

SPECTROSCOPIC STUDIES OF THE CRESOLS

III. Emission and Absorption Spectra of meta-Cresol in the Near Ultra-violet Region*

BY P. RAMAKOTESWARA RAO**

(Department of Spectroscopy, Banaras Hindu University)

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PART A. THE EMISSION SPECTRUM

EXPERIMENTAL PROCEDURE

THE meta-cresol used in the investigations was the laboratory reagent variety of the B.D.H. Company. It was purified by distillation before use. The emission spectrum of meta-cresol was excited by means of an uncondensed transformer discharge through the flowing vapour of the substance. The discharge tube employed and the electrical arrangement used for exciting the spectrum are similar to those described elsewhere (Ramakoteswara Rao, 1962, Part I). Even by running the discharge under the controlled conditions described in the paper on ortho-cresol (Ramakoteswara Rao, 1962, Part II), it was not possible to get the 'pure' emission spectrum of meta-cresol, *i.e.*, without the simultaneous appearance of the CO third positive bands. This meant that even under the mild conditions of excitation employed, some meta-cresol molecules dissociated with the consequent formation and excitation of the CO molecules. Therefore, still milder conditions of excitation were tried. Under these conditions, the discharge was not continuous. The total time for which the discharge took place varied between fifty and seventy-five per cent. of the actual time of exposure. Secondly, a mercury diffusion pump was included in the evacuating arrangement so that the rate of flow of the vapour and the rate of clearance from the discharge tube of the dissociation products were more rapid. Still, the CO bands persistently appeared on the spectrograms. Since only one CO band, the one at 2833.1 \AA , appeared in the region of the meta-cresol

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** Present address: Analytical Division, Atomic Energy Establishment, Trombay, Bombay, India.

emission bands, no further attempts were made to get the emission spectrum of meta-cresol free from all traces of CO bands. The voltage applied between the electrodes of the discharge tube varied between 1800 and 2050 volts. When the discharge was taking place, a feeble white glow could be seen in the discharge tube if there was complete darkness around it.

The emission spectrum of meta-cresol was recorded on the Hilger medium quartz (E_2) spectrograph. Kodak III-0 plates were used to photograph the spectrum and exposure times varied from eight to about thirty hours.

RESULTS

The emission spectrum of meta-cresol consists of fifteen bands in the region 2750–2920 Å, superposed over a continuum beginning at about 2770 Å and extending to beyond 3100 Å. The continuum has its intensity maximum at about 2960 Å and fades away towards both ends, the fading towards the long wavelength side being more gradual. The bands are, in general, diffuse. A typical emission spectrum of meta-cresol is shown in Fig. 1.

The spectrograms are measured on a Hilger comparator having a least count of 0.001 mm. The wavelength data presented in Table I are the averages of nine measurements on three spectrograms. The intensity of many of the bands does not differ much from that of the continuum over which they are superposed. The stronger bands are correct to within 8 cm^{-1} and the rest to about 15 cm^{-1} .

ANALYSIS AND DISCUSSION

A comparison of the emission spectrum with the near ultra-violet absorption spectrum of meta-cresol vapour, photographed on the same plate, has shown that the two are parts of the same band system. It is, therefore, clear that the carrier of the emission spectrum is the meta-cresol molecule.

It is assumed, as was done for the other two cresols, that the CH_3 and OH groups of meta-cresol 'behave' as single particles and that this near ultra-violet band system corresponds to the 2600 Å, ${}^1\text{B}_{2u} - {}^1\text{A}_{1g}$, system of benzene. It then follows that meta-cresol molecule has C_s symmetry and that the band system under discussion involves the transition ${}^1\text{A}' - {}^1\text{A}'$.

From a study of the absorption spectrum of meta-cresol vapour the zero-zero band was fixed at 35985 cm^{-1} (see Part B). Hence the band occurring in the emission spectrum of meta-cresol at 35983 cm^{-1} with medium strong intensity is taken as the zero-zero band.

A noteworthy feature in the emission spectrum of meta-cresol is the occurrence of two intense bands (more intense than the zero-zero band) on the short wavelength side of the zero-zero band. These two bands, which also occur with high intensity in the absorption spectrum of meta-cresol, are interpreted as due to transitions respectively from the 116 cm.^{-1} and 188 cm.^{-1} vibrational levels of the excited state of meta-cresol to the zero-vibrational level of its electronic ground state. The high intensity of these bands is to be understood in terms of the Franck-Condon principle and the change in equilibrium distances on electronic excitation, between atoms predominantly involved in the 116 cm.^{-1} and 188 cm.^{-1} excited state vibrations. The only other band to the short wavelength side of the zero-zero band is 251 cm.^{-1} away from it. This frequency difference is also suggested as an excited state vibrational frequency.

The medium intensity bands at 35248 cm.^{-1} and 34980 cm.^{-1} are separated from the zero-zero band by 735 and 1003 cm.^{-1} respectively. These frequency differences are taken as frequencies of fundamental vibrations in the ground state of the molecule. The Raman spectrum of meta-cresol (Herz, 1943) shows two strongly polarized lines of outstanding intensity at 734 cm.^{-1} and 1000 cm.^{-1} . It is obvious that the suggested ground state frequencies correspond to those involved in the above two Raman lines. Higher quanta of these frequencies are not observed in the emission spectrum.

The 1003 cm.^{-1} vibration of meta-cresol is interpreted as the carbon ring 'breathing vibration' corresponding to the 992 cm.^{-1} vibration of benzene. The 998 cm.^{-1} vibration of meta-xylene, which obviously involves the same vibrational mode as the 1003 cm.^{-1} vibration of meta-cresol, has been similarly interpreted by Pitzer and Scott (1943) and Singh (1956).

The 724 cm.^{-1} vibration of meta-xylene (Pitzer and Scott, 1943 and Singh, 1956), the 745 cm.^{-1} vibration of meta-dihydroxybenzene (Beck, 1950) and the 735 cm.^{-1} vibration of meta-cresol seem very likely to involve similar modes of vibration. Pitzer and Scott (1943) assign the 724 cm.^{-1} frequency of meta-xylene to the C-C-C parallel bending vibration corresponding to the b_{1u} 1011 cm.^{-1} vibration of benzene. Singh (1956), however, assigns it to the C-CH₃ valence vibration. Beck (1950) ascribes the 745 cm.^{-1} vibration of meta-dihydroxybenzene to the C-OH valence vibration. From the fact that these vibrations appear but with slightly different values in three different substituted benzene molecules, it appears that they are more likely to be associated with the carbon-ring vibrations rather than the carbon-substituent vibrations.

The 204 cm.^{-1} frequency involved in the weak band at 35779 cm.^{-1} is also suggested as a ground state vibrational frequency. This has also been observed in the absorption spectrum. This frequency is correlated with the depolarized Raman line at 215 cm.^{-1} . The weak band at 35579 cm.^{-1} separated from the zero-zero band by 404 cm.^{-1} may also involve a ground state vibration. In the absorption spectrum of meta-cresol a weak band occurs at 398 cm.^{-1} on the red side of the zero-zero band. The mean of these two values, namely, 401 cm.^{-1} is suggested as a possible ground state frequency. This frequency does not have support from the Raman spectrum.

The -85 cm.^{-1} and 54 cm.^{-1} frequencies appearing in the weak bands at 35898 and 36037 cm.^{-1} are difference frequencies involving $\nu - \nu$ and $\nu - \nu'$ transitions. These will be referred to in Part B.

The vibrational analysis of the emission spectrum of meta-cresol is presented in Table I.

TABLE I
Emission spectrum of meta-cresol

Wave-length Å	Wave-number cm.^{-1}	Intensity	Separation from 0-0 band	Assignment
2758.5	36241	2 <i>d</i>	258	0+251
63.5	175	8 <i>d</i>	192	0+188
69.2	101	9	118	0+116
74.1	037	2 <i>d</i>	54	0+54
78.3	35983	6	0	0-0
84.9	898	2	- 85	0-82
94.1	779	3	- 204	0-204
2809.8	579	3	- 404	0-401
15.7	505	2	- 478	0-401-82
36.2	248	5	- 735	0-735
42.8	166	4 <i>d</i>	- 817	0-735-82
48.9	091	4 <i>d</i>	- 892	0-735-2×82
57.9	34980	4 <i>d</i>	-1003	0-1003
98.3	493	5	-1490	
2919.5	242	3 <i>d</i>	-1741	0-735-1003

d, diffuse.

The origin of the continuous emission spectrum occurring in the region of the discrete bands and beyond has not been investigated.

PART B. ABSORPTION SPECTRUM

The absorption spectrum of meta-cresol vapour was investigated in the temperature range 0° – 32° C. using absorption cells of lengths 100, 150, 200 and 250 cm. The experimental details are similar to those given elsewhere (Ramakoteswara Rao, 1962, Part I). The absorption spectrum was photographed on the Hilger large quartz (E_1) spectrograph (dispersion 3.5 \AA/mm. at 2700 \AA) Kodak B-4 and B-20 plates were employed to photograph the spectrum and exposure times ranged between half an hour and forty-five hours.

RESULTS

The absorption spectrum of meta-cresol, recorded under the above-mentioned experimental conditions consists of about fifty-five bands in the region 2580 – 2810 \AA . On spectrograms corresponding to smaller cell lengths and lower temperatures, two band groups, headed on their short wavelength sides by the bands at 36173 cm.^{-1} and 37139 cm.^{-1} , can be recognized. The longer wavelength band group, namely, the one headed by the band at 36173 cm.^{-1} is the more prominent one. On spectrograms corresponding to longer absorption paths, both the band groups expand on either side resulting in a number of discrete absorption bands. In the spectrogram corresponding to 250 cm. absorption path and 30° C. temperature, there is total absorption in the region 2580 – 2810 \AA and beyond.

The absorption bands of meta-cresol can be classified regarding their appearance, into four broad categories. There are bands which are diffuse and exhibit on closer examination a degradation towards the long wavelength side. Over fifty per cent. of the total bands come under this category. There are eight to ten bands which are diffuse and very broad, the width of an individual band being 15 cm.^{-1} or more. Then there are bands which are narrow and line-like and those which show a sharp degradation towards the long wavelength side. About half a dozen bands come under each of these two categories. A typical absorption spectrum of meta-cresol vapour is reproduced in Fig. 2.

The wavelengths of the absorption bands are given in Table II. They are the average results of eight measurements made on four spectrograms. The stronger and sharper bands are correct to 5 cm.^{-1} and the rest to 12 cm.^{-1}

TABLE II
Absorption spectrum of meta-cresol

Wave-length Å	Wave-number cm. ⁻¹	Intensity	Separation from 0-0 band	Assignment
2809·2	35587	2	— 398	0—401
03·6	658	2 <i>d</i>	— 327	0—4×82
2799·4	711	3 <i>d</i>	— 274	0—200—82
97·4	737	4	— 248	0—248; 0—3×82
93·6	785	5	— 200	0—200
90·8	821	4	— 164	0—2×82
87·9	859	5	— 126	0—126
84·4	903	6	— 82	0—82
81·8	938	6	— 47	0—47
78·1	985	9	0	0—0
74·7	36029	9	44	0+44
73·6*	043	9 <i>b</i>	58	0+58
69·2	101	10	116	0+116
67·1	128	6	143	0+188—47
63·7	173	10 <i>b</i>	188	0+188
58·9	236	6	251	0+251
54·5	294	5	309	0+188+116; 0+469—2×82
52·0	326	2	341	0+469—126
49·9	354	2	369	0+696—4×82
47·9	381	2	396	0+469—82
45·5	412	4	427	
42·4	454	5	469	0+469
40·1	484	2	499	0+696—200
2737·4	36520	4	535	0+696—2×82
34·5	559	2	574	0+469+116; 0+696—126
31·3	602	4	617	0+696—82
28·1	645	4 <i>b</i>	660	0+469+188
25·4	681	9	696	0+696
17·1	793	6	808	0+696+116; 0+964—2×82
14·7	826	4	841	0+964—126
11·8	865	6 <i>d</i>	880	0+696+188; 0+964—82
05·6	949	8 <i>b</i>	964	0+964
00·7	37016	8 <i>b</i>	1031	0+1031
2697·4	062	8 <i>d</i>	1077	0+964+116; 0+964+188—82

TABLE II—(Contd.)

Wave-length Å	Wave-number cm. ⁻¹	Intensity	Separation from 0-0 band	Assignment
96.2	079	6	1094	0+1031+58
91.8	139	8 <i>d</i>	1154	0+964+188; 0+1031+116; 0+696+469
87.0	205	5 <i>b</i>	1220	0+964+251; 0+1031+188; 0+2×696-2×82
82.2	272	4	1287	0+1031+251; 0+696+469 +116
81.0	289	5	1304	0+2×696-82
74.7	376	5	1391	0+2×696
71.4	422	4 <i>d</i>	1437	0+964+469
67.1	483	6	1498	0+1031+469
59.5	590	5 <i>d</i>	1605	
55.4	648	6	1663	0+964+696
51.2	708	5 <i>d</i>	1723	0+1031+696
47.5	760	5 <i>d</i>	1775	0+964+696+116
2643.0	37825	5 <i>d</i>	1840	0+964+696+188; 0+1031 +696+116; 0+2×964 -82
37.1	909	4	1924	0+2×964; 0+1031+696 +188
32.0	983	3 <i>d</i>	1998	0+1031+964; 0+3×696 -82
28.9	38027	3 <i>d</i>	2042	0+2×964+116
25.3	080	3 <i>d</i>	2095	0+3×696
07.2	344	3 <i>d</i>	2359	0+2×696+964
2599.7	454	3 <i>d</i>	2469	0+1031+964+469
89.2	610	4	2625	0+2×964+696
85.1	672	1	2687	0+1031+964+696
82.8	706	1	2721	

b, broad. *d*, diffuse.

ANALYSIS AND DISCUSSION

The band at 35985 cm.⁻¹, one of the strongest bands in the absorption spectrum, is taken as the zero-zero band. The band is sharp and degraded towards the red.

The vibrational analysis presented in this section (*see* Table II) assumes seven excited state vibrational frequencies 116, 188, 251, 469, 696, 964 and 1031 cm^{-1} , three ground state frequencies 200, 248 and 401 cm^{-1} and five difference frequencies 44, 58, -47 , -82 and -126 cm^{-1} . One of the ground state frequencies proposed here, namely, the 248 cm^{-1} frequency, is not observed in the emission spectrum.

The bands involving the 116 cm^{-1} and 188 cm^{-1} excited state frequencies appear very prominently in both the absorption and the emission spectra of meta-cresol. In emission spectrum they are more intense than the zero-zero band. These frequencies appear in combination with all the other excited state frequencies. The 116 cm^{-1} and 188 cm^{-1} excited state frequencies are correlated with the 200 cm^{-1} (Raman effect 215 cm^{-1}) and 248 cm^{-1} (Raman effect 243 cm^{-1}) ground state frequencies respectively.

The 696 cm^{-1} and 964 cm^{-1} frequencies involve two very intense bands in the absorption spectrum of meta-cresol. They form progressions of three and two members respectively and occur in combination with all the other excited state frequencies and with many difference frequencies. Cave and Thompson (1950) and Sreeramamurty (1951) also reported these excited state frequencies from their analysis of the absorption spectrum of meta-cresol. The 696 cm^{-1} and 964 cm^{-1} excited state frequencies are correlated with the 735 cm^{-1} and 1003 cm^{-1} ground state frequencies observed in the emission spectrum.

Some correlations have been suggested between the remaining excited state frequencies and some ground state frequencies observed in the Raman spectrum (*see* Table III). Those ground state frequencies have not been observed in the emission spectrum.

The strong bands at 36029 cm^{-1} separated from the zero-zero band by 44 and 58 cm^{-1} respectively, are interpreted as involving $v - v'$ transitions.

The bands on the longer wavelength side of the zero-zero band and separated from it by -47 , -82 and -126 cm^{-1} can, as usual, be understood as resulting from 1-1 transitions, mostly involving non-totally symmetric vibrations. Of these, the -82 cm^{-1} frequency is the most prominent. Four multiples of this difference frequency appear superposed on the zero-zero band and its second and third multiples appear in association with a number of excited state frequencies. The 116 cm^{-1} excited state-frequency has been correlated above with the 200 cm^{-1} ground state frequency. It appears very likely that the -82 cm^{-1} difference frequency is due to 1-1 transition involving the 200 cm^{-1} ground state frequency. The occur-

TABLE III

Fundamental vibrational frequencies of meta-cresol molecule

Ground state frequencies in cm. ⁻¹		Excited state frequencies in cm. ⁻¹		
Raman effect (Herz, 1943)	Near u-v. emission spectrum. Present research	Near u-v. absorption spectrum		
		Present research	Sreeramamurthy Cave & Thompson (1951)	Thompson (1950)
215	200*	116*		
243	248†	188*	183	
			199	
303		251*		
	401*			423
518 } 540 }		469		
734	735	696	696	693
			808	
			950	
1000	1003	964	962	963
1086		1031		
			1150	
				1199
			1219	

* These frequencies are observed both in the absorption and emission spectra.

† This frequency is observed only in the absorption spectrum.

rence of higher multiples of the — 82 cm.⁻¹ difference frequency can be understood in view of the low value of the ground state vibration with which it is associated.

The analysis of the absorption spectrum of meta-cresol is given in Table II. In cases where a band has more than one assignment, the various assignments have been arranged in the order of decreasing significance. It can be seen from Table II that, in the absorption spectrum of meta-cresol, a fairly large number of transitions of the type $0 + \nu_i + \nu_j + \nu_k$ occur. Table III gives most of the fundamental vibrational frequencies of the ground and excited states of meta-cresol suggested so far.

A word may be said in the end about the diffuseness characteristic of the meta-cresol bands. The diffuseness is a characteristic of the bands of only meta-cresol and not so much of ortho and para-cresol. A similar situation is met with in the near ultra-violet band systems of the isomeric xylenes. Cooper and Spomer (1952) traced the diffuseness of meta-xylene bands to the following possible causes:

- (1) due to overlapping $\nu - \nu$ transitions;
- (2) due to the overlapping of gross and fine structures of band; and
- (3) due to internal rotation of the CH_3 group; the potential restricting such a rotation being only 500 cal./mole.

The first two in this list are of a general nature and apply not only to meta-xylene but also (may be to different extents) to other polyatomic molecules for example to ortho- and para-xylene and to other substituted benzene molecules. The third cause should effect the spectra of meta-xylene and para-xylene molecules to the same extent, since the potential hindering the rotation of the CH_3 group about the C-C bond in para-xylene is about the same as that in meta-xylene (Pitzer and Scott, 1943). Therefore it appears that there are other more important reasons responsible for the diffuseness of the bands in the spectra of meta-xylene and meta-cresol.

SUMMARY

Part A:—The emission spectrum of meta-cresol, obtained by means of a controlled transformer discharge through the flowing vapour, is recorded on the Hilger medium quartz (E_2) spectrograph. The emission spectrum consists of fifteen bands in the region 2750–2920 Å superposed over a continuum beginning at about 2770 Å and extending to beyond 3100 Å. The discrete emission spectrum is the counterpart of the near ultra-violet absorption spectrum of meta-cresol vapour (Part B). The electronic transition involved in the discrete band system is interpreted as ${}^1A' - {}^1A'$. A vibrational analysis of the band system is proposed in terms of the ground state vibrational frequencies 200, 401, 735 and 1003 cm^{-1} and the excited state frequencies 116, 188 and 251 cm^{-1} .

Part B:—The absorption spectrum of meta-cresol vapour, using absorption paths ranging from 100–250 cm. and temperatures from 0–30° C., is recorded on the Hilger large quartz (E_1) spectrograph. About fifty-five bands are obtained in the region 2580–2810 Å. A vibrational scheme for the band system is proposed in terms of the excited state vibrational frequencies 116, 188, 251, 469, 696, 964 and 1031 cm.^{-1} and the ground state frequencies 200, 248 and 401 cm.^{-1}

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EXPLANATION OF PLATES

PLATE XXIII

FIG. 1. Emission spectrum of meta-cresol photographed on Hilger medium quartz (E_2) spectrograph; exposure time 15 hours.

PLATE XXIV

FIG. 2. Absorption spectrum of meta-cresol obtained with 100 cm. absorption path at 30° C. Spectrogram taken on Hilger large quartz (E_1) spectrograph; exposure time 10 hours.

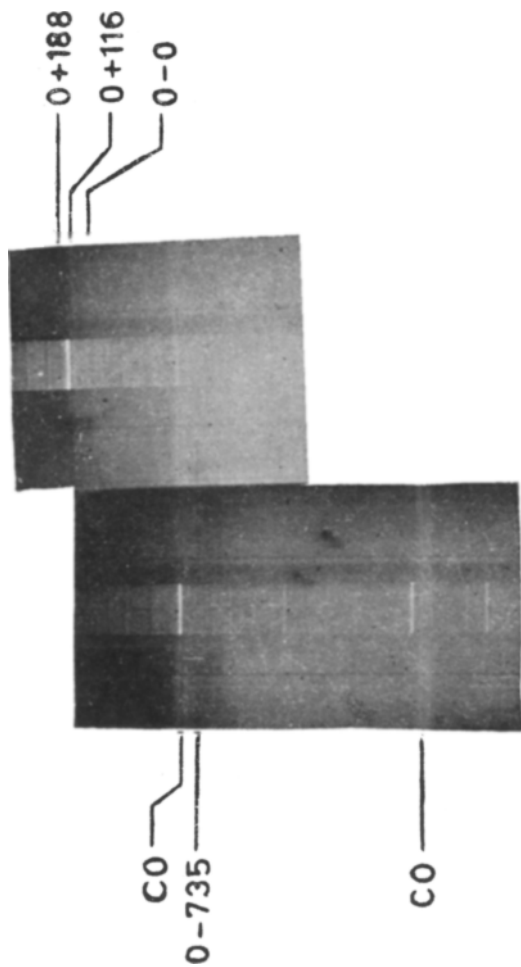


FIG. 1

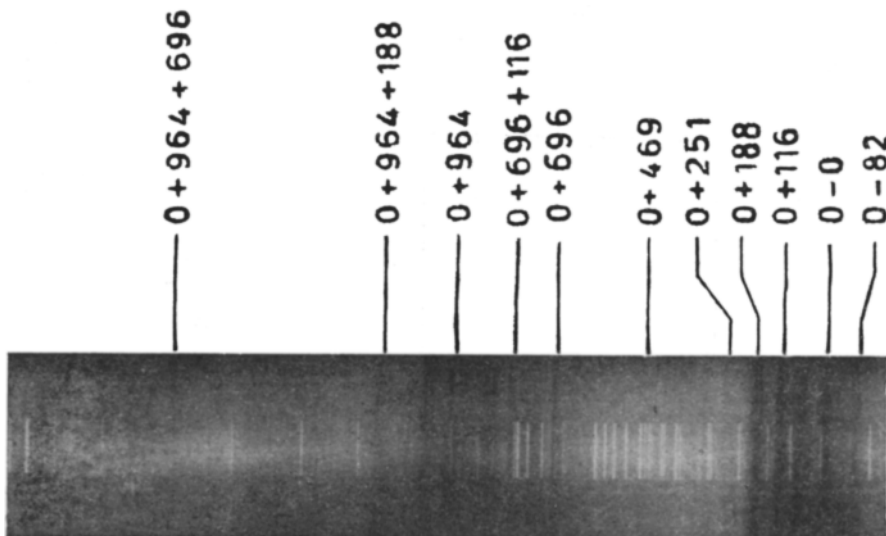


FIG. 2