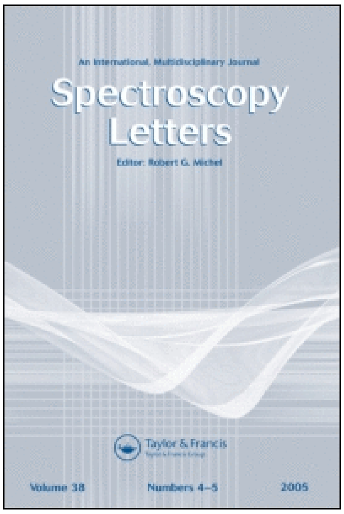

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ELECTRONIC ABSORPTION SPECTRUM OF MESITYLENE VAPOUR

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ABSTRACT

The electronic absorption spectrum of mesitylene vapour has been photographed on a Q-24 Medium Quartz Spectrograph. The molecule belongs to D_{3h} symmetry and the transition is $A_1' \rightarrow A_2'$ which is forbidden and due to that the (0,0) band does not appear in the spectrum. The position of (0,0) band in this case has been fixed at 36562 cm^{-1} with the help of $0 \rightarrow 1$ and $1 \rightarrow 0$ transitions. There are 66 bands and most of them are assigned in terms of two ground state frequencies of magnitudes 278 and 519 cm^{-1} and 7 excited state frequencies of magnitudes 267, 436, 554, 968, 1268, 1386 and 1575 cm^{-1}.

INTRODUCTION

The ultraviolet absorption spectra of some trisubstituted methyl benzenes vapours were photographed and the analyses were done by Verma et al. (1). But it seems that the analysis presented there about mesitylene is not properly correct. The analysis does not always follow the permitted selection rules. Therefore it is worthwhile to again analyse the spectrum of mesitylene and the problem has been undertaken here. The related references and other details can be seen in reference (1).

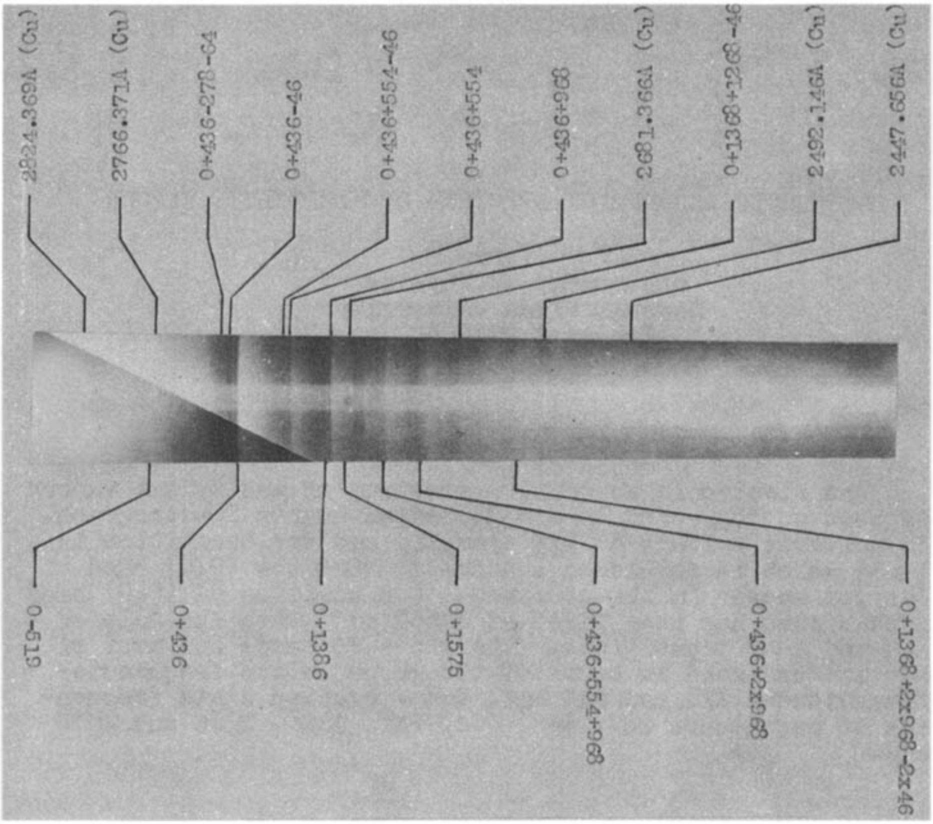

Fig. 1: Electronic Absorption Spectrum of Mesitylene Vapour.

EXPERIMENTAL

The electronic absorption spectrum of mesitylene has been photographed on a Q-24 Medium Quartz Spectrograph in the region 2400-2800 A. The sharp bands are observed at 30°C with the absorption path of 70 cm. The other details are exactly the same as mentioned in the previous paper. The spectrogram is shown in Fig. 1.

RESULTS AND DISCUSSION

We observed 66 bands and all bands are red degraded. Their wavelengths have been evaluated in the usual manner and converted to wavelengths in vacuum.

The frequencies of the observed bands alongwith their related intensities and proposed assignments are given in Table 1.

TABLE 1

Analysis of the Observed Bands in the Ultraviolet Absorption Spectrum of Mesitylene in Vapour Phase

Wavenumbers (cm^{-1})	Intensity	Separation from (0,0) Band	Assignments
35853	w	-709	0-519-3x64
35902	w	-660	0-519-3x46
35935	w	-627	0-519-46
35979	w	-583	0-519-64
36043	ew	-519	0-519
36562(calculated)		0	(0,0)

The molecule belongs to D_{3h} symmetry and the transition is $A_1' \rightarrow A_2'$. This transition is forbidden and due to this, the (0,0) band does not appear in vapour phase. But it does appear with moderate intensity in the liquid and solid phases of the molecule (2) at 36265 cm^{-1} and at 36326 cm^{-1} respectively. These observations however do not help in locating the (0,0) band in the vapour spectrum as

TABLE 1 (Contd.)

36653	w	91	0+436-278-64
36716	m	154	0+436-278
36764	m	202	0+267-64
36829	ms	267	0+267
36901	ms	339	0+436-2x46
36952	vs	390	0+436-46
36998	vvs	436	0+436
37287	w	725	
37367	m	805	0+2x407
37403	m	841	0+436+554-3x46
37459	s	897	0+436+554-2x46
37504	s	942	0+436+554-46
37552	vs	990	0+436+554
37779	w	1217	0+267+968
37814	m	1252	0+436+2x407
37856	m	1294	0+1386-2x46
37892	m	1330	0+1386-46
37919	s	1357	0+436+968-46
37948	s	1386	0+1386
37967	vs	1405	0+436+968
38137	m	1575	0+1575
38284	m	1722	0+436+554+2x407-2x46
38293	s	1731	0+436+1268
38351	s	1789	0+436+554+2x407
38392	m	1830	0+436+1386
38443	s	1881	0+436+554+968-64
38498	vs	1936	0+436+554+968
38698	w	2136	0+267+2x968-64

TABLE 1 (Contd.)

38810	m	2248	0+436+2x968-2x64
38868	s	2306	0+436+2x968-64
38931	vs	2369	0+436+2x968
39034	m	2472	0+436+2x554+968-46
39100	m	2538	0+1575+968
39172	s	2610	0+1386+1268-46
39221	s	2659	0+1386+1268
39263	s	2701	0+436+968+1268
39524	w	2962	0+1575+554+968-2x64
39584	w	3022	0+1575+554+968-64
39654	m	3092	0+1575+554+968
39691	m	3129	0+1386+554+1268-2x46
39753	s	3191	0+267+3x968
39802	m	3240	0+1386+2x968-2x46
39868	m	3306	0+1386+2x968
39942	w	3380	0+1575+2x968-2x64
40048	w	3486	0+1575+2x968-46
40129	m	3567	0+436+2x968+1268-64
40154	m	3592	0+436+2x968+1268-46
40196	w	3634	0+436+2x968+1268
40245	w	3683	
40289	m	3727	0+1386+2x1268-3x64
40346	m	3784	0+1386+1268-3x46
40575	w	4014	0+1575+2x1268-2x46
40612	w	4050	0+15752x1268-46
40655	m	4093	0+1386+3x968-3x64
40926	w	4346	0+1386+554+2x1268-46-64

TABLE 1 (Contd.)

40991	ew	4429	0+1386+2x1268+554-46
41039	ew	4477	0+1575+2x968+2x554-2x46
41077	ew	4515	0+1386+1268+2x968-64
41138	ew	4576	0+1575+2x968+2x554-46
41185	ew	4623	0+1575+2x968+2x554

N.B.: vvs=very very strong; vs=very strong; s=strong; ms=medium strong; m= medium; w=weak and ew=extremely weak.

the spectra in the condensed phases are generally shifted. The analysis of the corresponding transition in benzene also presented similar difficulty which was resolved by the observation that the transition becomes allowed due to the interaction of vibration of e_{2g} symmetry. The 0→1 and 1→0 bands involving this vibration frequency were detected on either side of the expected (0,0) band. The mutual separation between these two bands was found to the sum of the ground and excited magnitudes of e_{2g} mode of vibration. A similar procedure may be adopted to locate the (0,0) band in this case also. We have observed a strong band at 36998 cm^{-1} and a weak band at 36043 cm^{-1} and have taken these to correspond to 0→1 and 1→0 transition involving this particular vibration frequency which makes the transition allowed. The separation between these two bands is 955 cm^{-1} and should be equal to the sum of the bands in the ground and excited state magnitudes of some non-totally symmetric vibration of

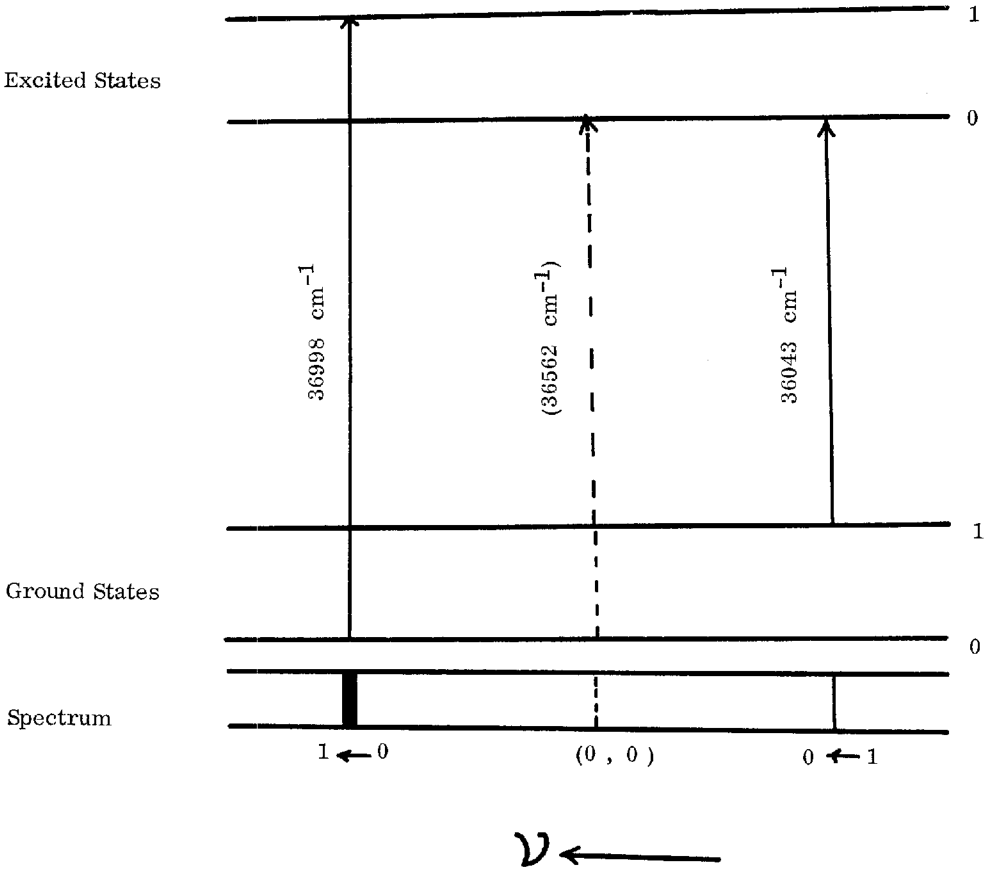

Fig. 2: Schematic Representation of Forbidden Vibronic Transition in Mesitylene.

this molecule. In the Raman spectrum of this molecule a depolarised line has been observed at 519 cm^{-1} and has been correlated with the 606 cm^{-1} (e_{2g}) mode of benzene. If this vibration is assumed to be responsible for the appearance of the transition, the missing (0,0) band is located at 36562 cm^{-1}. This is shown diagramatically in Fig. 2. The position of the (0,0) band has been reported at 36511 cm^{-1}

(3). The complete spectrum has been analysed in terms of two ground state frequencies 278 and 519 cm^{-1} and 7 excited state frequencies of magnitudes 267, 436, 554, 968, 1268, 1386 and 1575 cm^{-1} bands involving difference frequencies of 46 and 64 cm^{-1}.

It has already been mentioned that $A_1' \rightarrow A_2'$ is a forbidden transition for D_{3h} symmetry. Therefore, only vibrations of e' and a_1'' symmetry would appear strongly in the electronic transition. In the first case the total vibronic symmetry is $A_2'e'=E'$ and in the second case the total vibronic symmetry is $A_2'a_1''=A_2''$. Mesitylene, however, does not have any a_1'' vibration so that only vibrations of e' symmetry are expected to appear strongly in the electronic transition. The e_{2g} (606), e_{2g} (3046), e_{2g} (1596), e_{2g} (1178), e_{1u} (1033), e_{1u} (1485) and e_{1u} (3080) modes of benzene give rise to e' type vibrations in D_{3h} symmetry. One may expect a strong coupling of the electronic transition with the skeletal vibration and four frequencies: 278, 519, 1438 and 1611 cm^{-1} may render the transition allowed (Infrared and Raman data). The corresponding frequencies in the excited state are observed at 267, 436, 1386 and 1575 cm^{-1} in the absorption spectrum.

The vibrations corresponding to the a_{1g} (992), a_{1g} (3037), b_{1u} (1010) and b_{1u} (3060) modes of benzene have a symmetry a_1' in D_{3h} point group and as vibrations of a_1' symmetry can be excited only in combination with the e' vibrations so we do not expect these modes to occur singly in the absorption spectrum of mesitylene. Three a_1' type vibrations appear in combination with e' type vibrations in the absorption spectrum. These are the vibrations corresponding to the a_{1g} (992), b_{1u} (1010) of benzene modes and in phase C-CH_3 stretching mode. The magnitudes of these modes have been established in the excited state at 554, 968 and 1268 cm^{-1} respectively (4). The vibrations arising from e_{1g}(846), e_{2u} (404) and e_{2u} (967) modes of benzene give rise to e" type vibrations in D_{3h} symmetry. These vibrations are forbidden in the single quantum; but their second quanta may appear. Such a overtone of an e" vibration appears at 806 cm^{-1} (2x407=814). The ground state magnitude of this frequency is 453 cm^{-1} as observed in the infrared spectrum. This explains difference frequency of 46 cm^{-1} which appears rather often in the spectrum.

We observed a medium strong band at the separation of 267 cm^{-1} from the (0,0) band on the shorter wavelength side. This band corresponds to the C-CH_3 in-plane bending mode of e' symmetry. The ground state magnitude of this mode is at 278 cm^{-1}.

A very strong band is observed at 36998 cm^{-1}. We have already discussed that this refers to the 0→1 transition of the e' vibration which makes the transition allowed. The separation from the (0,0) band is 436 cm^{-1}. We have observed an extremely weak hot band at the separation of 519 cm^{-1}. This is the 1→0 band of the same vibration. These modes correspond to the 606 cm^{-1} mode of benzene in the excited and ground states respectively. These are assigned to C-C-C in-plane ring deformation mode.

TABLE 2

Observed Fundamental Frequencies in the Ultraviolet Absorption Spectrum and their Corresponding Mode in Infrared and Raman Spectra of Mesitylene

Ground State			Excited State
Infrared	Raman	U.V. Absorption	U.V.Absorption
278	275		267
453			407*
	519	519	436
	578		554*
	998		968*
	1255		1268*
	1438		1386
1601	1611		1575

* First quantum will not be observed.

Another strong band is observed at 37948 cm^{-1} at a separation of 1386 cm^{-1} from the (0,0) band. This corresponds to C-C ring stretching vibration corresponding to the 1485 cm^{-1} mode of benzene. The magnitude of this mode is 1438 cm^{-1} (Raman) in the ground state. Similarly another band of medium intensity is observed at a separation of 1575 cm^{-1} and has been assigned to a fundamental mode corresponding to the 1595 cm^{-1} mode of benzene. The magnitude of this mode is at 1611 cm^{-1} in the ground state.

All other bands observed in the spectrum could be satisfactorily explained in terms of the above fundamental frequencies in combination with difference frequencies corresponding to v-v transitions. The fundamental frequencies observed in the absorption spectrum and their magnitudes in the Raman and infrared spectra are compared in Table 2.

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