

Electronic absorption spectra of some difluorophenols

M S Navati and M A Shashidhar

Department of Physics, Karnatak University, Dharwad-580 003, India

Received 22 February 1994, accepted 5 May 1994

Abstract : The electronic absorption spectra of 2,4- 2,5- 3,4- and 3,5-difluorophenols in the ultraviolet region in vapour phase has been recorded on Medium Quartz Spectrograph and Hilger Large Quartz Spectrograph and analysed

Keywords : Electronic absorption, phenol

PACS Nos. : 33.10 Gx, 33.20.Ea, 33.20.Fb

Many investigators have studied the ultraviolet absorption spectra of phenols and their mono-derivatives [1-29]. Very little work has been done on the electronic absorption spectra of tri-substituted benzenes in the vapour phase. In view of the limited studies, particularly on the electronic spectra of tri-substituted benzenes, it was felt that an extension of the studies to the electronic absorption spectra of some more tri-substituted benzenes would be worthwhile as this would enable one to have more insight into the structure of the molecules in their ground and excited electronic states. As a part of our research programme, the present note reports the vibrational analyses of the electronic absorption spectra of 2,4-, 2,5-, 3,4-, 3,5-difluorophenols.

The experimental technique used to record the vapour absorption electronic spectra and accuracies in the positions of the bands are the same as those reported in our earlier work [30]. The samples of the compounds were obtained from Aldrich Chemical Co., USA and were further purified before use and were used immediately to record their spectra.

2,4-, 2,5-, and 3,4-difluorophenols (DFP) may be considered as belonging to the point group C_s , whereas 3,5-difluorophenol to C_{2v} point group, if we consider -OH group to be coplanar with the ring. The electronic absorption spectra of all the molecules studied

Table 1. Correlation of the fundamental vibrational frequencies (cm^{-1}) of 2,4-, 2,5-, 3,4- and 3,5-difluorophenols.

IR	2,4-DFP				2,5-DFP				3,4-DFP				3,5-DFP				Symmetry species C_2/C_{2v}	Assignments
	Electronic		Electronic		Electronic		Electronic		Electronic		Electronic		Electronic					
	GS	ES	IR	ES	GS	ES	IR	GS	ES	IR	GS	ES	IR	GS	ES			
275 m	274 mw	201 m	265 m	260 mw	200 m	245 s	246 mw	183 m	265 ms	261 mw	149 m	149 m	261 mw	149 m	a'' / b_1	X-sensitive		
330 ms	329 m	265 ms	315 ms	315 ms	253 s	325 ms	321 w	216 s	345 s	342 m	280 m	280 m	342 m	280 m	a' / b_2	X-sensitive		
420 s	417 ms	313 ms	410 s	407 m	293 s	405 s	402 m	293 ms	415 ms	415 mw	300 m	300 m	415 mw	300 m	a' / b_2	X-sensitive		
475 ms	477 mw	361 ms	455 s	460 m	325 s	435 s	434 w	359 ms	445 s	444 mw	383 ms	383 ms	444 mw	383 ms	a' / b_2	X-sensitive		
510 ms	-	431 s	515 m	-	440 s	475 s	476 mw	407 s	490 ms	488 w	404 mw	404 mw	488 w	404 mw	a' / a_1	X-sensitive		
620 ms	-	471 s	625 s	-	478 m	625 s	601 mw	483 mw	615 ms	609 m	477 s	477 s	609 m	477 s	a' / b_2	C=C in-plane bend		
740 s	-	695 s	745 s	-	650 s	635 s	632 mw	578 s	680 s	670 m	580 m	580 m	670 m	580 m	a' / a_1	X-sensitive		
805 s	-	758 s	820 s	-	742 vs	800 s	-	708 s	1020 ms	-	888 s	888 s	-	888 s	a' / a_1	X-sensitive		
1110 s	-	897 s	1120 s	-	932 s	1100 ms	-	918 s	1120 s	-	966 vs	966 vs	-	966 vs	a' / a_1	C-H In-plane bend		
1150 ms	-	980 ms	1145 ms	-	1032 ms	1140 s	-	971 ms	1140 s	-	1059 m	1059 m	-	1059 m	a' / a_1	C-H In-plane bend		
1200 s	-	1149 m	1205 s	-	1147 ms	1190 s	-	1123 ms	1200 ms	-	1124 s	1124 s	-	1124 s	a' / a_1	X-sensitive		
1240 s	-	1205	1235 ms	-	1190 s	1230 s	-	1151 m	1250 ms	-	1150 m	1150 m	-	1150 m	a' / a_1	X-sensitive		
1275 s	-	1253 s	1280 s	-	1222 s	1270 s	-	1248 mw	1280 s	-	1246 m	1246 m	-	1246 m	a' / a_1	X-sensitive		
1380 s	-	1287 mw	1375 s	-	1273 s	1380 s	-	1312 m	1385 s	-	1308 w	1308 w	-	1308 w	a' / a_1	C=C stretch		

GS = Ground state; ES = Excited State; DFP = Difluorophenol; vs = very strong; s = strong; ms = medium strong; m = medium; mw = medium weak; and w = weak.

shows a $\Pi^* \leftarrow \Pi$ system in the vapour phase and they spread over the region λ 2870 Å – λ 2470 Å and consists in each case rather well defined red degraded bands. This system observed in the spectra of all the compounds has been identified as corresponding to the forbidden electronic transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ of benzene. Under the reduced symmetry of C_s or C_{2v} of the compounds, the above forbidden transition becomes ${}^1A' \leftarrow {}^1A'$ or ${}^1B_2 \leftarrow {}^1A_1$ and it is allowed.

The effect of temperature on the band system has facilitated the choice of the bands at 35730, 36454, 35492 and 37614 as the 0,0 band in compounds 2,4-, 2,5-, 3,4- and 3,5-difluorophenols respectively. The identification of the fundamentals chosen in the compounds has been mainly done on the basis of intensities of the bands and the available literature on the analysis of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of other tri-substituted benzenes. The fundamentals so chosen are listed in Table 1 along with their IR data [31] and their probable assignments. The longer wave length side bands with spacings 46, 72, cm^{-1} in compound 2,4-DFP, 41, 90, cm^{-1} in compound 2,5-DFP, 37, 59 cm^{-1} in compound 3,4-DFP and 78 cm^{-1} in compound 3,5-DFP from their respective 0,0 bands have been identified as sequence intervals. It is found that most of the excited state fundamentals appear up to two or three quanta and also they combine with most of the other fundamentals in the excited state and thus most of the observed bands could be explained. The analyses of the electronic spectra of the molecules show a red shift in the order of 3,4- > 2,4- > 2,5- > 3,5-difluorophenol with respect to 0,0 band of benzene. Such a trend has been reported in the literature [32].

Acknowledgments

One of the authors (MAS) thanks the Karnatak University authorities for the financial support in the form of a research scheme and another author (MSN) for the financial assistance in the form of a fellowship.

References

- [1] F A Masten, Ginsburg Nathan and W W Robertson *J. Chem. Phys.* **13** 309 (1945)
- [2] J Christoffersen, J M Hollas and G H Kirby *Proc. Roy. Soc.* **A307** 97 (1968)
- [3] L N Tripathi *Ph D Thesis* (Gorakhpur University, Gorakhpur, India) (1966)
- [4] G N R Tripathi *J. Mol. Spectrosc.* **37** 486 (1971)
- [5] G N R Tripathi *Indian J. Pure Appl. Phys.* **7** 517 (1969)
- [6] M A Shashidhar and K Suryanarayana Rao *Curr. Sci.* **35** 62 (1966)
- [7] M A Shashidhar and K Suryanarayana Rao *Proc. Int. Conf. on Spectroscopy* (Bombay, India) **1** 242 (1967)
- [8] A N Pathak *Curr. Sci.* **36** 429 (1967)
- [9] N K Sanyal and A N Pandey *Indian J. Pure Appl. Phys.* **11** 913 (1973)
- [10] K Chandra *Indian J. Phys.* **39** 464 (1965)
- [11] S B Banerjee *Indian J. Phys.* **30** 353 (1956)
- [12] S K Sen *Indian J. Phys.* **30** 553 (1956)
- [13] J R Dearden and W F Forber *Can. J. Chem.* **37** 1294 (1956)

- [14] (Miss) J V Shukla, K N Upadhya and S K Tiwari *Indian J. Phys.* **44** 128 (1970)
- [15] V Suryanarayana and V Ramakrishna Rao *J. Sci. Industr. Res.* **15B** 260, 548 (1956)
- [16] C G Rama Rao, B R K Reddy and P Tiruvenganna Rao *Indian J. Phys.* **44** 212 (1970)
- [17] V K Mehrotra *Indian J. Pure Appl. Phys.* **6** 206 (1968)
- [18] H Kaemmerer and W Lewenz *Spectrochim. Acta* **24A** 2059 (1968)
- [19] S L Srivastava and L N Tripathi *Indian J. Pure Appl. Phys.* **6** 151 (1968)
- [20] B J Ansari and S L Srivastava *Indian J. Pure Appl. Phys.* **9** 820 (1971)
- [21] T C Sharma and I A Rao *Indian J. Pure Appl. Phys.* **1** 230 (1963)
- [22] D Sharma and L N Tripathi *Indian J. Pure Appl. Phys.* **1** 229 (1963)
- [23] K Chandra *Indian J. Pure Appl. Phys.* **2** 134 (1964)
- [24] S B Roy *Indian J. Phys.* **32** 525 (1958)
- [25] K N Upadhya *Indian J. Pure Appl. Phys.* **6** 344 (1968)
- [26] T N Misra and S B Banerjee *Indian J. Phys.* **35** 203 (1961)
- [27] P V Shanbhag *Ph D Thesis* (Karnatak University, Dharwad, India) (1980)
- [28] G D Baruah, R Ammimi Amma and K P R Nair *Indian J. Pure Appl. Phys.* **8** 239 (1970)
- [29] P V Shanbhag, M A Shashidhar and K Suryanarayana Rao *Indian J. Phys.* **52B** 349 (1978)
- [30] M A Shashidhar *Spectrochimica Acta* **27A** 2363 (1971)
- [31] M S Navati, G B Kalkoti, P R Jeergal, M K Aralakkanavar and M A Shashidhar *Proc. Int. Conf. on Spectroscopy and Astrophysics* (Allahabad, India) **28** (1993)
- [32] M R Padheye and T S Varadarajan *Indian J. Pure Appl. Phys.* **1** 25 (1963)