

THE RAMAN SPECTRA OF *m*- AND *p*-XYLENE IN THE SOLID STATE AT DIFFERENT LOW TEMPERATURES*

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Plates X A—C

ABSTRACT. The Raman spectra of meta and para xylenes in the liquid state and in the solid state at different low temperatures were recorded. Both the substances in the liquid state yield a few feeble extra Raman lines not reported in earlier publications. Some of the prominent Raman lines of both these compounds shift slightly with solidification of the compounds, but the number of lines undergoing such changes in their frequency-shifts is much greater in the case of meta xylene than in the case of the para compound.

Three new lines appear in the low-frequency region when the meta compound is solidified while two such lines in the low frequency region appear in the case of the para compound. With lowering of temperature of the solidified mass to -185°C the low-frequency lines of the former substance show little change except that the band at 81 cm^{-1} shifts to 90 cm^{-1} while in the case of the other compound the number of low-frequency lines increases from two to five with the lowering temperature to -185°C . The probable origin of these low frequency lines is discussed. The difference in the Raman spectra of these two isomers in the solid state is explained by assuming that the influence of the intermolecular field on the molecules of the substance depends on the relative positions of the substituent groups in the benzene ring.

INTRODUCTION

It was pointed out earlier (Biswas, 1954) that the study of the influence of temperature on the intensities and positions of the low-frequency Raman lines which appear when some organic liquids are solidified may lead to the proper understanding of the origin of such lines. The results obtained by Swamy (1951, 1952 and 1953) and Deb (1952, 1953, 1954) in their investigations on the ultraviolet absorption spectra of substituted benzenes and naphthalene compounds show that the influence of intermolecular field on the electronic energy level in the solid state depends on the relative positions of the substituent groups. A comparison of the Raman spectra of ortho and meta compounds in the solid state at different temperatures may indicate to what extent the intensities and positions of the lines can be correlated with the relative positions of the substituent groups and also with the intermolecular field indicated by the results of investigation of the ultraviolet absorption spectra under similar conditions. With this object in view the Raman spectra of meta and para xylene in the solid state at different low temperatures have been investigated and the results have been discussed in the present paper.

*Communicated by Professor S. C. Sirkar.

EXPERIMENTAL

The liquids of the present investigation were secured from Fischer Scientific Co., New York and were of chemically pure quality. They were distilled in vacuum, as usual. The Raman spectra of the substances in the liquid state were photographed and compared with the Raman shifts of these liquids reported by previous workers to test the purity of the samples. The technique for recording the Raman lines of the solidified substances is same as that described earlier (Biswas, 1954). In all the cases the spectra were recorded on Ilford Zenith plates using a Fuess glass spectrograph having a dispersion of about 11 Å° in the 4047 Å° region. Each spectrogram contains an iron arc spectrum for comparison.

RESULTS AND DISCUSSIONS

The calculated Raman shifts of the substances both in the liquid state and in the solid state at different temperatures are given in Tables I and II.

TABLE I

m-Xylene C₆H₄(CH₃)₂,Δν in cm⁻¹

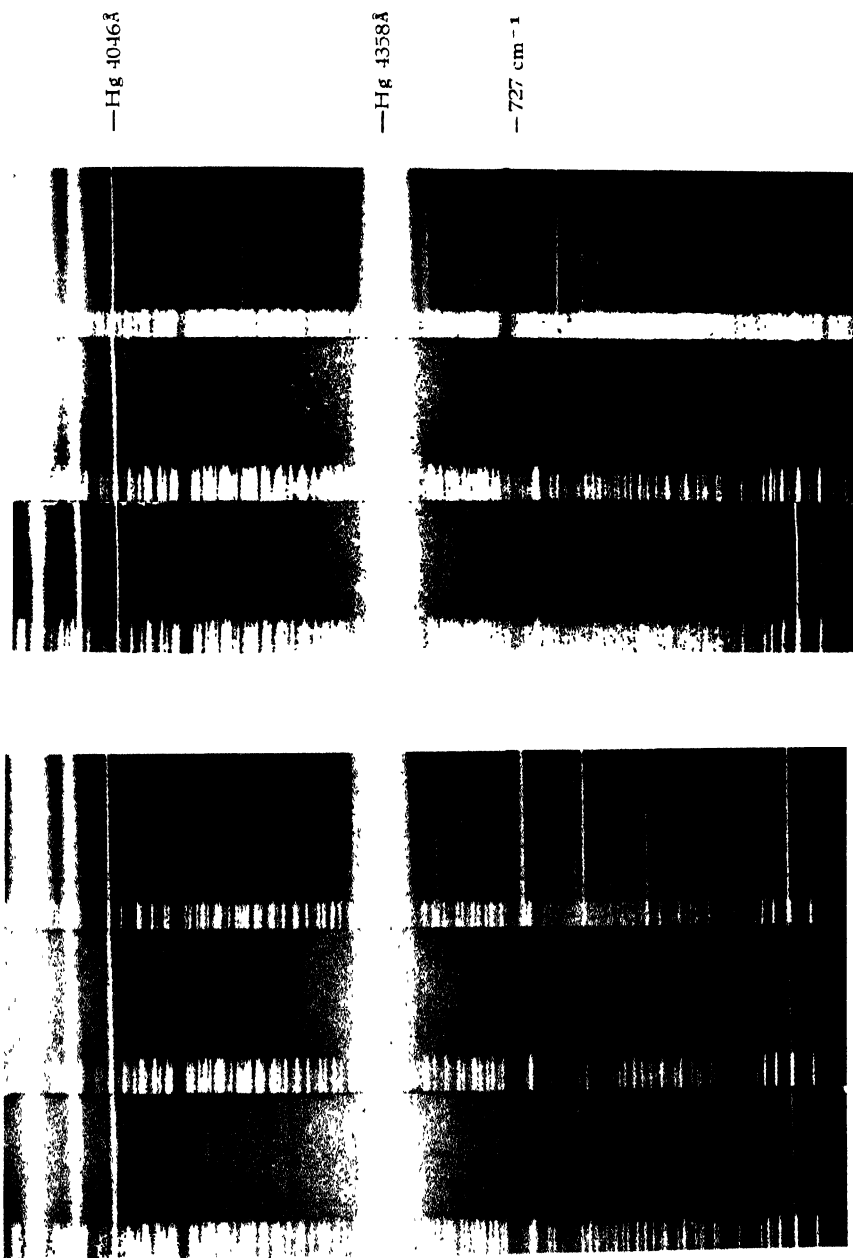
Liquid		Solid (present author)	
Magat (1936)	Present author	At about -85°C	At -180°C
		41 (2) e	41 (1) e
		59 (2) e	59 (2) e
		81 (6) e, k	90 (2b) e, k
200 (4)	206 (3) ± e		
224 (6)	231 (5) ± e, k	236 (1) e, k	236 (0) e, k
295 (3)	282 (3) ± e, k	282 (0) e, k	282 (0) e, k
	318 (1b) e, k		
	461 (2) ± e, k		
514 (4)	517 (4) e, k	513 (1) e, k	513 (0) e, k
538 (6)	549 (7) ± e, k	536 (2) e, k	534 (1) e, k
	588 (0) e		
	647 (1) e		
	679 (0) e		
725 (10)	727 (10) ± e, k, i	721 (5) e, k	721 (3) e, k
770 (0.5)	766 (1) e, k		

TABLE I—*contd.*

Liquid		Solid (present author)	
Magat (1936)	Present author	At about -80°C	At -180°C
819 (3b)	812 (0) e 828 (3) e, k 887 (1b) e 943 (1) e 968 (1) e	826 (0) e, k	826 (0) e, k
1000 (12)	1000 (12) e, k, i	1000 (7) e, k	1000 (5) e, k
1032 (1)	1035 (2) e, k	1035 (0) e, k	1035 (0) e, k
1094 (1)	1093 (2) e, k	1093 (0) e, k	1093 (0) e, k
1167 (1)			
	1210 (2) e, k	1210 (0) e, k	1210 (1) e, k
1246 (4)	1250 (4) e, k	1248 (2) e, k	1248 (1) e, k
1268 (0.5)	1265 (2) e, k		
1342 (5)	1349 (1) e		
1375 (5)	1380 (5) e, k	1374 (2) e, k	1374 (1) e, k
1448 (1b)	1446 (2b) e, k		
1592 (1)	1592 (3) e, k	1592 (0) e	1592 (0) e
1613 (3)	1616 (5) e, k	1610 (1) e, k	1610 (1) e, k
2571 (0)			
2731 (0.5)			
2866 (3)	2874 (3b) e, k	2868 (1) k	2868 (0) k
2917 (8b)	2920 (6b) e, k	2911 (4b) e, k 2962 (1) k	2911 (2b) e, k 2962 (1) k
3014 (3)			
3045 (7b)	3058 (4) e, k	3045 (2) k	3045 (1) k
3217 (1b)			

TABLE II
p-Xylene, C₆H₄(CH₃)₂
 $\Delta\nu$ in cm⁻¹

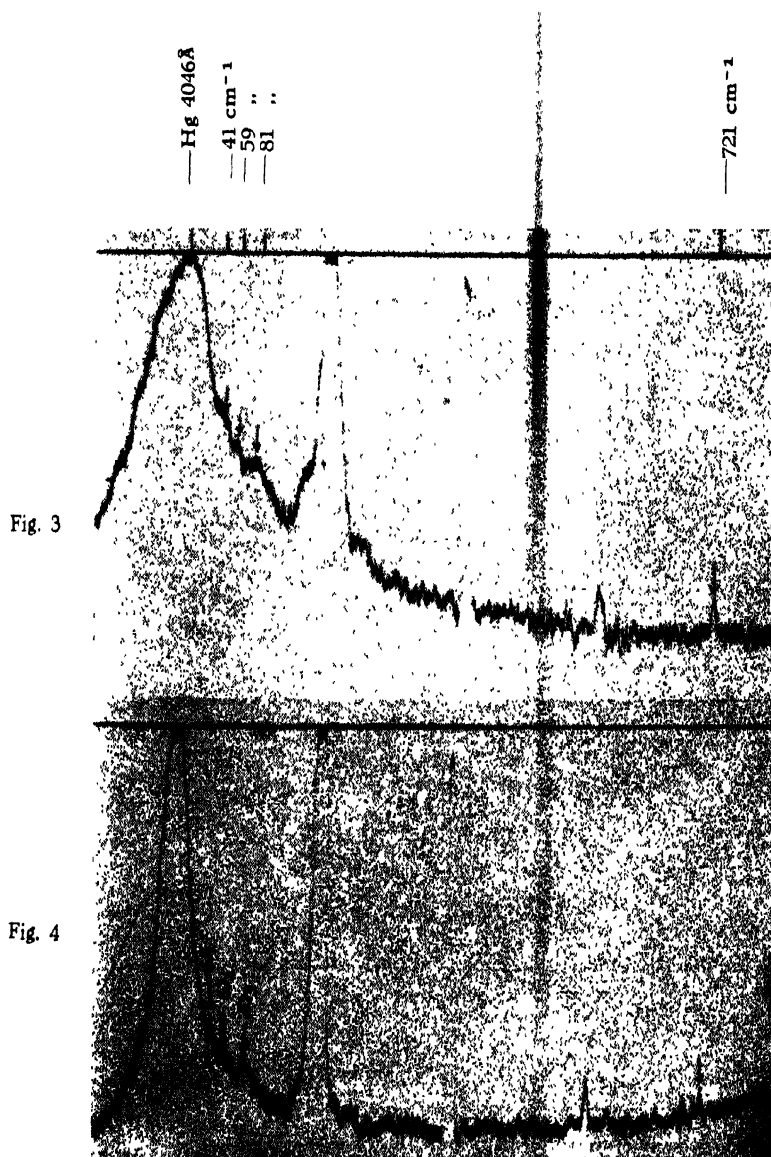
Liquid		Solid (present author)	
Magat (1936)	Present author	At about -30°C	At -180°C
		55 (0) e	50 (1) e, k
			68 (1) e, k
			87 (2) e, k
		91 (2b) e, k	108 (2) e, k
			118 (1b) e
170 (0.5)			
311 (7)	310 (7) \pm e, k	316 (1) e, k	316 (1) e, k
389 (0)	389 (1) e		
460 (8)	460 (10) + e, k	460 (1) e, k	460 (1) e, k
540 (0)			
	593 (0) e		
643 (6)	617 (1) \pm e, k	647 (1) e, k	617 (1) e, k
697 (0)	697 (1) e		
	725 (1) e		
	754 (1) e		
811 (4)	800 (4) \pm e, k	800 (0) e	800 (0) e
827 (12)	820 (12) \pm e, k, i	820 (3) e, k	820 (3) e, k
	1000 (1) e, k		
1036 (0)			
	1120 (2) e, k		
1182 (2)	1180 (2) e, k	1185 (0) e	1185 (0) e
1212 (8)	1210 (10) e, k, i	1210 (5) e, k	1210 (5) e, k
1310 (2)	1319 (1) e		
	1360 (0) e		
1382 (6)	1380 (6) e, k	1371 (0) e, k	1375 (1b) e, k
-1452 (2b)	1450 (2b) e, k	1448 (0) e	1448 (1b) e, k
	1466 (1b) e		



Raman spectra

Fig. 1. Meta xylene
 (a) Liquid at 30°C
 (b) Solid at -30°C
 (c) Solid at -180°C

Fig. 2. Para xylene
 (a) Liquid at 30°C
 (b) Solid at -30°C
 (c) Solid at -180°C

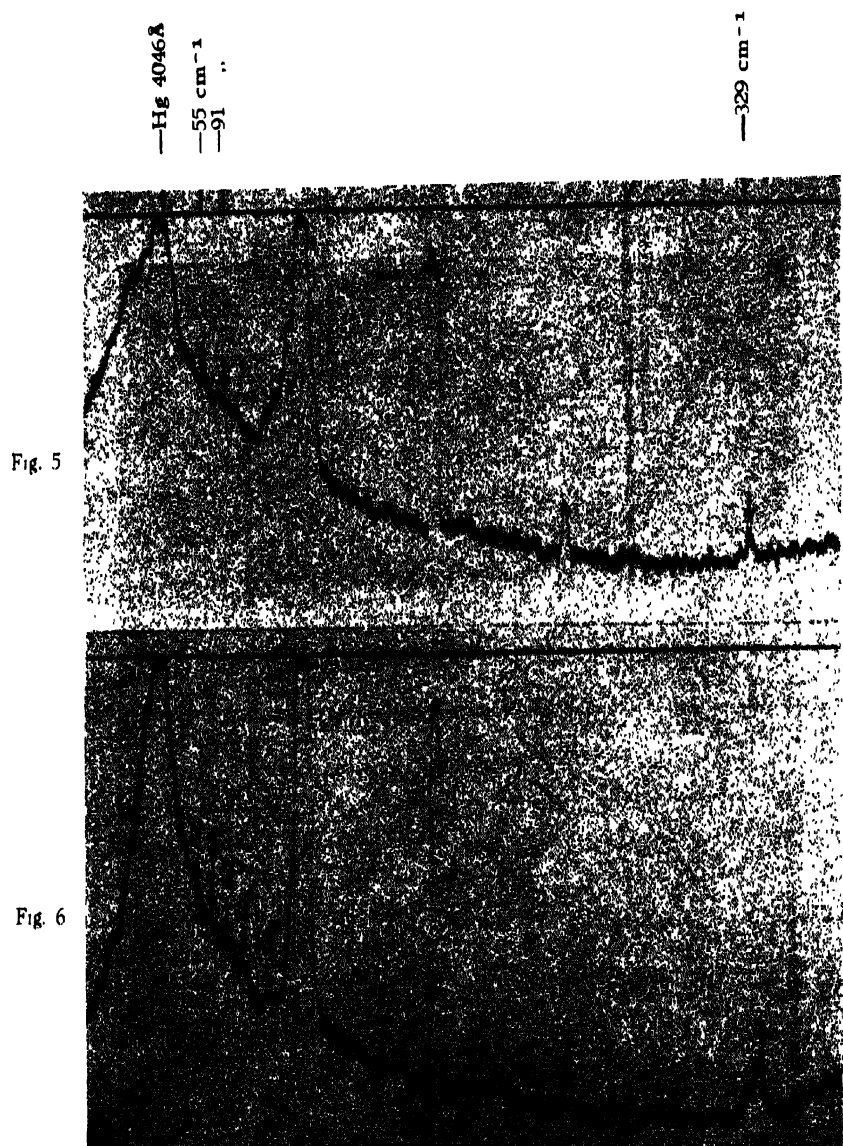


Microphotometric records of Raman spectra

Fig. 3. Meta xylene at -80°C

Fig 4. " " at -180°C

($\omega_1 = 41 \text{ cm}^{-1}$, $\omega_2 = 59 \text{ cm}^{-1}$, $\omega_3 = 90 \text{ cm}^{-1}$)



Microphotometric records of the Raman spectra

Fig. 5. Para xylene at -30°C

Fig. 6. „ „ at -180°C

($\omega_1 = 50 \text{ cm}^{-1}$, $\omega_2 = 68 \text{ cm}^{-1}$, $\omega_3 = 87 \text{ cm}^{-1}$, $\omega_4 = 108 \text{ cm}^{-1}$, $\omega_5 = 148 \text{ cm}^{-1}$)

TABLE II—*contd.*

Liquid		Solid (present author)	
Magat (1936)	Present author	At about -30°C	At -180°C
	1519 (o) e		
1575 (1)	1580 (2) e, k	1580 (o) e	1580 (o) e, k
1616 (f)	1622 (8) e, k	1620 (o) e	1620 (3) e, k
273 (2)	2740 (2) e, k	2740 (o) k	2740 (o) k
	2805 (1b) e, k		
2867 (5)	2870 (3b) e, k	2868 (1b) k	2868 (1b) k
2920 (9b)	2922 (5b) e k	2921 (1b) e	2921 (2b) e, k
		2942 (c) e	2942 (2) e k
3017 (51)	3014 (2) e, k	3014 (2) e	3014 (2) k
	3026 (2) e, k	3026 (2) e	3026 (2) k
3050 (7b)	3063 (4) e, k	3061 (3) e, k	3061 (4) e, k
3214 (1b)			

The tables also include for comparison the Raman shifts of these substances in the liquid state reported by some previous workers. The spectrograms are reproduced in figures 1 and 2, Plate XA. Microphotometric records showing the intensities of the low frequency lines at different temperatures relative to some other lines due to intramolecular oscillations are also reproduced in figures 3—6 (Plates X B—C).

(a) Raman lines of the substances in the liquid state :

Tables I and II show that some of the weak lines observed in the present investigation for these two compounds have not been recorded by previous workers. Such extra lines observed in the case of *m*-xylene are at 318 (1b), 461 (2), 588 (o), 647 (1), 812 (o), 887 (1b), 943 (1), 968 (1) and 1210 (2) cm^{-1} and in the case of the other compound the extra lines are at 593 (o), 725 (1), 754 (1), 1000 (1), 1120 (2), 1360 (o), 1466 (1b), 1519 (o) and 2805 (1b) cm^{-1} . As the extra lines 461 (2), 647 (1), 812 (o) and 1210 (2) cm^{-1} observed in the case of *m*-xylene coincide in positions with the strongest lines of the para compound, it is suspected that a small percentage of para compound is present as impurity in the experimental substance used as meta-xylene in this investigation. Similarly, the presence of the extra lines 725 (1) and 1000 (1) cm^{-1} in

the spectrum of the liquid para xylene indicates the contamination of the substance by minute traces of the meta compound. The other extra lines observed in the present investigation seem to be genuine Raman lines of the respective liquids.

Previous authors, on the other hand, have reported the existence of four lines not found in our spectrogram in the case of each of the two xylenes. For meta xylene such extra lines are at 1167 (o), 2571 (o), 2731 (o.5) and 3217 (1b) cm^{-1} while for the other compound they are at 170 (o.5), 540 (o)?, 1036 (o) and 3214 (1b) cm^{-1} . The lines assigned by previous workers as 2731 cm^{-1} and 3217 cm^{-1} in the case of meta xylene and as 3214 cm^{-1} in the case of the para compound cannot be attributed to the C—H valence oscillation, because although there are traces of the lines at their positions corresponding to 4046 Å excitation, no trace of them is found at the positions corresponding to the much stronger excitation by 4358 Å Hg line. They can be satisfactorily attributed to the C—C valence vibration and the C—H deformation vibration excited by the 4358 Å Hg line. These lines are assigned as the lines 943 cm^{-1} and 1446 cm^{-1} of the meta compound and the line 1466 cm^{-1} of the para compound as given in Tables I and II respectively.

(b) Raman lines of the substances in the solid state :

It can be seen from Tables I and II that meta xylene when solidified and cooled to -80°C , (m. p. of *m*-xylene is -52°C) gives rise to three new Raman lines in the low-frequency region while the para compound in the solid state at -30°C (m. p. of *p*-xylene is 13°C) gives rise to two new lines in the low-frequency region. When the solidified mass is cooled down to -180°C , the low-frequency lines of the meta compound show little change in their intensities and positions except the shift of the band at 81 cm^{-1} to 90 cm^{-1} . The low-frequency lines of the para compound, on the other hand, show remarkable changes with the lowering of temperature of the polycrystalline mass to -180°C . Two more low frequency lines at 68 cm^{-1} and 148 cm^{-1} respectively appear and the broad line at 91 cm^{-1} breaks up into two equally intense lines at 87 cm^{-1} and 108 cm^{-1} when the solid mass is cooled to -180°C . Thus, with lowering of temperature of the solid para xylene from -30°C to -180°C , the number of low-frequency lines increases from two to five. Moreover, it is evident from the microphotometric records reproduced in figures 3—6 that the intensities of some of the low-frequency lines do not diminish appreciably with the lowering of temperature of the crystals of meta and para xylenes to -180°C . On the other hand, the intensities of some of the low-frequency lines increase while those of the other lines practically do not show any change with lowering of temperature.

We can now try to understand the above results of our investigation from the points of view of different theories regarding the origin of these low-frequency lines. The ultraviolet absorption spectra of these xylenes were

studied previously by Swamy (1952). It was observed that the absorption bands of these substances become sharper with the solidification of the samples and with the lowering of the temperature to -180°C . He concluded from these results that with the lowering of temperature angular oscillation of the molecules tends to cease. We can, therefore, see that if the low-frequency lines originate from the angular oscillations of the molecules fixed in the crystal lattice as postulated by some previous workers their intensities should invariably diminish with the lowering of temperature of the solid mass. The evidence being on the contrary, we conclude that at least some of these lines cannot be due to the angular oscillations of the xylene molecules fixed in the crystal lattice. An alternative explanation of the origin of these low-frequency lines was given by Sirkar (1936). According to his theory, the low-frequency lines are due to the intermolecular vibrations in groups of molecules formed by virtual bonds amongst the molecules in each group. In this associated group, the molecules may execute both translational and rotational oscillations giving rise to the new Raman lines in the low-frequency region observed in the case of crystals. The enhancement of the frequency shifts of the low-frequency lines with the lowering of temperature can be easily understood to be the result of the increase in the strength of the virtual bonds which are formed between neighbouring molecules in the solid state with the lowering of temperature. Moreover, at lower temperatures the molecules come closer together and association between next neighbours may take place. These new virtual bonds may be responsible for the increase in the number of low-frequency lines at lower temperature.

This hypothesis of association of the molecules in the solid state in this particular case seems to be unavoidable in view of the fact that the intermolecular field in the liquid state is too weak to make the frequency of angular oscillation as high as $10^{12}/\text{sec}$. This can be seen from the results of investigation on the absorption of U. H. F. radio waves in meta xylene reported by Ghosh (1953). He observed an absorption peak of frequency $8.2 \times 10^8/\text{sec}$ in the case of *m*-xylene at -30°C and this peak was attributed to dimers. The peak due to monomer was expected to have a frequency of the order of $10^9/\text{sec}$. The frequency of the angular oscillation of the single molecule in the solid state, therefore, cannot be greater than $10^9/\text{sec}$ in this case, unless there is a thousandfold increase in the intermolecular field. As the frequencies of the new lines are of the order of $10^{12}/\text{sec}$ the intermolecular field is much stronger in the solid state than that in the liquid, as pointed out recently by Sirkar (1951).

A comparison of the number and positions of the low-frequency lines of the two compounds studied in the present investigation show that the relative positions of the substituents in the benzene ring have considerable influence on the low-frequency lines exhibited by these crystals. Also it is clear that the low-frequency lines of the para compound show considerable changes with lowering of temperature to -180°C , while those of the meta compound

practically do not show such changes under similar condition. This difference in the behaviour of these two compounds with lowering of temperature is certainly related with the relative positions of the substituent groups in the benzene ring. The molecule of the meta compound, due to their unsymmetrical structure, possesses permanent electric moment. Hence the polar molecules of the meta compound get associated more easily even at a temperature just below the freezing point than the symmetrical molecules of the para compound, and with further lowering of temperature only the virtual bond may strengthen a little in the former case. The molecules of the para compound, however, come closer and closer together when the temperature is brought down to -180°C and the molecules probably disturb the symmetry of their neighbours only when they are sufficiently close to each other. The association of molecules in the case of the para compound is, therefore, complete only at very low temperatures and not at a temperature just below its freezing point.

(c) *Lines of single molecule in the solid state :*

All the prominent Raman lines of both the meta and the para compound in the liquid state are found in the Raman spectra of these substances in the solid state and the relative intensities of these lines remain unaltered with solidification. The frequency-shifts of the intense lines 517 , 540 , 727 , 1380 , 1616 and 2920 cm^{-1} diminish slightly while that of the line 231 cm^{-1} increases with solidification of the substance. In the case of the para compound also the lines 310 and 1380 cm^{-1} shift respectively to 316 and 1375 cm^{-1} while a new line at 2942 cm^{-1} appears with solidification. This probably indicates that the influence of the intermolecular field on the modes of vibration of the molecules in the solid state depends on the symmetry of the molecule and that meta xylene molecule being more asymmetric than the para xylene molecule greater number of vibrations are affected by intermolecular field in the former case than in the latter case.

The line at 2874 cm^{-1} of the meta xylene due to C—H valence oscillation shifts to 2868 cm^{-1} with the solidification of the substance. Another line at 2920 cm^{-1} of meta xylene due to this C—H valence oscillation splits up into two lines at 2911 cm^{-1} and 2962 cm^{-1} with the solidification of the substance. Similarly for the para compound the line at 2922 cm^{-1} breaks up into two lines at 2921 cm^{-1} and 2942 cm^{-1} with the solidification of the substance. Such changes in the lines due to C—H valence oscillation of the xylene molecules, when the other intramolecular oscillations of xylene molecule are little affected with solidification, may lead one to conclude that the association of the neighbouring molecules in the solid state in case of xylenes probably takes place through the hydrogen atom. It may be pointed out here that even when polymerization takes place at the expense of a regular C—C bond in methylmethacrylate, the other lines of the methylmethacrylate molecule do

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not change appreciably (Roy, 1953). Hence in the case of the xylenes also considerable changes in the positions and intensities of other lines are not expected if association takes place through C—H bonds.

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