

INTENSITY STUDIES IN RAMAN EFFECT—POSITIONAL ISOMERISM

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1. INTRODUCTION

THE infra-red absorption spectra of the various isomers of the *o*, *m*, *p* cresols, xylenes, ethyl toluenes and dichlorobenzenes have been investigated by Whiffen *et al.*¹ Their spectra reveal the existence of intense absorptions in the regions 700–800 cm^{-1} and 1200–1300 cm^{-1} . The region 700–800 cm^{-1} is characteristic of benzenoid substances, with the substituents attached to the nucleus. It has been found that there is a shift of this 'aromatic band' towards higher frequencies in passing along the series *o-m-p* in most of the disubstituted benzenes regardless of the nature of the substituents.

The Raman spectra of the three isomeric cresols were investigated by Biswas,² in both liquid and solid states. The Raman spectra of *o-p*-chlorotoluenes and of *o-p*-xylenes in liquid and solid states were studied by Sanyal³ and Biswas⁴ respectively. According to Sanyal, *p*-chlorotoluene does not yield any line with a frequency below 306 cm^{-1} whereas there is an intense line at 163 cm^{-1} in the case of *o*-chlorotoluene. This line, he has attributed to the presence of dimers in *o*-chlorotoluene.

Very little work has been done in the case of these isomers with reference to the intensities of the Raman lines. A study of the frequencies and the intensities of the various Raman lines with reference to the position of the substitution has been attempted in the present investigation.

2. EXPERIMENTAL

Extra pure samples of the substances distilled at constant boiling-points have been used in the present investigation. A Hilger E 612 two-prism glass

spectrograph, in conjunction with a Raman Source Unit, was used. The spectra of each series have been recorded under identical conditions. A set of graded intensity marks were also given on the same plate and the intensities were computed using a Moll microphotometer.

3. RESULTS AND DISCUSSION

Tables I to IV contain the frequencies and the integrated intensities of the Raman lines in different isomers.

TABLE I

Xylenes

<i>o</i> -Xylene		<i>m</i> -Xylene		<i>p</i> -Xylene	
Frequency cm. ⁻¹	Intensity	Frequency cm. ⁻¹	Intensity	Frequency cm. ⁻¹	Intensity
..	170	0.846
..	313	2.147
..	459	0.467
506	0.738	514	0.360
582	1.065	538	0.581	644	0.599
733	2.768	724	1.057	784	1.034
..	827	2.781
1051	0.936	1182	0.286
1222	2.452
1384	0.494	1375	0.414	1376	0.732
1606	0.780	1613	0.408	1606	0.768
..	..	2866	0.389	2860	3.081
2920	1.223	2916	1.982	2920	2.226
3047	1.999	3048	2.767	3052	1.414

TABLE II

Cresols

<i>o</i> -Cresol		<i>m</i> -Cresol		<i>p</i> -Cresol	
Frequency cm. ⁻¹	Intensity	Frequency cm. ⁻¹	Intensity	Frequency cm. ⁻¹	Intensity
190	3.266
274	1.431	214 } 239 }	0.476	337	3.130
445	2.946	455	0.468	464	1.980
584	1.776	612	0.084	646	0.919
749	11.298	735	3.012	841	8.379
		833	1.931		
1044	4.407	1002 1042 1081	2.190 0.211 0.629	1100	0.227
1252	3.390	1251	2.083
1378	1.209	1378	0.772	1380	1.740
1400	2.625	1400	2.680	1400	2.638
1598 } 1620 }	2.396	1597 } 1614 }	3.549	1598 } 1612 }	4.873
2920	3.279	2929	2.292	2927	2.857
3057	3.922	3057	5.746	3048	6.850

From the results given in the above tables the following conclusions can be drawn:—

(1) The intensities of the corresponding lines are, in general, low in the *meta*-isomer.

(2) *In xylenes*.—(a) The strong line in the region 700–800 cm.⁻¹ represents the benzenoid vibration. According to Whiffen and Thompson this

TABLE III
Chloroanilines

<i>o</i> -Chloroaniline		<i>m</i> -Chloroaniline	
Frequency cm. ⁻¹	Intensity	Frequency cm. ⁻¹	Intensity
168	1.900	193	2.060
257	1.473	244	1.362
467	1.433	408	1.366
555	1.008	530	0.683
678	1.415	694	1.641
833	1.878	893	1.071
1020	1.843	1073	1.092
1304	2.231	1300	4.271

TABLE IV
Chlorotoluenes

<i>o</i> -Chlorotoluene		<i>p</i> -Chlorotoluene	
Frequency cm. ⁻¹	Intensity	Frequency cm. ⁻¹	Intensity
164	1.692
247	2.383	307	1.180
675	1.167	634	0.801
801	1.366	796	1.803
1040	1.243	1090	1.866
1204	0.947	1208	0.639
1590	1.545	1608	0.819
2920	1.149	2927	0.497
3062	1.543	3050	1.078

line in the infra-red appears at 743, 765 and 790 cm.^{-1} in passing from *ortho*- to the *para*-compound. In the present investigation strong lines have been observed at 733 cm.^{-1} , 724 cm.^{-1} and 784 cm.^{-1} in the three isomers respectively, thus showing a diminution in frequency in the *meta*-isomer.

(b) The line in the region 2880–2860 cm.^{-1} represents the symmetrical stretching of the methyl group attached to the benzene nucleus. This line has a maximum intensity in *para*, but it is very weak in *meta* and is absent in *ortho*-isomer.

(c) The line at 2916 cm.^{-1} , representing the asymmetrical stretching of the methyl group, shows a gradual increase in intensity from *ortho* to *para*-isomer.

(3) *In cresols.*—(a) Strong lines at 749, 735 and 841 cm.^{-1} have been observed corresponding to the benzenoid vibration, while Whiffen and Thompson recorded it at 752, 775 and 827 cm.^{-1} in the *o-m-p* cresols respectively.

(b) The intensities of the C-C vibration at 1000 cm.^{-1} and the CH_3 asymmetric stretching in methyl attached benzene ring at 2916 cm.^{-1} behave in the same way.

(c) No line has been observed in the region 2880–2860 cm.^{-1} which represents the CH_3 symmetric stretching mode.

(4) *In chloroanilines.*—(a) There is a slight increase in intensity of the C-Cl vibration at 678 cm.^{-1} in the *meta*-compound. This observation is different from what has been found in the other substances.

(b) The line at 1300 cm.^{-1} in *meta*-isomer shows a doublet structure as a result of which the integrated intensity has been considerably enhanced.

(5) In chlorotoluenes the intensities of the lines in *ortho*-compound are greater than in the corresponding *para*-isomer.

The *para*-chloroaniline and *meta*-chlorotoluene were not investigated due to non-availability of the substances.

Since the vibrational intensity of a Raman band is a dependent function of the derivative of the polarisability, which is a related function of the electronic state of the bond, the observed variation in intensity in the three isomers may be explained, by considering the inductive effects brought into play by the various substituents attached to the benzene ring.

Shorygin⁵ while studying the influence of the second substituent on the mono-derivatives of benzene has observed that the intensity of the first substituent depends upon the electronegativity of the second substituent group.

In the case of the intensity of the nitrogroup band, the intensity increases very sharply when electropositive radicals are introduced in the *para* position. He has also pointed out that the halogen atoms behave as electropositive groups as far as the intensity of the Raman scattering is concerned.

The compounds studied in the present investigation have the following groups: CH_3 groups in xylene; OH and CH_3 in cresols; NH_2 and Cl in chloroaniline; and CH_3 and Cl in chlorotoluene. All these groups are known to be electropositive. The degree of electronegativity is different for each group.

When an electropositive group like CH_3 is attached to the benzene ring, this group will force the electron into the ring due to the electron repelling character and consequently increases the electron density at the *ortho* and the *para* positions with respect to it and the effect at the *meta* is much less. If another methyl group is substituted in the *para* position, as in *para*-xylene, the positions *a* and *b* (Fig. 1) possess high electron density owing to the repulsive inductive effect of the alkyl group in the *ortho* position. Thus both the groups aid each other and the electron density will be increased.

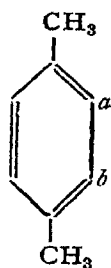


FIG. 1.

When the methyl group is attached to the *meta* position, due to cumulative effect of the electric charges induced in the *ortho* and the *para* positions, the electron density will be maximum.

In the *ortho* position, the inductive effects due to both the groups oppose each other and consequently change in the electron density induced in the ring will be minimum.

Thus it is seen that the changes in electron density induced in the ring follow the order $meta > para > ortho$. This will be the case with all the electropositive substituents though the changes may vary depending upon the degree to which they are electropositive. The observed results may thus qualitatively be explained on the basis that the increase in the electron density may cause a decrease in intensity of the Raman lines.

4. SUMMARY

The Raman spectra of the *o-m-p* isomers of some substances have been investigated. It has been found that in all the cases the intensities of the corresponding Raman lines have a maximum value in the *ortho*-compound and a minimum value in the *meta*-isomer. An attempt has been made to explain the observed results on the basis of the change in electron density caused by the inductive effect of the various substituents attached to the benzene nucleus.

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