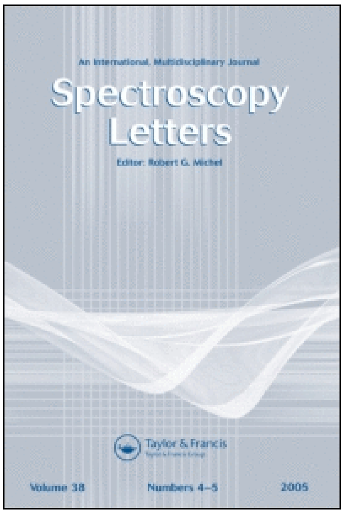

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S. P. Sinha[a]; C. L. Chatterjee[a]
[a] Department of Physics, T. N. E. College Bhagalpur- University, Bhagalpur (Bihar), INDIA

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THE NEAR ULTRA-VIOLET ABSORPTION SPECTRUM OF PARA-FLUORO PHENETOLE VAPOUR

S. P. Sinha and C.L.Chatterjee
Department of Physics,
T.N.B.College
Bhagalpur- University
Bhagalpur (Bihar) INDIA.

ABSTRACT

The near ultra-violet absorption spectrum of para- fluoro phenetole has been studied in vapour phase. About 135 red degraded Bands have been measured. These have been explained in terms of five ground state (187, 258, 345, 633 and 855 cm^{-1}) and seven excited state (151,306, 527,816, 966, 1279 and 1328 cm^{-1}) fundamental frequencies. A red shift of 1243 cm^{-1} of (o,o) band relative to that of Phenetole is also observed.

INTRODUCTION

The present study of the ultra-violet absorption spectrum of p-fluoro phenetole has the aim of extending the analysis of the spectra of mono substituted phenetoles. A brief report on the ultra-violet absorption spectrum of this compound was published by Sharma and Singh (1967). The present paper is the first detailed report on its ultra-violet absorption spectrum in which the electronic transition has been classified, the frequencies of the ground and excited electronic states have been identified and their probable mode of assignments has been discussed.

EXPERIMENTAL

The absorption spectrum of para-fluoro phenetole was photographed in the region 2930-2620 A° using special illford N-30 plates on the Hilger medium and large qartz spectrograph, in the vapour phase having path length 10,25,50,75 and 100 cm. Temperature varied from 0°c to 60°C The sample p-fluoro phenetole was of specpure grade obtained from Messers Koch Light Laboratories Ltd; England. The source of Continuous radiation was a Hilger and Watts hydrogen lamp, run on a direct current 0.5 amp drawn from a stablised power supply. Exposures varied from 10 mts to 4 hours. Generally, all the bands on the violet and a few on the red-side of the (o,o) band appeared with fairly good intensity, with path length 75 cm and temperature 30°C. To develop bands on the higher wave length side a 100 cm tube was used with the temperature varying from 30°C to 60°C.

To prevent the deposition of Vapours on windows, temperature of the vapours exposed to light was always kept higher than its reservoir's temperature. The bands have been measured with the help of a comparator of least count 0.001 mm. The expected accuracy is ± 1 cm^{-1} for the very sharp bands (those having line like structure), with the accuracy diminishing to ±5 cm^{-1} for the extremely diffuse bands. The cross-wire of the comparator was focused at the edges of the sharp bands and at the intensity peaks for the diffuse bands.

RESULTS:

About 135 bands, all degraded to the red, have been measured in the region 2930-2620 A^{o}. At 0^{o}c only two bands could be recorded at 2846.6 A^{o} and 2782.0 A^{o}, of which 2846.6 A^{o} probably represents (0,0) band of p-fluoro phenetole molecule. With the rise of temperature, a few more bands appear on the longer wave length at room temperature all the bands to the violet and a few to the red of the (0,0) band begin to appear. Bands on the longer wave length side of spectrum appear in the region 2896.2 - 2927.7 A^{o} with path length 100 cm in the temperature range 0^{o}c to 60^{o}c. Bands lying below 2896.2 A^{o} merge in the continuous absorption. The wave length and the corresponding wave numbers of the observed bands are given in table I. Visual estimated intensity is on the Scale vvw - very very weak, vw - very weak, mw - medium weak, w- weak, ms - medium strong, S- Strong, Vs- Very Strong, VVS- very very strong. The bands fall into several groups,

TABLE I

Wave length in A^{o}	Wage number in cm^{-1}	Intensity		Shift from the 0,0 band.	Assignment.
		Path length 150 cm	Temp 40°C		
2927.7	34147	vvw		-972	0-855-4x29 = 971 0-633-345 = 978
2925.8	34169	vw		-950	0-888-3x29 = 942
2922.7	34205	mw		-914	0-855-2x29 = 913
2920.5	34231	w		-888	0-855-29 = 884
2917.7	34264	ms		-855	0-855
2914.9	34296	w		-823	0-633-187 = 820 0-855 + 32 = 823
2912.0	34331	mw		-788	0-855+2x32 = 791
2906.9	34391	vvw		-728	0-633-3x29 = 720
2904.6	34418	vw		-701	0-633-2x29 = 691 0-855+151 = 704
2901.8	34451	mw		-668	0-633-29 = 662
2898.9	34486	w		-633	0- 633
2896.2	34518	ms		-601	0-345-258 = 603 0-633+32 = 601 ?
2894.2	34542	vw		-577	0-2x258-2x29=574
2891.8	34570	w		-549	0-2x258-29 = 545 0-855 + 306 = 549
2888.3	34612	mw		-507	0-258-187-2x29=503 0-2 x258 = 516
2885.3	34648	w		-471	0-258-187-29=474
2883.0	34676	ms		-443	0-258-187 = 445
2880.2	34710	w		-409	0-2x187-29 = 403
2876.8	34751	mw		-368	0-345-21 = 366 0-2 x 187 = 374
2871.9	34774	s		-345	0-345
2872.9	34799	w		-320	0-258-2x29 = 316 0-855+527 = 328
2870.6	34826	ms		-293	0-258 - 29 = 287
2869.5	34839	mw		-280	0-258 - 21 = 279
2867.7	34861	s		-258	0-258
2865.9	34883	ms		-236	0-187-42 = 229 0-258 + 32 = 226
2864.2	34904	s		-215	0-187 - 29 = 216

TABLE I (continued)

Wave length in A°	Wave number in cm^{-1}	Intensity Path length 75 cm Temp 45°C	Shift from the 0,0 band.	Assignment.
2861.9	34932	s	- 187	0-187
2860.4	34950	w	-169	0-187 + 15 = 172
2859.0	34967	ms	-152	0-187 + 32 = 155
2855.9	35005	ms	-114	0-4 x 29 = 116
2853.9	35030	s	- 89	0-3 x 29 = 87 0-2 x 42 = 84
2851.8	35055	s	- 64	0- 42 -21 = 63
2850.0	35066	vs	- 53	0-2x29 = 58 0-21 - 29 = 50
2850.0	35077	vs	- 42	0- 42
2849.0	35090	vvs	- 29	0 -29
2848.3	35098	s	- 21	0- 21
2846.6	35119	vvs		0, 0
2845.4	35134	ms	15	0 + 15
2844.0	35151	sb	32	0 + 32
2841.6	35181	w	62	0 + 2x32 = 64
2837.3	35234	ms	115	0+ 151-42 = 109 0+ 966-855 = 111
2835.5	35257	w	138	0 + 151-21 = 130
2834.4	35270	s	151	0 + 151
2832.2	35298	w	179	0 + 151 + 32 = 183 0 + 816 -633 = 183
2829.6	35330	mw	211	0 + 151+2x32 = 215
2827.1	35362	vw	243	0 + 306-42-21= 243
2825.3	35384	ms	265	0 + 306-42 = 264
2823.4	35408	mw	289	0 + 306-21 = 285
2822.0	35425	s	306	0 + 306
2819.7	35454	ms	335	0 + 306 + 32 = 338
2817.6	35481	mw	362	0 + 1279-855-2x29=366 0 + 306 + 2x32 =370
2815.3	35510	w	391	0 + 1279-855-29 = 395
2812.7	35543	ms	424	0 + 1279-855 =424

TABLE I (continued)

Wave length in A°	Wave number in cm^{-1}	Intensity Path length 75 Cm Temp. 45°C	Shift from the 0,0 band	Assignment	
2810.4	35572	w	453	0+151+306	=457
2809.1	35589	w	470	0+1328-855 0+527 -2x29	=473 =469
2809.1	35602	wBD	483	0+527-45	=485
3806.9	35616	ms	497	0+527-29	=498
2805.8	35630	w	511	0+527-21	=506
2804.5	35646	s	527	0+527	
2803.5	35659	mw	540	0+527+15	=542
2802.1	35677	w	558	0+527+32 0+816-258	=559 =558
2799.2	35714	w	595	0+2x306-21 0+816-258+32	=591 =590
2798.2	35727	ms	608	0+2x306	=612
2795.0	35768	w	649	0+2x306+32 0+1279-633	=644 =646
2791.0	35819	ms	700	0+816-4x29	=700
2788.6	35850	s	731	0+816-3x29	=729
2786.4	35878	vs	759	0+816-2x29	=758
2784.5	35903	vvs	784	0+816-29	=787
2783.6	35914	s	795	0+816-21	=795
2782.0	35935	vvs	816	0+816	
2781.0	35948	ms	829	0+816+15	=831
2779 .7	35965	s	846	0+816+32	=848
2776.3	36009	w	890	0+966-2x42 0+816+2x32	=882 =880
2774.8	36028	w	909	0+966-2x29	=908
2773.3	36048	ms	929	0+966-29 0+966-42	=937 =924
2772.1	36063	w	944	0+966-21	=945
2770.4	36085	s	966	0+966	
2768.0	36117	ms	998	0+966+32	=998
2765.5	36146	w	1030	0+966+2x32	=1030
2761.7	36199	w	1080	0+966+151-42	=1075
2759.0	36234	ms	1115	0+966+151	=1117
2756.1	36272	vw	1153	0+966+151+32	=1149

TABLE I (continued)

Wave length in A°	Wave number in cm^{-1}	Intensity Path length 75 cm.	 Temp 45°C	Shift from the 0,0 band.	Assignment.	
2754.4	36295	vvw		1176	0+966+151+2x32	≐1181
2752.8	36316	w		1197	0+1279-3x29	≐1192
2751.0	36340	ms		1221	0+1279-2x29	≐1221
2749.1	36365	s		1246	0+1279-29	≐1250
2747.9	36381	ms		1262	0+1279-21	≐1258
2746.6	36398	vs		1279	0+1279	
2744.8	36422	w		1303	0+1328-21	≐1307
2742.9	36447	s		1328	0+1328	
2739.6	36491	mw		1372	0+2x816-258	≐1374
2737.4	36520	mw		1401	0+1279+151-21 0+2x816-258+32	≐1409 ≐1406
2735.2	36548	ms		1429	0+1279+151	≐1430
2732.7	36583	mw		1464	0+966+527-29	≐1464
2730.9	36607	w		1488	0+966+527	≐1496
2729.3	36629	w		1510	0+2x816-4x29	≐1516
2726.6	36665	ms		1546	0+2x816-3x29	≐1545
2724.5	36693	s		1574	0+2x816-2x29	≐1574
2722.7	36717	vs		1598	0+2x816-29	≐1603
2721.8	36730	ms		1611	0+2x816-21	≐1611
2720.4	36748	vs		1629	0+2x816	≐1632
2717.8	36784	w,ms		1665	0+2x816 +x32	≐1664
2715.5	36815	mw		1696	0+2x816+2x32	-1696
2713.4	36843	w		1724	0+ 966+816-2x29	≐1724
2711.4	36870	ms		1751	0+816+966-29	≐1753
2709.1	36902	s		1783	0+816+966	≐1782
2707.3	36926	w		1807	0+1279+527	≐1806
2705.5	36951	vvw		1832	0+1328+527-21	≐1834
2704.2	36969	mw		1850	0+2x966-2x42 0+1328+527	≐1848 ≐1855
2701.7	37003	w		1884	0+2x966-42	≐1890
2698.2	37051	msB		1932	0+2x966	≐1932
2695.5	37088	w		1969	0+2x966+32	≐1964

TABLE I (continued)

Wave length in A°	Wave number in cm^{-1}	Intensity Path length 75 cm.	Intensity Temp. 45°C	Shift from the 0,0 band.	Assignment.	
2692.5	37129	mw		2010	0+1279+816-3x29	=2008
2690.3	37160	w		2041	0+1279+816-2x29	=2037
2688.2	37189	ms		2070	0+1279+816-29	=2066
2686.5	37212	s		2095	0+1279+816	=2095
2684.7	37237	w		2118	0+1328+816-29	=2115
2683.3	37256	ms		2137	0+1328+816	=2144
2679.9	37304	vw		2185	0+3x816-258	=2190
2677.8	37333	vvw		2214	0+3x816-258+32	=2222
2667.9	27472	mw		2353	0+3x816-3x29	=2361
2664.6	37518	wB		2399	0+3x816-2x29	=2390
2663.4	37535	ms		2416	0+3x816-29	=2419
2661.6	37560	s		2441	0+3x816	=2448
2658.4	37605	ms		2486	0+3x816+32	=2480
2655.6	37645	mw		2526	0+2x1279-29	=2529
2652.7	37686	w		2567	0+1279x2	=2558
2650.0	37725	w		2606	0+1279+1328	=2607
2640.3	37863	w		2744	0+2x966+866	=2748
2635.6	37931	vvw		2812	0+3x966-3x29	=2811 ?
2633.1	37967	vw		2848	0+3x966-2x29	=2840
2631.4	37991	mw		2871	0+3x966-29	=2869
2629.6	38017	wB		2898	0+3x966	=2898
2628.2	38038	w		2919	0+2x816+1279	=2911
2625.8	38072	w		2953	0+2x966+1328	=2960

intensity of which decreases as one goes to shorter wave length side of (0,0) band. In general, these bands are broader than those of its lower homologue p-fluoro anisole.

ANALYSIS AND DISCUSSION OF THE SPECTRUM:

p- fluoro phenetole molecule, [p- f c_6H_4 O c_2H_5] is obtained by replacing two hydrogen atoms by - F and - Oc_2H_5 groups at para Carbon atoms of benzene. Treating - OC_2H_5 as one unit, p-fluoro phenetole molecule belongs to the C_{2v} point group. The forbidden electronic transition $^1A_{1g}$ - $^1B_{2u}$ or ^1L_b - ^1A for Benzene (D_{6h} point group) becomes allowed. similarly A_1-B_1 for C_{2v} point group, with the transition moment lying in the molecular plane is also allowed.

The appearance of spectrum with high intensity suggests that the electronic transition, A_1- B_1 is an allowed one. This confirms the assumed symmetry C_{2v} for p-fluoro phenetole molecule. As (0,0) band will appear with strong intensity on the longer wave length side of the spectrum the band at 2846.6 A° (35119 cm^{-1}) is obviously the (0,0) band. Frequency shifts of the various bands from the (0,0) band are given in column 4 of table I. The strong bands with shifts 151, 306, 527, 816, 966, 1279 and 1328 cm^{-1} are easily identified as the excited state fundamentals and 258, 345, 633 and 855 cm^{-1} are identified as ground state fundamentals.

The (0,0) band of p-fluoro phenetole is shifted by 1243 cm^{-1} towards red side relative to the phenetole (36362 cm^{-1}). Cooper (1954) has pointed out that the spectral shift produced by a fluorine atom substituted in para position

TABLE - II

CO-RELATION BETWEEN GROUND AND EXCITED STATE FUNDAMENTAL FREQUENCIES OF Para- fluoro phenetole

Ground State (cm^{-1})		Excited State (cm^{-1})	Assignment
*Infrared (liquid)	Ultra violet (Vapour)		
-	187	151	Out of plane C-X bending mode.
-	258	-	
-	345	306	Components of e_g^+ vibration (608cm^{-1}) of benzene.
635	633	527	
860	855	816	ring breathing.
1010	-	966	C-C-C trigonal mode (1010 B_{1u} of benzene)
1290	-	1279	C-F stertching.
1392	-	1328	-CH_3 bending in ethoxy group ?

* Author's work under publication.

X- Stands for substitution.

?- Conveys doubtful.

depends on the directing power of the substituent. Thus the red shift of (0,0) band indicates that - OC_2H_5 group is orthopara directing.

On substitution, degenerate e_g^+ vibration in benzene (608 cm^{-1}) splits up into two components are lying around 600 cm^{-1} known as non-totally symmetric vibration (6b vibration) does not change very much but other component known as totally symmetric vibration (6 a vibration) is effected to a large extent, lies much below it. The band at 633 cm^{-1} to red side of (0,0) band represents non-totally symmetric component

B_1 of ϵ_g^+ vibration and corresponding excited state is at 527 cm^{-1} to the violet of the (0,0) band. The band at 306 cm^{-1} in the excited electronic state and corresponding ground state frequency 345 cm^{-1} represent $1 \rightarrow 0$ and $0 \rightarrow 1$ bands of totally symmetric component α_1 of ϵ_g^+ vibration of benzene.

Of all the excited state fundamental frequencies the frequency 816 cm^{-1} appears frequently at low and saturated vapour pressure with an intensity comparable to (0,0) band. It also occurs in progressions and combinations which suggests that it is probably a totally symmetric vibration. The frequency 855 cm^{-1} represents the ground state value of the excited state frequency 816 cm^{-1}. On comparision with other disubstituted benzenes, it was found that a frequency of this order generally exists in all benzene compounds. The values are 810, 794, 819, 794, 816, 796 and 771 cm^{-1} in the excited state and 857, 844, 815, 860,858 and 808 cm^{-1} in the ground state in p-fluoro anisole, p-fluoro toluene, p-difluoro benzene, p-fluoro chloro benzene, p-fluoro phenol, p-fluoro benzaldehyde and p-fluoro anisole respectively. In all these compounds, this frequency lying around 800 cm^{-1} has been assigned as a totally symmetric carbon vibration. Thus the excited state frequency 816 cm^{-1} (855 cm^{-1} in the ground state) is possibly a ring breathing vibration and is correlated to W_1' (Sponer's notation) or 1 (Wilson notation) mode of vibration of benzene.

As the upper state frequency 966 cm^{-1} forms progressions and occurs with a strong intensity it represents totally symmetric carbon vibration, on comparision with other substituted benzenes. The corresponding ground state frequency could not be observed as the spectrum did not extend beyond 2927. 7 A^{o} even at 100 cm path length and temperature of 60^{o}C.

Para-fluoro phenetole molecule may be expected to have two fundamentals in the region 1250-1350 cm^{-1}, one due to C-F stretching and the other due to CH_3 bending in ethoxy group. We have identified two fundamentals at 1279 cm^{-1} and 1328 cm^{-1} in the excited state. Assuming the fundamentals given by Sreeramamurthy (1957), the frequency at 1328 cm^{-1}explaining a few un-interpreted bands. One such band is at a separation of 258 cm^{-1} from the 0,0 band to its red side, which is the most intense band.

The excited state frequency 1279 cm^{-1}, on comparision is probably C-F stretching frequency (table III). Close to this the CH_3 bending frequency also occurs. An alternative interpretation of 1279 cm^{-1} is that it may present CH_3 bending frequency in ethoxy group.

The ground state frequencies 187 and 258 cm^{-1} and the excited state frequencies 151 cm^{-1} are of poor intensity. Their definite interpretation has not been possible. The 258 cm^{-1} (ground state) is possibly a C-F bending mode. Similar frequency also occurs in fluorinated aromatics.

Close to the 0,0 band on the red and violet side occur bands at 21, 29, 42 and 15, 32 cm^{-1} . of these, the 29 cm^{-1} occurs as 1 x 29, 2 x 29, 3 x 29 and 4 x 29. It is also found to occur in combination with nearly all of the ground and excited state fundamentals, and as summation bands and also with overtones. This has been ascribed to a difference frequency between a ground state and an excited state vibration

TABLE - III

"VALUE OF C- F STRETCHINGFREQUENCY IN SOME DISUBSTITUTED BENZENES"

Molecule	Ground State (cm^{-1})	Excited State (cm^{-1})	References
m - difluorobenzene	1277	1267	(10)
m - fluoroanisole	1280	1277	(11)
m - fluoro Benzonitrile	1278	1269	(11)
o - Difluorobenzene	1279	1265	(12)
o - fluorobenzaldehyde		1242	(13)
p - fluorophenol	1257	1247	(14)
p - fluorochlorobenzene	1293	1237	(15)
p- Difluoro benzene	1260	1250	(9)
p - fluoro phenetole	1290	1279	Present work.

that is, a so called 1 → 1 type of transition. Possibly the ground state frequency 855 cm^{-1} and corresponding excited state frequency 816 cm^{-1} are responsible (855- 816 = 29 cm^{-1}) for its appearance. The frequency 32 cm^{-1} on the violet of 0,0 band also occurs with a large number of fundamentals (ground and excited) combination frequencies and overtones.

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