Vibrational Analysis of the 2400—2800 Å Bands of 1,2,3- and 1,3,5-Trimethylbenzenes in Vapour Phase

V.N. Verma, K.P.R. Nair, and D.K. Rai

Department of Spectroscopy, Faculty of Science, Banaras Hindu University, Varanasi-5, India

(Received October 13, 1970)

The near ultraviolet absorption spectra of 1,2,3- and 1,3,5-trimethylbenzenes have been photographed in vapour phase at different vapour pressures on a Q-24 Zeiss Medium Quartz Spectrograph. Assuming C_{2v} symmetry for the 1,2,3- and D_{3h} symmetry for the 1,3,5-isomer, tentative assignments of the observed bands have been made in terms of various ground state and excited state fundamentals. The respective vibrational modes have also been suggested.

The electronic spectrum of mono-methylbenzene (toluene) has been studied by many workers.[1-5] Price *et al.*[6] reported the vacuum ultraviolet absorption spectra of the three isomeric dimethylbenzene(xylenes) in vapour phase. Complete analysis of the electronic spectra in the near ultraviolet region for the three xylenes has been made by Cooper *et al.*[7,8] and also by Singh.[9-11] For trimethylbenzenes, however, the work done is very limited and further work is clearly needed.

The Raman spectrum of 1,3,5-trimethyl benzene has been studied[12,13] and the polarization measurements are reported. The infrared spectrum of this molecule has been studied[14] in the range 600—3100 cm^{-1} in vapour, liquid and in solutions. Sponer[15] and Sponer and Stallcup[16] photographed the ultraviolet absorption spectrum of 1,3,5-trimethylbenzene in vapour phase and located the forbidden (0,0) band and assigned some of the other bands. Sen[17] studied the electronic absorption spectrum of this molecule in the liquid and solid states and discussed the shift in the (0,0) band on change of phase. Sreeramamurty[18] studied the absorption spectrum of 1,2,4-trimethylbenzene in vapour phase and discussed the substituent effect of CH_3 group. The vibrational analysis of the electronic spectra of 1,2,3-trimethylbenzene has not yet been reported, though Kohlrausch and Pongratz[13] have reported its Raman spectrum. An investigation of the absorption spectra of 1,2,3- and 1,3,5-trimethylbenzenes has been undertaken here and a complete analysis of the observed bands is being proposed.

1) K. Masaki, This Bulletin, **11**, 346 (1936).
2) J. Savard, *Ann. de. Chim.*, **11**, 287 (1929).
3) N. Ginsberg, W. W. Robertson, and F. A. Matsen, *J. Chem. Phys.*, **14**, 511 (1946).
4) M. R. Padhye, *Indian J. Phys.*, **23**, 331 (1949).
5) H. Sponer, *J. Chem. Phys.*, **10**, 672 (1942).
6) W. C. Price, V. J. Hammond, J. P. Teegan, and A. D. Walsh, *Discuss. Faraday Soc.*, **9**, 53 (1950).
7) C. D. Cooper and H. Sponer, *J. Chem. Phys.*, **20**, 1248 (1952).
8) C. D. Cooper and M. L. N. Sastri, *ibid.*, **20**, 607 (1952).
9) I. S. Singh, *J. Sci. Res. Banaras Hindu University*, **7(2)**, 171 (1956—1957).
10) I. S. Singh, *ibid.*, **8(1)**, 19 (1957—1958).
11) I. S. Singh, *ibid.*, **8(1)**, 32 (1957—1958).
12) S. Venkateshwaran, *Phil. Mag.*, 17th Series **15**, 263 (1933).
13) K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, **65**, 13 (1934).
14) S. B. Banerjee and K. C. Medhi, *Indian J. Phys.*, **34**, 1 (1960).
15) H. Sponer, *Chem. Rev.*, **41**, 281 (1947).
16) H. Sponer and M. J. Stallcup, Contribution al'Elude de la Structure Moleculaire, Victor Henri Memorial Volume (Deseor, liege) (1948), p. 222.
17) S. K. Sen, *Indian J. Phys.*, **33**, 41 (1959).
18) K. Sreeramamurty, *Proc. Natl. Inst. of Sci., India*, **17**, 385 (1951).

Experimental

Pure samples of 1,2,3- and 1,3,5-trimethylbenzenes have been obtained from Koch-Light Laboratories and were used after redistillation under reduced pressure. The vapour absorption spectra were photographed on Q-24 Zeiss Medium Quartz Spectrograph. Absorption cells of various lengths were used. The temperature of the bulb attached to the middle of the tube and which acted as reservoir of experimental liquid was varied from -10 to 30°C. The source for continuous radiation from a Beckman hydrogen lamp was used. The bands were best developed with a cell of 75 cm and a bulb temperature at 25°C in the case of 1,2,3-isomer and with a cell of 70 cm and a bulb temperature of 30°C for the other isomer. They were recorded on Ilford N-40 plates with a slit width of 20 μ. Typical spectrograms are shown in Figs. 1 and 2. The spectra lie in the region 2400—2800 Å for both the isomers and the dispersion of the spectrograph in this region is about 9 Å/mm. The bands were measured on a Hilger L-76 comparator having a least count of 0.001 mm. The accuracy of measurement for the sharp bands is ± 5 cm^{-1} and for the diffuse bands is ± 10 cm^{-1}.

Results and Discussion

Nearly 56 bands for 1,2,3-isomer and 66 bands for 1,3,5-isomer have been observed. The bands are degraded towards the longer wavelength side. The frequencies of the observed bands along with their relative intensities and proposed assignments are given in Tables 1 and 2. The correlation of the observed fundamentals in the ultraviolet absorption spectra of 1,2,3- and 1,3,5-trimethylbenzenes with the corresponding Raman frequencies is given in Table 3. The prominent vibrational transitions are shown in Figs. 3 and 4 for 1,2,3- and 1,3,5-trimethylbenzenes respectively.

Under the usual approximation, *i.e.*, considering the CH_3 group as a mass-point, the six fold symmetry, D_{6h}, of benzene drops to C_{2v} for 1,2,3-isomer. The forbidden $A_{1g} \rightarrow B_{2u}$ transition of benzene therefore reduces to an allowed $A_1 \rightarrow B_2$ transition. On the other hand for 1,3,5-isomer remains as D_{3h} and the electronic transition is A'_1—A'_2. The transition therefore is still forbidden.

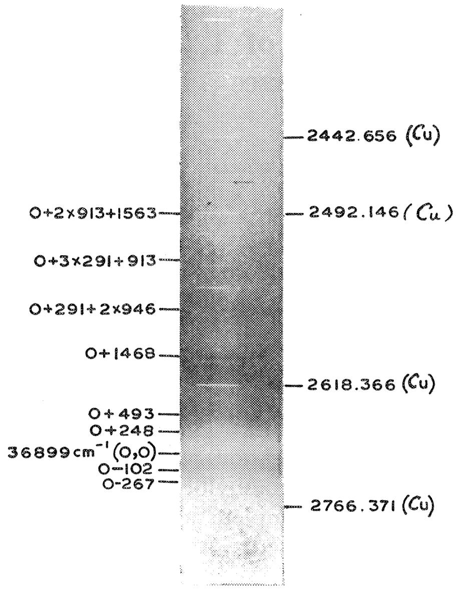

Fig. 1. Electronic absorption spectrum of 1,2,3-trimethylbenzene in vapour phase.

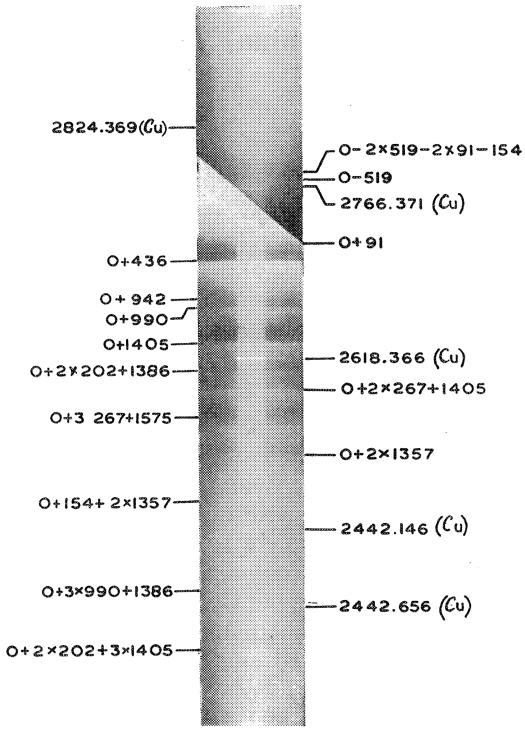

Fig. 2. Electronic absorption spectrum of 1,3,5-trimethylbenzene in vapour phase.

According to the Franck-Condon principle, if the internuclear distances in the ground and excited electronic states of the molecule are nearly the same, the (0,0) band of an allowed transition should either be most intense or one of the intense bands of the system. The strongest band at 36899 cm^{-1} appearing even at the lowest vapour pressure is assigned as the (0,0) band for 1,2,3-trimethylbenzene. The entire spectrum is analysed in terms of one ground state frequency of

TABLE 1. VIBRATIONAL ANALYSIS OF THE OBSERVED BANDS IN THE ULTRAVIOLET ABSORPTION SPECTRUM OF 1,2,3-TRIMETHYLBENZENE IN VAPOUR PHASE

Wave number (cm^{-1})	Intensity	Separation from (0,0) band	Assignment	Wave number (cm^{-1})	Intensity	Separation from (0,0) band	Assignment
36632	ew	267	0−267	38249	m	1350	0+1350
36686	ew	213	0−2×52−102	38272	m	1373	0+453+913
36726	w	173	0−69−102	38317	m	1418	0+2×248+913
36742	w	157	0−52−102	38367	s	1468	0+1468
36797	m	102	0−102	38408	m	1509	0+2×493+523
36830	s	669	0−69	38462	m	1563	0+1563
36847	vs	52	0−52	38500	m	1601	0+523+1530−267
36865	vs	34	0−34	38542	w	1643	0+2×913−34−2×69
36899	vvs	0	(0,0)	38581	w	1682	0+2×913−2×69
37147	w	248	0+248	38790	w	1891	0+2×946
37190	m	291	0+291	38861	w	1962	0+2×523+913
37233	m	334	0+453−52−69	38897	m	1998	0+913+1350−267
37285	m	386	0+453−69	38920	m	2021	0+453+3×523
37318	ms	419	0+453−34	38961	m	2062	0+2×248+2×523
37352	s	453	0+453	38998	m	2099	0+3×248+1350
37392	s	493	0+493	39038	m	2139	0+248+2×946
37422	m	523	0+523	39082	m	2183	0+291+2×946
37588	w	689	0+946−267	39184	w	2285	0+453+2×931
37645	m	746	0+746	39252	w	2353	0+523+2×913
37695	w	796	0+2×248+291	39531	w	2632	0+3×248+2×946
37733	m	834	0+834	39556	w	2657	0+3×248+453+1468
37777	m	878		39589	m	2690	0+3×291+913
37812	s	913	0+913;0+2×453	39647	m	2748	0+3×291+523+1350
37845	m	946	0+946	39682	m	2783	0+2×913+946
37895	w	996	0+2×493	39779	m	2880	0+2×493+2×946
37944	w	1045	0+291+3×248	40136	w	3237	0+248+291+2×1350
38143	w	1244	0+291+946	40190	w	3291	0+2×913+1468
38200	w	1301	0+1563−267	40289	ew	3390	0+2×913+1563

TABLE 2. VIBRATIONAL ANALYSIS OF THE OBSERVED BANDS IN THE ULTRAVIOLET ABSORPTION SPECTRUM OF 1,3,5-TRIMETHYLBENZENE IN VAPOUR PHASE

Wave number (cm^{-1})	Intensity	Separation from (0,0) band	Assignment	Wave number (cm^{-1})	Intensity	Separation from (0,0) band	Assignment
35853	w	709	0−2×519+2×91+154	38698	w	2136	0+2×436+1252
35902	w	660	0−2×519+390	38810	m	2248	0+2×436+1386
35935	w	627	0−519−583+202+267	38868	s	2306	0+942+1357
35979	w	583	0−583	38931	vs	2369	0+3×267+1575
36043	ew	519	0−519	39034	m	2472	0+154+436+2×942
36562	(Calculated)	0	(0,0)	39100	m	2538	0+2×814+1386−519
36653	w	91	0+91	39172	s	2610	0+91+3×841
36716	m	154	0+154	39221	s	2659	0+91+154+841+1575
36764	m	202	0+202	39263	s	2701	0+2×1357
36829	ms	267	0+267	39524	w	2962	0+1386+1575
36901	ms	339	0+2×91+154	39584	w	3022	0+202+3×942
36952	vs	390	0+390	39654	m	3092	0+2×841+1405
36998	vvs	436	0+436	39691	m	3129	0+2×942+1252
37287	w	725	0+725	39753	s	3191	0+91+154+436+2×1252
37367	m	805	0+91+267+436	39802	m	3240	0+267+3×990
37403	m	841	0+841	39868	m	3306	0+154+1357
37459	s	897	0+990+436−519	39942	w	3380	0+2×990+1405
37504	s	942	0+942	40048	w	3486	0+990+3×1252
37552	vs	990	0+990	40129	m	3567	0+841+2×1357
37779	w	1217	0+267+942	40154	m	3592	0+436+2×1575
37814	m	1252	0+1252	40196	w	3634	0+2×435+2×1386
37856	m	1294	0+2×91+267+841	40245	w	3683	0+2×267+2×1575
37892	m	1330	0+267+1575−519	40289	m	3727	0+2×91+841+2×1357
37919	s	1357	0+1357	40346	m	3784	0+3×841+1252
37948	s	1386	0+1386	40576	w	4014	0+2×436+1575
37967	vs	1405	0+1405	40612	w	4050	0+1252+2×1405
38137	m	1575	0+1575	40655	m	4093	0+3×841+1575
38284	m	1722	0+2×154+1405	40926	w	4364	0+3×990+1386
38293	s	1731	0+3×391+202+1252	40991	ew	4429	0+942+3×1357−583
38351	s	1789	0+2×202+1386	41039	ew	4477	0+2×154+3×1386
38392	m	1830	0+436+1386	41077	ew	4515	0+436+3×1357
38443	s	1881	0+2×942	41138	ew	4576	0+436+990+2×1575
38498	vs	1936	0+2×267+1405	41185	ew	4623	0+2×202+3×1405

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

magnitude 267 cm^{-1} and 12 excited state frequencies of the magnitudes 248, 291, 453, 493, 523, 746, 834, 913, 946, 1350, 1468, and 1563 cm^{-1}. Difference bands at the separation of 34, 52, 69, and 102 cm^{-1} are observed on the longer wavelength side of the (0,0) band.

In the spectrum of the 1,3,5-isomer, because of the forbidden nature of the transition, the (0,0) band is not observed in the vapour phase. The (0,0) band appears with moderate intensity in the liquid and solid phase[17] at 36265 and 36326 cm^{-1} respectively, however, because of the expected shift in its position due to the intermolecular interactions, this by itself does not help in the location of the (0,0) band. A similar situation arises in the corresponding transition of benzene. It has been suggested that in benzene the transition becomes allowed due to interaction of a vibration of e_{1g} symmetry. In such a case bands would be observed on either side of the (0,0) band whose mutual separation would be the sum of the ground and excited state magnitudes of this vibration. A similar method can be used for the location of the (0,0) band in 1,3,5-trimethylbenzene also. We observed a strong band at 36998 cm^{-1} and a weak band at 36043 cm^{-1} and have taken these to correspond to $0\rightarrow1$ and $1\rightarrow0$ transitions involving this particular frequency making the transition allowed. In the Raman spectrum of 1,3,5-trimethylbenzene a depolarized line has been observed at 519 cm^{-1} and has been correlated to the 606 $cm^{-1}(e_{1g})$ in benzene. Taking this to be the frequency responsible for the appearance of the transition we can locate the missing (0,0) band at 36562 cm^{-1} (36043+519). A similar discussion by Sponer and Stallcup[16] leads to the estimated location of the (0,0) band at 36557 cm^{-1}. The entire spectrum is analysed in terms of two ground state frequencies of magnitudes 519 and 583 cm^{-1} and 12 excited state frequencies of magnitudes 267, 390, 436, 725, 841, 942, 990, 1252, 1357, 1386, 1405, and 1575 cm^{-1}. Bands are also observed at separation of 91, 154, and 202 cm^{-1} in the lower wavelength side of the main band and are assigned as due to $v'-v''$ transition.

In *o*-, *m*-, and *p*-xylenes the frequencies 720, 724, and 740 cm^{-1} respectively are assigned to the C–CH_3 stretch-

TABLE 3. CORRELATION OF THE FUNDAMENTALS OF 1,2,3- AND 1,3,5-TRIMETHYLBENZENES OBSERVED IN THE ULTRAVIOLET ABSORPTION SPECTRUM WITH THEIR RAMAN FUNDAMENTALS

1,2,3-Trimethylbenzene	UV Absorption		1,3,5-Trimethylbenzene	UV Absorption	
Raman[13]	Ground	Excited	Raman[12]	Ground	Excited
228			233		
269	267	269	275		267
318			519	519	
484		453	578	583	
509		493	847		841
536		523	976		942
654			998		990
744		746	1036		
810			1255		1255
888		834	1301		
990		946	1380		1357
1163					
1240			1611		1575
1377		1350			
1468		1468			
1589		1553			

ing vibration in the ground state.[19] Sreeramamurty[18] assigned this mode at 711 cm^{-1} in 1,2,4-trimethylbenzene. In the present study this mode is assigned at 746 cm^{-1} and 725 cm^{-1} for 1,2,3- and 1,3,5-isomers respectively.

There is a great controversy in the assignment of ring breathing mode arising from 992 cm^{-1} (a_{1g}) mode of benzene for the substituted benzenes. It is observed in many cases that the value of this mode usually decreases as the number of substituents increases. The frequencies of magnitude 834 and 841 cm^{-1} observed in the observed bands at 37733 cm^{-1} and at 37403 cm^{-1} for 1,2,3- and 1,3,5-isomers respectively have been assigned to this mode.

There is a band observed at 37422 cm^{-1} with medium intensity for the 1,2,3-isomer involving a separation of 523 cm^{-1} from (0,0) band. This is taken as an excited state fundamental. The Raman data show a band at 536 cm^{-1}. The corresponding frequency in 1,3,5-trimethylbenzene is observed at 36043 cm^{-1}. This mode of vibration has been identified as one of the components of the 606 cm^{-1} (e_{1g}) mode of benzene.

The band at 37814 cm^{-1} having separation of 1252 cm^{-1} from the (0,0) band is observed with medium intensity and can be correlated with the strong and polarized Raman line observed at 1255 cm^{-1} for 1,3,5-trimethylbenzene. In analogy with toluene,[3] this mode is identified as the a_1 part of the degenerate (e_{1g}) benzene vibration 3047 cm^{-1}. No such band is observed for 1,2,3-trimethylbenzene.

The medium strong band observed at 38249 cm^{-1} at a separation of 1350 cm^{-1} can be correlated with a band observed at 1377 cm^{-1} in the Raman spectrum of 1,2,3-isomer. Similarly a strong band at 37919 cm^{-1} at a separation of 1357 cm^{-1} can be correlated with 1380 cm^{-1} in Raman spectrum of 1,3,5-trimethylbenzene. In methyl substituted benzenes a strong Raman line always appears at about 1375 cm^{-1} which has been assigned to the C–H in-plane bending vibration in methyl groups. Similarly, the bands at 38367 cm^{-1} *i.e.* at the separation of 1468 cm^{-1} from the zero band for 1,2,3-isomer and at 37967 cm^{-1} *i.e.* at the separation of 1405 cm^{-1} for 1,3,5-trimethylbenzene are assigned to C–H out-of-plane (asymmetric) bending mode in the methyl group.

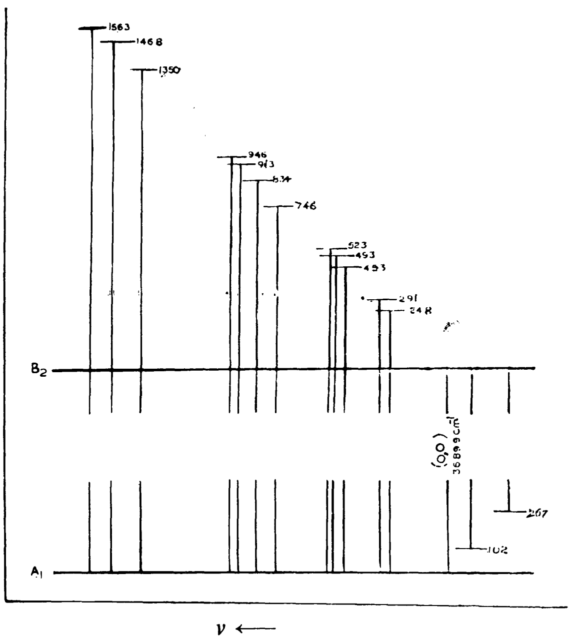

Fig. 3. Prominent vibrational transitions in the UV absorption spectrum of 1,2,3-trimethylbenzene in vapour phase.

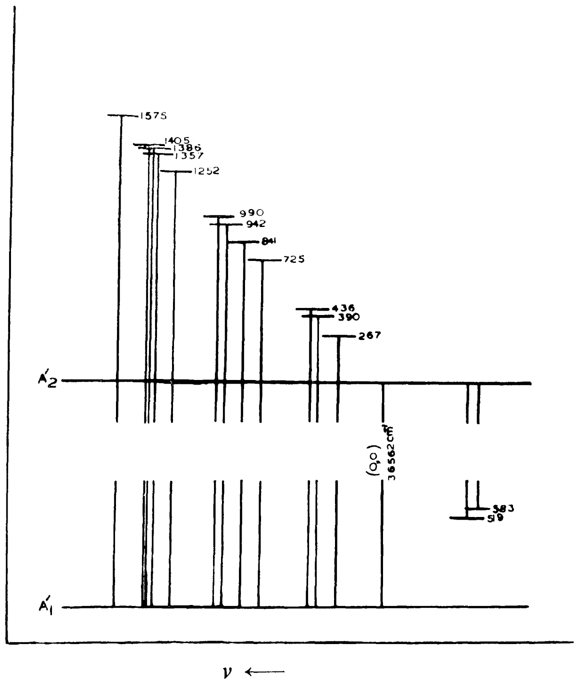

Fig. 4. Prominent vibrational transitions in the UV absorption spectrum of 1,3,5-trimethylbenzene in vapour phase.

19) K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, **65**, 803 (1943).

The medium strong band observed at 38462 cm^{-1} at a separation of 1563 cm^{-1} from the zero band for 1,2,3-trimethylbenzene on the lower wavelength side can be correlated with 1589 cm^{-1} reported in Raman spectrum. Another medium strong band at 38137 cm^{-1} at a separation of 1575 cm^{-1} from the zero band can be correlated with 1611 cm^{-1} in Raman spectrum of 1,3,5-trimethylbenzene. These Raman bands are polarized. This totally symmetric frequency may be assigned to the a_1 part of 1600 cm^{-1} (e_{1g}) benzene vibration.

The authors are thankful to Professor N. L. Singh for valuable discussions. Two of them (Verma and Nair) are grateful to C.S.I.R. New Delhi, India, for financial assistance.