

Electronic and Vibrational Spectral Studies of 4-Dimethylamino Benzaldehyde, Solvent Effect and Effect of pH on $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ Transitions

B. S. Yadav and M. K. Yadav

Molecular Spectroscopy & Biophysics Laboratory, D. N. College, Meerut, India
Email: bsyadav@gmail.com

S. K. Tyagi

Department of Physics, C.S.S.S (P.G.) College, Machhra, India
Email: sktyagi12@rediffmail.com

(Received March 20, 2006)

Abstract: The vibrational (infrared and laser Raman) spectra of 4-dimethylamino benzaldehyde have been recorded. Electronic spectra of 4-dimethylamino benzaldehyde in various solvents have been recorded in the region 1900-4000 Å. The effect of solvents and pH effect on $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions have been studied. The analysis and assignments of various spectra have been given.

Key Words: Laser Raman spectrum, infrared spectra, ultraviolet spectra solvent effect, pH effect.

1. Introduction

Benzaldehyde is the simplest aromatic aldehyde and the substitution of a functional group in benzaldehyde changes the spectra markedly. The electronic and vibrational spectra of benzaldehyde and its derivatives have been extensively investigated by many earlier workers.¹⁻⁷

The present paper reports the vibrational and electronic spectra of 4-dimethylamino benzaldehyde which have not been reported earlier. The present study also includes the effect of change of solvent and effect of change in pH on $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ transitions.

2. Experimental

The spec. pure grade sample of 4-dimethylamino benzaldehyde (hereafter referred as 4-DMAB) was purchased from Aldrich Chemical Co., U.S.A. and used as such. Its purity was confirmed by elemental analysis and melting point determination. The infrared spectra of the compound 4-DMAB were recorded on Perkin Elmer spectrophotometer in the region 400-4000 cm^{-1} using KBr pellets and nujolmull solvent. The laser Raman spectrum in the region (40-4000 cm^{-1}) was recorded on "Spex Rama Lab" spectrophotometer using 52mg argon-krypton laser beam of wavelength 488 nm.

The near UV spectra of the above molecule have been recorded on UV-VIS double beam spectrophotometer in the region 190-400nm in liquid state, using various solvents viz. ethanol, methanol, water, benzene and chloroform. The pH is changed by adding acid or alkali and measured with a systronic digital pH meter.

3. Results and Discussion

The molecule 4-DMAB is assumed to belong to Cs point group symmetry. The molecular structure of 4-DMAB is shown in fig. 1 and its near ultraviolet absorption spectra (region 190-400nm) in various solvents (a) ethanol (b) methanol (c) water (d) benzene (e) chloroform are shown in fig. 2. Absorption spectra of the said molecule in various solvents at different pH are shown in figs. 2 - 4. The laser Raman spectrum as well as IR spectra in KBr pellets and nujolmul are shown in figs. 5, 6 and 7 respectively. Ring fundamentals along with CH_3 group vibrations are presented in Table 1 and effect of solvent and effect of pH on $n-\pi^*$ and $\pi-\pi^*$ transitions are presented in table 2.

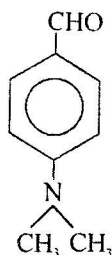


Fig. 1: Molecular structure of 4-DMAB.

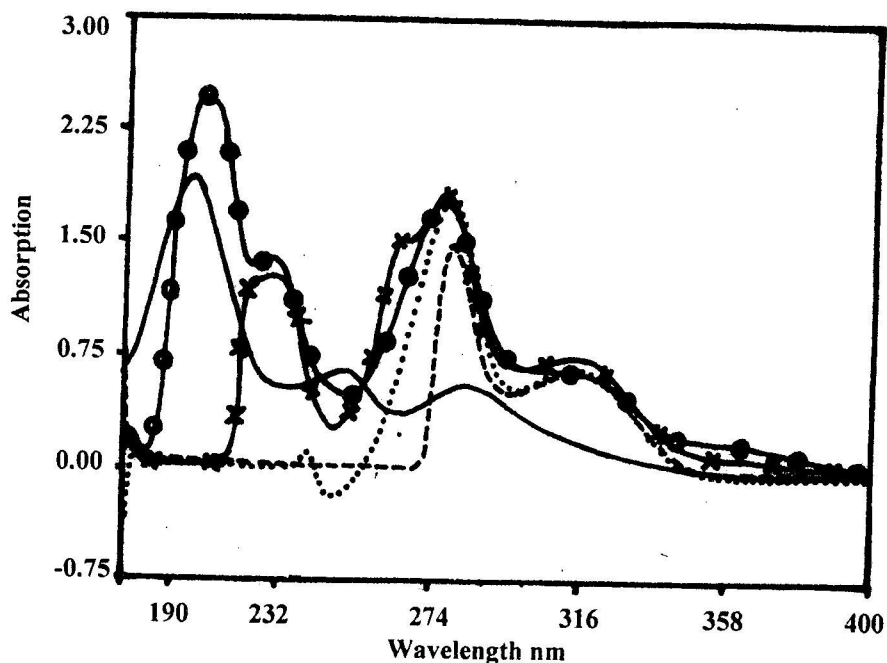


Fig-2: Ultraviolet absorption spectra of 4 DMAB in ethanol (x—x), methanol (o—o), water (—), chloroform (....) and benzene (- - -) medium.

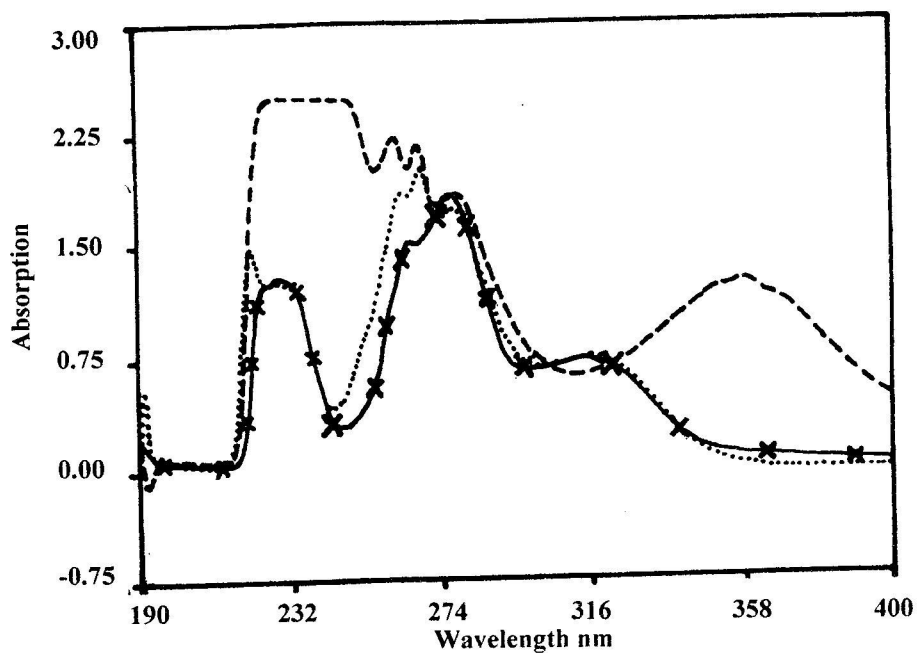


Fig-3: Ultraviolet absorption spectra of 4 DMAB in ethanol (x—x), acidic (....) and alkaline (- - -) medium.

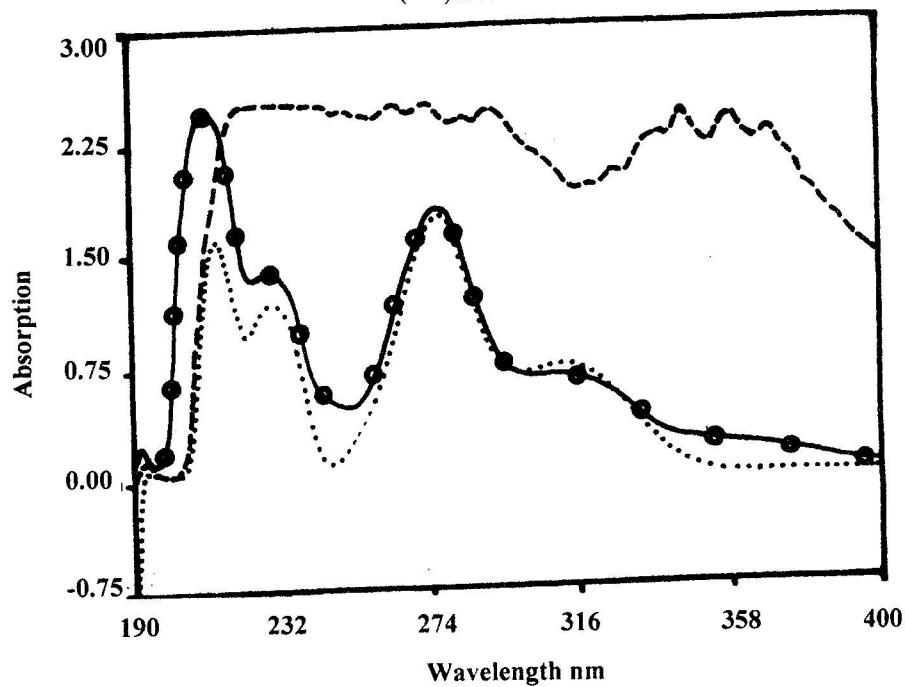


Fig-4: Ultraviolet absorption spectra of 4 DMAB in methanol (x—x), acidic (....) and alkaline (- - -) medium.

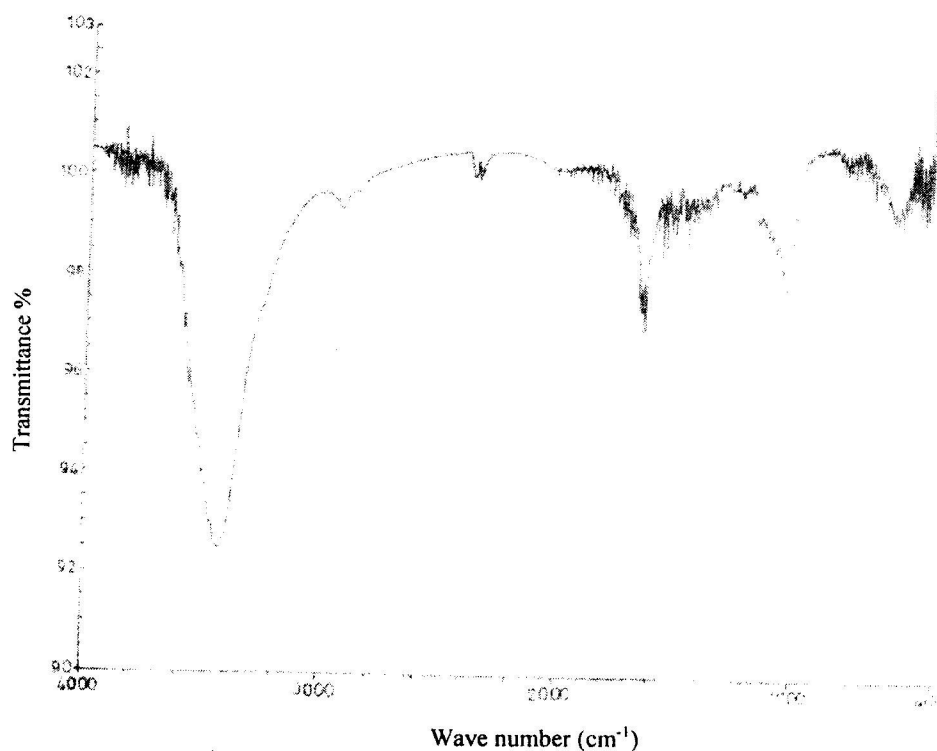


Fig-5: IR absorption spectrum of 4 – DMAB in nujolmull

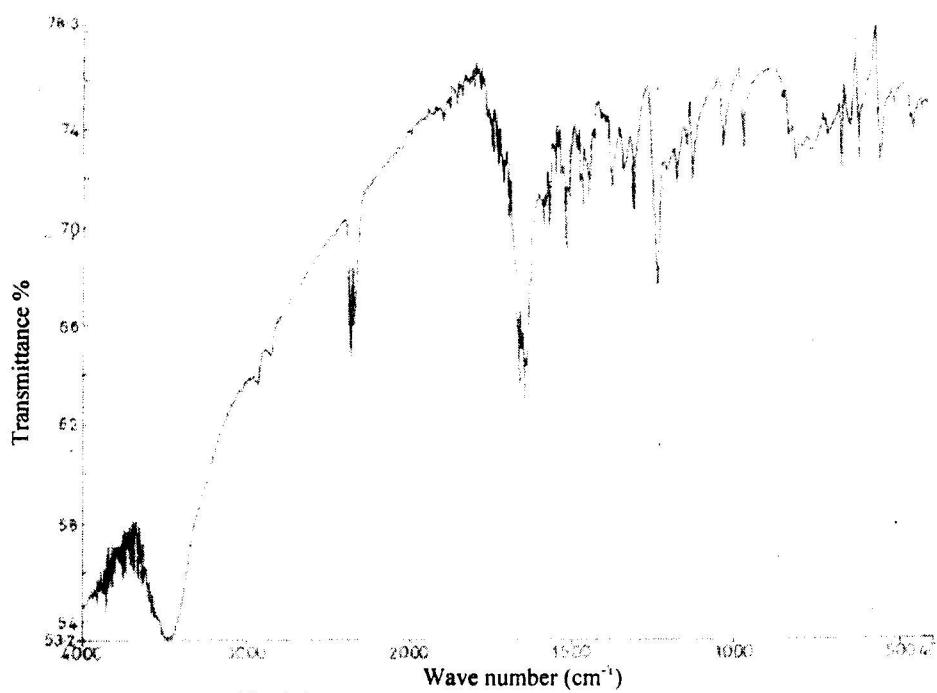


Fig-6: IR absorption spectrum of 4 – DMAB in KBr pellets

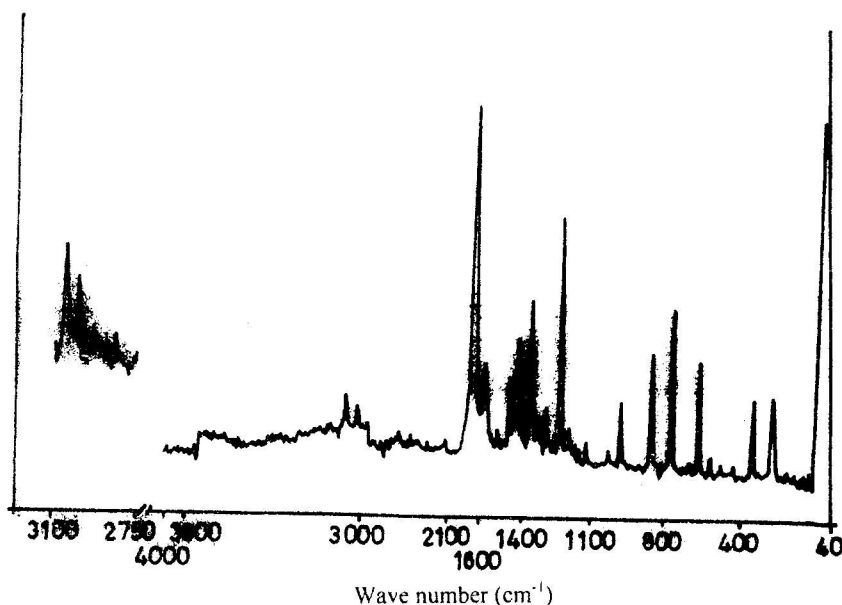


Fig-7: Laser Raman Spectrum of 4 - DMAB

Electronic Spectra: Srivastava et al⁸ have reported the electronic spectra of three isomeric dimethoxy benzaldehydes and reported three band systems in the regions (a) 2150-2300 Å° (b) 2550-2770 Å° and (c) 2950-3150 Å° in each case. Jaiswal⁹ and Dwivedi¹⁰ suggested that for isomeric methoxy benzaldehyde first two band correspond to π - π^* transition while the third band system is due to n - π^* transition. The largest wavelength system is very weak and the other two are intense. In the present study very strong band at 3140 Å° has been taken to represent the 0, 0 band corresponding to $^1A \rightarrow ^1U$ (3100 Å°) spectra while that at 2780 Å° corresponds to $^1A_{1g} \rightarrow ^1B_{2u}$ (2600 Å°) system. To represent the system $^1A_{1g} \rightarrow ^1B_{2u}$ (2100 Å°) as 0, 0 band has been taken at 2140 Å°.

Vibrational Spectra: The analysis of the bands and the assignments of the fundamental frequencies are made on the basis of magnitude and relative intensity of the observed bands and earlier assignments in the similar molecules.

(i) Ring Vibrations: The C-H stretching vibrations are very much prominent in the spectrum of benzene and its substituted derivatives, and are highly characteristics of the aromatic ring itself. Since the molecule 4-DMAB is a disubstituted benzene, four C-H valence oscillations are expected in the region 3000-3100 cm^{-1} . In the present study three C-H stretching vibrations are well assigned and are given in the Table 1. C-H in plane bending and out of plane bending modes lie in the region 1000-1500 and 750-100 cm^{-1} which are given in Table 1.

The group of four bands appearing between 1400-1650 cm^{-1} in the spectra of substituted benzenes represents the characteristics skeletal stretching modes. These correspond to doubly degenerate stretching vibrations of benzene i.e. e_{2g} (1595) and e_{1u} (1485) modes. There are two more C-C stretching modes b_{2u} (1310) and a_{1g} (995) of benzene. Except for the ring breathing mode, all these are known to remain practically unaffected by the substitution. In the present study the very strong bands observed at 746 and 975 cm^{-1} in Raman spectrum may be assigned to ring breathing mode and triangular

bending mode respectively which finds support from the work of Gupta et al¹, Varsanyi¹² & Sanyal et al¹³.

(ii) C-X Vibrations: The medium strong band at 1155cm^{-1} has been assigned to C-N (CH_3)₂ stretching vibration which finds support from the work of Gupta et al¹⁴ while the strong band at 554 cm^{-1} in KBr with its Raman counter part at 565cm^{-1} may be assigned to C-N (CH_3) in plane-bending vibration. The strong band at 1220 cm^{-1} in KBr with the counter part of Raman band at 1210 cm^{-1} may be assigned to C-CHO stretching mode while the very strong band observed at 290 cm^{-1} may be assigned to C-CHO in plane bending mode.

(iii) Group Vibration: 4-DMAB is the compound in which two hydrogen of amino group are replaced by two methyl groups. The CH asymmetric stretching vibrations have very nearly the same magnitude and usually appear with varying intensity at $2900\text{-}3000\text{ cm}^{-1}$. In the present study, out of the four asymmetric CH stretching modes only three in 4-DMAB have been observed (Table 1). The strong band at 1024 cm^{-1} (KBr) with the counter part of Raman band at 1031cm^{-1} and strong band at 1110cm^{-1} (KBr) have been assigned to CH_3 rocking vibration. According to Tylli and Konschim¹⁵ the CH_3 torsional vibration usually lies between $200\text{-}300\text{cm}^{-1}$. Hence the weak bands at 222 and 250 cm^{-1} have been assigned to above mode.

The aldehyde group give rise to six vibrations namely C=O stretching, C=O in plane bending, C=O out of plane bending, C-H stretching, C-H in plane bending and C-H out of plane bending vibrations. The possible vibrations are shown in Table 1.

Table-1
Assignment of vibrational frequencies (cm^{-1}) of 4-DMAB

IR		Raman	Assignment
KBr	Nujolnull		
-	-	125 ms	-N- (CH_3) ₂ torsion
-	-	152 w	γ C-N (CH_3) ₂
-	-	185 wb	CHO opw
-	-	222 w	CH_3 torsion
-	-	250 vw	CH_3 torsion
-	-	290 vs	β C-CHO
413 w	417 ms	-	γ (C-C)
477w	470 ms	-	γ (C-C)
554S	554 w	565 w	β C-N (CH_3) ₂
615S	621 w	626 vs	β (C-C)
639ms	638w		β (C=O)
669ms	672w	663 w	β (C-C)
704w	706w	-	γ (C-C)
-	723w		β (C-C)

-	740w	746 vs	Ring breathing
752 wb	757w		γ (C=O)
800 w	808w		γ (C-H)
836vw	842w	838 vs	γ (C-H)
-	-	893 w	γ (C-H)
.964 ms	-	975 vs	(C-C-C) trigonal bending
1024s		1031 ms	CH ₃ rocking
1110s	1095w	-	CH ₃ rocking
1155 ms	-	-	ν C-N (CH ₃) ₂
1190w	-	1180 w	β (C-H)
1220 s	-	1210 w	ν (C-CHO)
-	1232vw	1239 vs	β (C-H)
1298 ms	-	1309 s	β (C-H)
1330 ms	1342w	1340 ms	β (C-H)
1365 ms	1376vw	1373 vs	ν (C-N), ν (C-C)
1458 ms	1461w		CH ₃ asymm def.
1470 vs	1478vw	1474 ms	Ring stretching
1508S	1512 w		Ring stretching
1598 ms	-	1589	Ring stretching
1636 ms	1632 vs	1630 vs	Ring stretching
1654 ms	1669 w		ν (C=O)
-	-	2750 w	ν (C-H) symm aldehydic)
2834 vwb	-	2851 w	ν (C-H) symm.
2949 w	2933 wb	2960 m	ν (C-H) asymm.
2970 vw	-	2984 wb	ν (C-H) asymm.
3003 vw	-	-	ν (C-H) aromatic
		3036 m	ν (C-H) aromatic
-	-	3089	ν (C-H) aromatic

where ν = stretching, β = in plane bending, γ = out of plane bending, w = weak, m = medium, s = strong, ms = medium strong, mw = medium weak, vs = very strong, vw = very weak, def = deformation, symm = symmetric, asymm = asymmetric, wb = weak band.

Table-2
Effect of solvent and effect of pH on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in 4-DMAB

S. No.	Solvent	Refractive Index	pH	$n \rightarrow \pi^*$	$(\pi \rightarrow \pi^*)$	$(\pi \rightarrow \pi^*)$ II
1.	Water	1.3380	8.0	-	2830	2500
2.	Methanol+ NaOH		10.8	3410	2805	2240
	Methanol	1.3773	7.4	3110	2780	2290
	Methanol+ HCl		1.25	3125	2780	2305
3.	Ethanol+ NaOH		9.5	3520	2790	2290
	Ethanol	1.3362	8.1	3135	2775	2300
	Ethanol+ HCl		1.2	3140	2780	2305
4.	Chloroform	1.4580	7.85	3150	2805	2410
5.	Benzene	1.5236	7.25	3140	2800	2470

4. Effect of Solvents

Polar solvents generally shift the $\pi-\pi^*$ transition to longer wavelength and $n-\pi^*$ transition to shorter wavelength¹⁶. For $\pi-\pi^*$ system both ground and excited states are stabilized and absorption maximum moves towards longer wavelength with the increasing polarity of the solvent (Table 2). The $n \rightarrow \pi^*$ shifts towards shorter wavelength with the increase in the polarity of the solution because in these transitions ground state is more stabilized than the excited state. In the present study of 4-DMAB the $n \rightarrow \pi^*$ system shifts towards shorter wavelength with the increase of the polarity of solvent while going from ethanol to water. Benzene also shows blue shift while going from chloroform to benzene. A red shift is also observed in $\pi-\pi^*$ transitions while going from ethanol to water except in case of methanol ($\pi-\pi^*$).

5. Effect of pH

From Table 2 and figs. 3 and 4 it is evident that in 4-DMAB there is a marked red shift in $n-\pi^*$ and $(\pi-\pi^*)$ I transition and blue shift in $(n-\pi^*)$ II transition in both the solvents (ethanol and methanol) with increase in pH (on adding NaOH to solutions). In pure solvents, on the addition of HCl i.e. with decreasing pH a red shift is observed in all the transitions.

Acknowledgements

The authors are thankful to RSIC, IIT Bombay for recording IR and laser Raman spectra and Dr. Jagbeer Singh, Sr. Scientist, I.V.R.I., Bareilly for recording UV absorption spectra in various solvents.

References

1. S. P. Gupta, C. Gupta, S. Sharma and R.K. Goel, *Indian J. Pure Appl. Phys.*, **24** (1986) 111.
2. P. Venkoji, *Indian J. Pure Appl. Phys.*, **24** (1986) 166.

3. S. P. Gupta, C. Gupta, Seema and R. K. Goel, *Indian J. Phys.*, **62B(4)** (1988) 560.
4. N. R. Katti, M. K. Aralakkanvar, P. R. Jeergal, Rekha Rao and M. A. Shashidhar, *Indian J. Phys.*, **66B(2)** (1992) 221.
5. N. R. Katti, M. K. Aralakkanvar, P. R. Jeergal, G. B. Kalkati and M. A. Shashidhar, *Indian J. Phys.*, **66B(3)** (1992) 333.
6. D. N. Singh, I. D. Singh, R. A. Yadav, *Indian J. Phys.*, **76B(3)** (2002) 307.
7. D. N. Singh, I. D. Singh, R. A. Yadav, *Indian J. Phys.*, **76B(1)** (2002) 35.
8. S. C. Srivastava, B. B. Lal and I. S. Singh, *Indian J. Phys.*, **49** (1975) 494.
9. R. M. P. Jaiswal, *Indian J. Pure Appl. Phys.*, **3** (1965) 405.
10. C. P. D. Dwivedi, *Indian J. Pure Appl. Phys.*, **3** (1965) 452.
11. L. J. Bellamy, *The Infrared spectra of complex molecules*, New York, John Weley, 1975.
12. G. Varsanyi, *Assignments for Vibrational spectra of seven hundred benzene derivatives*, Vol. I and II Adam Hilger, London, 1974.
13. N. K. Sanyal, R. K. Goel and M. L. Agarwal, *Indian J. Pure Appl. Phys.*, **19-5** (1981) 480.
14. S. P. Gupta, Salik Ahmad and R K Goel, *Indian J. Phys.*, **1B** (1987) 427.
15. H. Tylli and H. Konschim, *J. Molec. Struct.*, **42** (1977) 7.
16. J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice Hall Inc. (U.K.), 1969.

