

THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF *ORTHO*- AND *META*-THIOCRESOLS

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ABSTRACT

The absorption spectra of *ortho*- and *meta*-thiocresols have been studied in the present investigation. The *ortho*-thiocresol spectrum consists of about forty-five bands of rather a diffuse nature and in general low intensity in the region from 2873 Å to 2600 Å. The maximum number of bands is obtained by using a path length of 330 cm. for absorption, the temperature of the bulb being maintained at 14° C. Several of these bands are assigned as due to *v-v*-transitions. The (0, 0) band is chosen at 35386 cm.⁻¹ which is the strongest band on the longer wavelength side. Vibrational frequencies in the excited state have values 729, 957 and 1159 and combinations and overtones of these are present.

The *meta*-thiocresol spectrum consists of about forty bands of rather a diffuse nature and very weak intensities in the region from 2900 Å to 2590 Å. The maximum number of bands is obtained by using a path length 200 cm. for absorption and by keeping the temperature of the bulb at 20° C. The (0, 0) band is chosen to be that at 34793 cm.⁻¹ which is the strongest band on the longer wavelength side. Vibrational frequencies in the excited state have values 492, 611, 720, 845, 965, 1016 and 1155 cm.⁻¹ and combinations and overtones of these are present.

INTRODUCTION

WORK on the absorption spectra of *ortho*- and *meta*-thiocresols has been reported in the collection of ultraviolet spectral data of the American Petroleum Institute Research Project 44, Serial Nos. 433 and 435. The spectrum of *ortho*-thiocresol in *iso*-octane solution shows one peak at about 2880 Å, the other at 2790 Å and the third at 2340 Å. In case of *meta*-thiocresol studied in *iso*-octane solution there are three peaks at 2890 Å, 2795 Å and at 2385 Å. Different concentrations were used to plot the graph showing the absorption against the wavelength. Work on the absorption spectrum of *para*-thiocresol has been recently reported by the author.¹ So far no

work on the vapour absorption spectra of *ortho*- and *meta*-thiocresols in the ultraviolet region appears to have been reported. The infra-red spectral data and the Raman spectrum data do not appear to have been reported for these molecules. The infra-red and Raman spectral data are being reported elsewhere. The ultraviolet absorption spectra in the vapour state and the effect of changing the temperature of the absorbing column and the length of the column have been studied and reported now. Assignments have been made and discussed.

EXPERIMENTAL

Ortho-thiocresol and *meta*-thiocresols are colourless liquids with boiling points 194.3°C . and 195°C . respectively. These chemicals were supplied by Eastman Kodak Company. The experimental procedure adopted is the same as described in detail in the absorption spectrum of *para*-thiocresol.¹

RESULTS

Ortho-thiocresol in vapour phase shows strong absorption below 2550 \AA . At room temperature 30°C . and an absorption path length of 100 cm. the bands appear in the region 2900 \AA to 2600 \AA . With increase in temperature of the absorbing column to 50°C . the bands on the shorter wavelength side begin to disappear and when the temperature is raised to 80°C ., there is continuous absorption from 2900 \AA to the lower wavelength side. No bands develop on the long wavelength side. On increasing the length of the absorbing column to 330 cm. and keeping the temperature of the bulb at 14°C . all the bands mentioned in Table I below were recorded.

Meta-thiocresol in solution phase absorbs in the region 2900 \AA to 2600 \AA , and there is strong continuous absorption below 2600 \AA . In the vapour absorption about forty bands were obtained between 2900 \AA to 2590 \AA . At room temperature and an absorption path length 100 cm. the bands are present in this region with weak intensities. When the temperature is raised to 50°C . most of the bands on the shorter wavelength side disappear and on raising the temperature to 80°C . there is continuous absorption starting from 2900 \AA towards the shorter wavelength side. No new bands appear to develop on the longer wavelength side. On increasing the length of the absorbing column to 200 cm. and evacuating the tube and keeping the bulb at 20°C . all the bands mentioned in Table II were recorded.

The data on the observed bands together with the proposed assignments are given in Tables I and II for *ortho*- and *meta*-thiocresols respectively, and the analysis discussed.

TABLE I
Ortho-thiocresol bands 2800 Å system

The intensities of the bands were visually estimated and explained as below. *s*, strong; *ms*, medium strong; *m*, medium; *w*, weak; *vw*, very weak.

λ in Å	ν in cm.^{-1}	Int. visual estimation	Separation from (0, 0), <i>i.e.</i> , 35386 cm.^{-1}	Assignment
2872.2	34806	<i>w</i>	— 580	
2866.8	34871	<i>w</i>	— 515	
2863.8	34908	<i>vw</i>	— 482	0—4 × 120
2857.2	34990	<i>vw</i>	— 396	
2854.9	35017	<i>w</i>	— 369	0—3 × 120
2849.9	35079	<i>w</i>	— 307	0—2 × 120—60
2844.4	35146	<i>w</i>	— 240	0—233
2841.4	35183	<i>w</i>	— 203	0—203
2837.8	35228	<i>w</i>	— 158	0—158
2834.7	35266	<i>w</i>	— 120	0—120
2830.0	35325	<i>vw</i>	— 61	0—61
2825.1	35386	<i>vs</i>	0	(0, 0)
2811.1	35562	<i>w</i>	176	
2803.0	35665	<i>w</i>	279	
2790.9	35820	<i>w</i>	434	
2779.4	35968	<i>w</i>	582	0+729—158
2773.0	36051	<i>w</i>	665	0+729—60
2768.1	36115	<i>s</i>	729	0+729
2765.3	36151	<i>w</i>	765	0+957—203
2760.7	36212	<i>w</i>	826	0+957—120
2755.9	36275	<i>w</i>	889	0+957—60
2750.7	36343	<i>s</i>	957	0+957
2744.1	36431	<i>w</i>	1045	0+1159—120
2739.8	36488	<i>w</i>	1102	0+1159—60
2735.5	36545	<i>s</i>	1159	0+1159
2729.1	36631	<i>w</i>	1245	0+2 × 729—203
2725.5	36679	<i>w</i>	1293	0+2 × 729—158
2721.3	36736	<i>w</i>	1350	0+2 × 729—120
2713.9	36836	<i>ms</i>	1450	0+2 × 729
2705.7	36948	<i>w</i>	1562	0+957+729—120
2700.4	37020	<i>w</i>	1634	0+957+729—60
2695.8	37083	<i>ms</i>	1697	0+957+729
2692.3	37131	<i>w</i>	1745	0+2 × 957—158
2684.5	37239	<i>w</i>	1853	0+2 × 957—60
2680.5	37295	<i>ms</i>	1909	0+2 × 957
2676.4	37352	<i>w</i>	1966	0+957+1159—158
2665.7	37502	<i>m</i>	2116	0+957+1159
2655.8	37642	<i>w</i>	2256	0+2 × 1159—60
2651.2	37707	<i>m</i>	2321	0+2 × 1159
2639.2	37878	<i>vw</i>	2492	0+2 × 957+729—158
2636.0	37924	<i>vw</i>	2538	0+2 × 957+729—120
2628.5	38033	<i>w</i>	2647	0+2 × 957+729
2620.5	38149	<i>w</i>	2763	0+3 × 957—120
2612.7	38263	<i>m</i>	2877	0+3 × 957
2604.1	38389	<i>vw</i>	3003	0+2 × 957+1159—60
2599.1	38463	<i>mw</i>	3077	0+2 × 957+1159

TABLE II
Meta-thiocresol bands 2900 Å to 2590 Å region

The intensities of the bands were visually estimated and explained as below. *vs*, very strong; *s*, strong; *ms*, medium strong; *m*, medium; *w*, weak; *mw*, medium weak; *vw*, very weak.

λ in Å	ν in cm.^{-1}	Int. visual estimation	Separation from (0, 0) <i>i.e.</i> , 34793 cm.^{-1}	Assignment
2901.5	34454	<i>w</i>	— 339	0—223—121
2892.0	34568	<i>w</i>	— 225	0—223*
2888.4	34611	<i>w</i>	— 182	0—177*
2885.6	34644	<i>w</i>	— 149	0—146*
2883.6	34668	<i>w</i>	— 125	0—121*
2881.9	34689	<i>w</i>	— 104	
2878.1	34734	<i>vw</i>	— 59	
2873.3	34793	<i>vs</i>	0	(0, 0)
2855.3	35012	<i>w</i>	219	
2846.0	35126	<i>w</i>	333	
2838.4	35220	<i>w</i>	433	
2833.2	35285	<i>s</i>	492	0+492
2827.8	35352	<i>w</i>	559	
2823.7	35404	<i>s</i>	611	0+611
2815.0	35513	<i>s</i>	720	0+720
2805.1	35638	<i>s</i>	845	0+845
2795.7	35758	<i>s</i>	965	0+965
2790.7	35809	<i>s</i>	1016	0+1016
2780.9	25948	<i>s</i>	1155	0+1155
2767.5	36123	<i>m</i>	1330	0+845+492
2757.1	36259	<i>m</i>	1466	0+965+492
2748.2	36376	<i>m</i>	1583	0+965+611
2742.6	36450	<i>m</i>	1657	0+1155+492
2740.9	36473	<i>m</i>	1680	0+965+720
2734.9	36553	<i>ms</i>	1760	0+1155+611
2730.9	36607	<i>ms</i>	1814	0+965+845
2726.0	36672	<i>ms</i>	1879	0+1155+720
2722.6	36718	<i>ms</i>	1925	0+965+965
2714.5	36828	<i>ms</i>	2035	0+2×1016
2709.0	36903	<i>ms</i>	2110	0+965+1155
2705.0	36957	<i>ms</i>	2164	0+1016+1155
2694.7	37098	<i>ms</i>	2305	0+2×1155
2669.3	37451	<i>ms</i>	2658	0+2×965+720
2660.7	37572	<i>w</i>	2779	0+2×965+845
2653.1	37680	<i>m</i>	2887	0+3×965
2647.3	37763	<i>w</i>	2970	0+845+965+1155
2642.4	37833	<i>w</i>	3040	0+3×1016
2639.7	37871	<i>w</i>	3078	0+2×965+1155
2613.5	38251	<i>w</i>	3458	0+3×1155
2603.0	38405	<i>w</i>	3612	0+3×965+720
2593.7	38543	<i>w</i>	3750	0+3×965+845

* Observed in Raman spectrum.

DISCUSSION AND ANALYSIS

Ortho-thiocresol

The strong band on the longer wavelength side at 2825 Å is taken as the (0, 0) band. The other strong bands at 2768 Å, 2750 Å and 2735 Å are separated from the (0, 0) band by 729, 957 and 1159 cm.⁻¹ respectively. Combinations and overtones of these frequencies are present as shown in the analysis. The excited state frequency 729 giving the strong band at 2768 Å is correlated with the medium strong Raman frequency of 795 cm.⁻¹ and the medium strong infra-red frequency 797 cm.⁻¹. The frequency near about 957 cm.⁻¹ is a frequency which is observed to be present in practically all the *ortho*-disubstituted molecules as shown in Table III. This frequency is correlated with the very strong Raman frequency 1047 cm.⁻¹ and the corresponding strong infra-red frequency 1046 cm.⁻¹. The spectrum of *ortho*-thiocresol is similar to that of *ortho*-cresol^{5, 6} and *ortho*-xylene.³ The excited state frequency 957 cm.⁻¹ in *ortho*-thiocresol, 944 cm.⁻¹ in *ortho*-cresol, 939 cm.⁻¹ in *ortho*-xylene, 957 cm.⁻¹ in *ortho*-dichloro-benzene⁸ perhaps involve similar modes of vibration. The third progression forming frequency is 1159 cm.⁻¹. This frequency is correlated with the medium strong Raman frequency 1209 cm.⁻¹ and the medium strong infra-red frequency 1217 cm.⁻¹. This may be tentatively assigned to the C—CH₃ stretching vibration. In addition to these fundamental vibration frequencies, there are bands separated by 60, 120, 158 and 203 cm.⁻¹ respectively from the progression forming frequencies. These bands may be assigned as due to *v-v* transitions. On comparing the shift of the (0, 0) band in the case of *ortho*-disubstituted molecules studied so far it is found that it is the largest in *ortho*-thiocresol.

Meta-thiocresol

It is observed that the *meta*-thiocresol bands are in general very diffuse. This has also been observed in case of the *meta*-cresol⁵ and *meta*-xylene bands.³ Spomer and Cooper put down the causes of diffuseness as (i) due to overlapping transitions, (ii) due to overlapping of the gross and fine structure of bands, and (iii) due to internal rotation of the CH₃ group. The first two of these are in general applicable to other substituted benzene molecules also. In case of *meta*-thiocresol the bands are very diffuse and the *v-v* transitions are overlapping to such an extent that it was difficult to measure the wavelengths of the bands due to *v-v*-transitions on account of the very low intensity of all the bands in the spectrum and specially extremely low intensity of the bands due to *v-v*-transitions. As such the analysis for the prominent bands only is given in Table II.

The band at 34793 cm.^{-1} , the strongest band in the absorption spectrum on the longer wavelength side, is taken as the (0, 0) band. The frequencies 492, 611, 720, 845, 965, 1016 and 1155 cm.^{-1} involved in the strong bands at 35285, 35404, 35513, 35638, 35758, 35809 and 35948 cm.^{-1} are taken as fundamental vibrational frequencies of the molecule in the electronically excited state in the analysis of the absorption spectrum of *meta*-thiocresol.

The frequency 492 cm.^{-1} may be correlated with the frequency 523 cm.^{-1} with medium intensity in the Raman spectrum. The frequency 611 cm.^{-1} can be correlated with the medium strong intensity frequency 685 cm.^{-1} observed in the Raman effect and the strong frequency 686 cm.^{-1} observed in the infra-red spectrum. The frequency 720 cm.^{-1} is correlated with the very strong frequency 772 cm.^{-1} observed in the infra-red spectrum. The frequency 845 cm.^{-1} is correlated with the strong frequency 853 cm.^{-1} in the infra-red and 855 cm.^{-1} in the Raman spectrum.

The excited state frequency 965 cm.^{-1} is correlated with the very strong Raman ground state frequency 1001 and 982 cm.^{-1} in the infra-red. This frequency appears in combination with all the other excited state frequencies. This frequency appears in the excited state in case of *meta*-fluoro-toluene,² *meta*-cresol,⁵ *meta*-xylene,³ *meta*-fluoro-chloro-benzene,⁴ and *meta*-dichloro-benzene⁸ as shown in Table IV, and involves similar mode of vibration. This seems to be the characteristic excited state frequency present in all the *meta*-disubstituted benzenes.

The 1016 cm.^{-1} excited state frequency may possibly be correlated with the Raman frequency 1084 cm.^{-1} appearing with medium intensity and with 1083 cm.^{-1} appearing with medium strong intensity in the infra-red spectrum. A similar frequency 1031 cm.^{-1} in the excited state with the corresponding Raman line at 1086 cm.^{-1} is observed in case of *meta*-cresol also.⁵

The frequency 1155 cm.^{-1} may be correlated with 1218 cm.^{-1} having medium intensity in the infra-red and 1222 cm.^{-1} with medium strong intensity in the Raman spectrum. This is assigned to C—CH₃ stretching vibration. It is also observed that the shift of the (0, 0) band towards longer wavelength from the (0, 0) band of benzene is in the case of *meta*-thiocresol the largest of all *meta*-disubstituted benzenes.

It is also observed that the (0, 0) band shifts to the longer wavelength side as we go from *ortho*- to *meta*- and to *para*-thiocresol. The (0, 0) band in *ortho*-, *meta*- and *para*-thiocresols being at 35386 cm.^{-1} , 34793 cm.^{-1} and 34222 cm.^{-1} respectively. It has also been observed by Cave and Thompson that along the series *o*-, *m*-, *p*- for cresols or fluoro-toluenes the position of the (0, 0) transition moves towards lower frequencies.²

TABLE III
Table showing the comparison of the excited state frequencies in ortho-disubstituted benzenes

O-Dichloro- benzene ¹⁰	O-Dichloro- benzene ⁸	O-Fluoro- chloro- benzene ⁴	O-Xylene ³	O-Cresol ⁵	O-Chloro- toluene ⁶	O-Fluoro- toluene ²	O-Thio- cresol	(0, 0) band in cm. ⁻¹
36232	36230	37035	37308	36418	36838	37576	35386	
307	944 (1041 R)	477	507	124	368	707	729	
437	957 (1020 R)	513	692	202	460	924	957	
610	1089 (1129 R)	639	939	360	530	1230	1159	
958		794 (830 R)	1195	702	625			
1089		929 (1031 R)		719	680			
1486		1076 (1127 R)		944	813			
		1248 (1237 R)		955	915			
				1251	1005			
					1084			
					1192			
^{uv} 24	^{uv} 25 cm. ⁻¹	^{uv} 99 cm. ⁻¹	^{uv} 56	^{uv} 63			^{uv} 60	
59	60 cm. ⁻¹	274 cm. ⁻¹	60	73			120	
			72	97			158	
			76	115			203	
			126					

TABLE IV
Table showing comparison of excited state frequencies of meta-disubstituted benzenes

M-Dichloro- benzene ⁸	M-Fluoro- chloro- benzene ⁴	M-Xylene ³	M-Cresol ⁵	M-Chloro- toluene ⁹	M-Fluoro- toluene ²	M-Thio- cresol	(0, 0) band in cm. ⁻¹
36186	37027	36955	35985	36619	37398	34793	
960 (1000 R)	160 (245)	470	116	418	282	492	
	325 (410)	675	188	476	457	611	
1089 (1070 R)	455 (519)	735	251	612	684	720	
	636 (683)	965	469	711	965	845	
1103 (1126)	846 (883)	1145	696	778	1261	965	
	966 (1003)	1250	964	851		1016	
	1023 (1063)		1031	981		1155	
	1218 (1221)			1211			
<i>vv</i>			<i>vv</i>				
63			47				
70			82				
147 cm. ⁻¹			126				
			200				

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It is further observed that the intensities in the case of *ortho*-, *meta*- and *para*-thiocresols are in agreement with the observation by Sklar⁷ the ratios of these being approximately as 1:1:4.

The absorption spectra in case of thiocresols are in general of very low intensity as compared to those of cresols. This may be due to the effect of the substitution of the SH group in place of OH in cresols.

SUMMARY

The spectra of the *ortho*-, *meta*-, and *para*-thiocresols are similar to those of the respective cresols. Excited state frequencies in *ortho*- and *meta*-thiocresols have been discussed. The frequency near 1210 cm.^{-1} is assigned to C—CH₃ stretching vibration. In thiocresols SH is substituted in place of OH in cresols. This substitution of SH in place of OH causes the (0, 0) band to shift to the longer wavelength side as compared to the (0, 0) band in respective cresols and of all the disubstituted benzenes the (0, 0) band in case of *ortho*-, *meta*- and *para*-thiocresols is to the longest wavelength side.

Substitution of SH in place of OH has also a marked effect on the intensity of the bands in the spectra. This intensity in case of thiocresol bands is very much low as compared to the intensity in case of the respective cresols.

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