

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