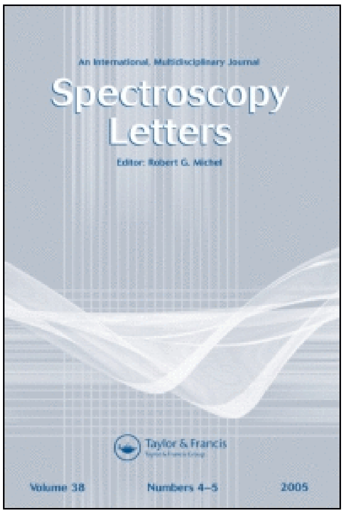

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An Analysis of π - π* Electronic Transition Observed in Absorption Spectrum of Meta-Fluoroanisole

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An Analysis of π - π* Electronic Transition Observed in Absorption Spectrum of Meta-Fluoroanisole*.

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ABSTRACT:- The electronic absorption spectrum, photographed in the region 2790-2510A, is assigned as allowed A' - A' transition between the two lowest-lying singlet states (ππ*) of meta-fluoroanisole vapour. An analysis of the observed absorption bands is proposed in terms of excited state: 155, 217, 509, 691, 838, 964 and 1277 cm^{-1} and ground state: 225, 330, 583 and 734 cm^{-1} fundamental vibrations. The 0-0 transition of the system is found at 36664 cm^{-1}. Intense bands with their separation 43, 70, 80 and 96 cm^{-1} on lower frequency

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side of the 0-0 transition are due to difference of the fundamental vibrations. A correlation of the normal vibrations with the vibrations observed in ortho and para isomers of fluoroanisole together with infrared vibrations of the meta isomer has also been made.

I. INTRODUCTION

On account of the extreme electronegativity of the fluorine atom, the fluorinated benzenes have unique physical and chemical properties which make the investigation of their ultraviolet and infrared absorption spectra of considerable interest. Extensive studies of normal vibrations of ortho-and para-fluoroanisole have been made, the former by absorption (IR&UV)[1,2], Raman[3], fluorescence[4] - emission[4] and the later by absorption[6,5] (IR&UV) techniques. There does exist a systematic study of fundamental vibrations in the lowest singlet state (A') of meta-fluoroanisole by infrared-absorption technique[7]. To the writer's knowledge, no work on the vibrational structure of the spectrum (~2650A) of meta-fluoroanisole has yet appeared in the literature. The present paper illustrates vibrational analysis of the singlet spectrum of meta-fluoroanisole (MFA) vapour.

II. EXPERIMENTAL PROCEDURE

The sample of meta-fluoroanisole was obtained from Messrs. Koch-Light Laboratories, England and was of specpure grade. When examined by infrared spectroscopy no impurity was detected. The sample was then used to obtain absorption spectrum on the medium & large quartz spectrographs using vapour absorption lengths varying from 10 to 150 cm over a temperature range of 0°C to 80°C. Ilford N30 and N40 plates were used to photograph the spectrum. Exposures were varied from 10 minutes to 2 hours depending on the experimental conditions. The meta-fluoroanisole molecule is found to have two absorption band systems-one consisting of mostly discrete red degraded bands in the region 2790 - 2510A and the other below 2300A - a continuous absorption. The wavelength measurements were made on four different plates, twice on each, taking iron lines as standard, with the help of a Hilger comparator which allowed readings up to 0.001 mm. The accuracy of these measurements depends largely upon the definition of bands. It varies from ±5 cm^{-1} for well defined heads to ±10 cm^{-1} for broad and diffuse bands and for overlaping bands not sufficiently resolved. Table 1 shows the positions in wavenumbers, visual estimated intensities, separation from the 0-0 transition and assignments of the observed absorption bands.

III. DISCUSSION

Considering, in first approximation, $-OCH_3$ group as a mass point the meta-fluoroanisole molecule approximates to the C_s point groupthe molecular plane containing all atoms being the only element of symmetry. The forbidden singlet electronic transition ~2600A of benzene (D_{6h}) transforms to allowed electronic transition (C_s) and is generally observed at wavelength >2600A in substituted benzenes. Thus, for meta-fluoroanisole, it is expected that the 0-0 transition of electronic absorption spectrum (A' - A'), observed in the region 2790 - 2510A, should be present with fairly strong intensity toward longer wavelength side of this spectrum. Besides, numerous progressions of different symmetric vibrations and combinations between them are expected to be on the shorter wavelength side of the 0-0 transition. On the long wavelength side of the principal bands v-v transitions, due to low frequency vibrations with favorable Boltzmann factors, are also expected.

The most important characteristic of the uv absorption spectrum of m-fluoroanisole vapor is the group of bands cumulating in the very strong band with an extremely sharp edge on uv side which occurs at 36664 cm^{-1}. Being allowed transition, it is, in accordance with group theory and

Franck-Condon principle, the 0-0 transition of the uv absorption system. The vibrations: 225, 330, 583 and 734 cm^{-1} on lower frequency side of the 0-0 transition, are the normal vibrations of the singlet ground electronic state (A'). In the main portion of the spectrum, all the bands on the shorter wavelength side of the 0-0 transition, arise from transitions to excited vibrational levels in the upper electronic state and their differences in cm^{-1} from the 0-0 transition, obviously, give the values of vibrations in the singlet excited electronic state. Amongst them, the normal vibrations are: 155, 217, 509, 691, 838, 964 and 1277 cm^{-1}.

The e_{2g}(608 cm^{-1}) vibration of benzene (D_{6h}) is found to split up into two components - thus breaking the degeneracy - in substituted benzenes of reduced symmetry. One of the components keeps its ground state value ~600 cm^{-1} and the order reduces its magnitude considerably. The ground state frequency 583 cm^{-1} (correlated with infrared[7] vibration 573 cm^{-1}) is identified to have its counterpart excited state frequency 509 cm^{-1}. The vibration 509 cm^{-1} occurs with good intensity and does not show a change in intensity on increasing the vapour pressure of the absorbing column. The strong band at 36881 cm^{-1}, shifted 217 cm^{-1} towards violet of the 0-0 transition, involves a bending mode usually observed in the spectra of disubstituted benzenes[8,9]. The intensity of this band is found to be a function of number of absorbing molecules. The vibrations: 217 and 509 cm^{-1} are, tentatively, assigned as the representatives of the vibration 608 cm^{-1} of benzene in the upper electronic state of m-fluoroanisole.

Amongst the excited state vibrations, the vibration 691 cm^{-1} is of great particular interest. It occurs with extremely strong intensity, comparable to 0-0, in the absorption spectrum and combines with all the excited state vibrations. The progressions of 691 cm^{-1} are at 37355, 38042, 38739 and 39428 cm^{-1} with intensity in descending order (Table 1). From its intensity and combining power it is inferred that 691 cm^{-1} frequency, with its counterpart 734 cm^{-1} (= 729 cm^{-1} of infrared[7]) in the ground electronic state, in all probability represents a totally symmetric vibration — the C - OCH_3 stretching vibration. Its assignment is further supported by the following facts:-

1) If MFA is treated as equivalent to meta-fluorochlorobenzene[9] by weight - the vibration C - OCH_3 valence is espected to be nearer to C - Cl valence which appears with good intensity at 636 cm^{-1} in the UV absorption spectrum of meta-fluorochlorobenzene[9]. Further, experimental evidence shows that the C-Cl valence lies at ~650cm^{-1} in the singlet excited electronic state of most of the monosubstituted chlorobenzenes. An increase of ~50 cm^{-1}in ν(C-Cl) is expected as the - OCH_3 unit is lighter than Cl atom.

2) the substituted anisoles have been found to possess a frequency of ~690 cm^{-1} in the excited electronic state which has undoubtedly been assigned to ν(C-OCH_3) valence. The observation of upper state vibration: 672 cm^{-1} in o - fluoroanisole[1], 685 cm^{-1} in meta-methoxyanisole[10], 720 cm^{-1} in p - fluoroanisole[6] and 679 cm^{-1} in meta-chloroanisole[11] are a few examples in support of the 691 cm^{-1} to ν(C - OCH_3) vibration.

The two bands at 37502 and 37628 cm^{-1} are found to involve frequencies 838 and 964 cm^{-1}, respectively, in the upper electronic state. Both these appear with strong intensity and are found to combine with each other and with other fundamentals. Members of the 964 cm^{-1} progression are at 37628, 38596 and 39562 cm^{-1} with decreasing intensity. Its counterpart in the ground state could not be observed as the spectrum did not extend beyond 2787.3 Å. The medium strong infrared band[7] at 1000 cm^{-1} may be correlated with it. Experiments (Table 2) show that a frequency ~950 cm^{-1} occurs in the excited state of the spectra of meta-disubstituted benzenes. It suggest that this frequency is insensitive to substituents and, thus, belongs to totally symmetric carbon ring vibration.

The remarkable feature of C-F stretching vibration in the spectra of fluorinated benzenes has been that it retains its magnitude in both the electronic states and is found to appear in the frequency range 1218 - 1298 cm^{-1}. In the spectrum of meta-fluoroanisole vapour, the C-F stretching vibration is identified at 1277 cm^{-1} (E.S.) and is correlated with strong infrared[7] band 1280 cm^{-1}. The excited state vibration 155 cm^{-1} may be correlated to the ground state vibration 225 cm^{-1}. The 155 cm^{-1} occurs with strong intensity and combines with few vibrations indicating, thus, its non-sym-

TABLE 1

ABSORPTION BANDS OF META-FLUOROANISOLE MOLECULE IN VAPOUR PHASE

Position of the band νvac	Intensity 150 cm 80°C	 75 cm 30°C	Separation from the 0-0 Transition	Assignment
1	2	3	4	5
35866	w		-798	0-734-70
35900	vw		-764	0-583-96-80
35930	ms		-734	0-734
35985	w		-679	0-583-96
35998	w		-666	0-2(330),0-583-80
36037	vw		-627	0-583-43
36081	ms		-583	0-583
36132	mw		-532	0-2(225)-80
36165	vw		-499	0-2(225)-43
36221	ms		-443	0-2(225)
36253	w		-411	0-330-80
36280	vw		-384	0-225-2(80)
36307	vw		-357	0-225-96-43
36334	ms		-330	0-330
36348	w		-316	0-225-96
36360	w		-304	0-225-80
36373		w	-291	0-225-70
36391		mw	-273	0-225-43
36409		ms	-255	0-2(80)-96
36439		s	-225	0-225
36475		s	-189	0-2(96)
36494		s	-170	0-96-70;0-96-80
36506		s	-158	0-2(80)
36526		s	-138	0-2(70),0-96-43
36568		vs	-96	0-96
36584		vs	-80	0-80;0-583+509
36594		vs	-70	0-70;0-225+155
36621		sb	-43	0-43;0-734+691
36664		vvs	0	0- 0 Transition

contd.

Table 1 (contd.)

1	2	3	4	5
36686		w	+22	
36717		vs	+53	0+155-96
36731		vs	+67	0+155-80
36755		vs	+91	0+155-70
36766		w	+102	0+838-734;0+691-583
36775		s	+111	0+155-43
36801		ms	+137	0+217-80
36809		ms	+145	0+217-70
36819		vvs	+155	0+155
36831		w	+167	0+217-43
36850		vw	+186	0+509-330
36881		s	+217	0+217
36906		mw	+242	0+217+22
36964		wbd	+300	0+2(155)
36985		mw	+321	0+509-2(96)
37012		mw	+348	0+509-2(80)
37048		vw	+384	0+964-583
37074		w	+410	0+509-96
37096		w	+432	0+2(217);0+509-80
37129		mw	+465	0+509-43;0+691-225
37155		ms	+491	0+691-2(96)
37173		s	+509	0+509
37198		mw	+534	0+509+22
37220		s	+556	0+691-96-43
37256		vs	+592	0+691-96
37288		vs	+624	0+691-70
37315		s	+651	0+691-43
37355		vvs	+691	0+691
37376		w	+712	0+691+22
37404		s	+740	0+838-96
37415		s	+751	0+838-80
37436		s	+772	0+838-70;0+964-2(96)

contd.

Table 1 (contd.)

1	2	3	4	5
37460		ms	+796	0+838-43
37469		s	+805	0+964-2(80)
37502		vs	+838	0+838
37515		ms	+851	0+691+155
37529		vs	+865	0+964-96
37542		vs	+878	0+964-80
37557		vs	+893	0+964-70
37576		sb	+912	0+964-43;0+691+217
37604		ms	+940	0+1277-330
37628		vvs	+964	0+964
37645		w	+981	0+964+22
37675		ms	+1011	0+2(509);0+838+217-43
37693		w	+1029	0+964+155-96
37720		s	+1056	0+838+217;0+1277-225
37736		mw	+1072	0+964+155-43
37752		mw	+1088	0+1277-2(96)
37767		mw	+1103	0+964+217-80
37780		s	+1116	0+964+155
37809		vvw	+1145	0+1277-96-43; 0+1277-2(70)
37826		vvw	+1162	0+2(691)-225
37843		w	+1179	0+1277-96;0+964+217
37872		w	+1208	0+1277-70;0+691+509
37892		mw	+1228	0+1277-43
37909		ms	+1245	0+2(691)-2(70)
37941		s	+1277	0+1277
37975		s	+1311	0+2(691)-70
37996		ms	+1332	0+2(691)-43
38014		w	+1350	0+838+509
38042		vs	+1378	0+2(691)
38074		mw	+1410	0+2(691)+22
38104		ms	+1440	0+838+691-96, 0+1277+155
38135		ms	+1471	0+964+509

contd.

Table 1 (contd.)

1	2	3	4	5
38158		w	+1494	0+838+691-43;0+1277+217
38194		s	+1530	0+838+691
38208		vw	+1544	0+838+691+22
38247		ms	+1583	0+964+691-70
38272		w	+1608	0+2(838)-70;0+264+691+43 0+2(691)+217
38312		vs	+1648	0+964+691
38341		ms	+1677	0+2(838)
38366		ms	+1702	0+964+838-96
38392		ms	+1728	0+964+838-70
38421		mw	+1757	0+964+838-43
38434		vvw	+1770	0+1277+691-2(96)
38472		s	+1808	0+964+838
38500		mw	+1836	0+2(964)-96
38535		mw	+1871	0+1277+691-96
38570		mw	+1906	0+1277+691-70
38596		ms	+1932	0+2(964)
38634		w	+1970	0+1277+691
38685		mwb	+2021	0+3(691)-43
38739		msb	+2075	0+3(691)
38759		vvw	+2095	0+3(691)+22
38841		mw	+2177	0+1277+964-70
38858		vw	+2194	0+1277+964-43
38891		w	+2227	0+2(691)+838; 0+3(691)+155
38911		w	+2247	0+1277+964
38949		w	+2285	0+2(691)+964-70; 0+3(691)+217
39005		ms	+2341	0+2(691)+964
39033		w	+2369	0+2(838)+691
39061		vvw	+2397	0+2(838)+691+22; 0+2(691)+2(509)
39095		vw	+2431	0+2(964)+509

contd.

Table 1 (contd.)

1	2	3	4	5
39113		mw	+2449	0+2(1277)-96
39162		w	+2498	0+838+691+964
39221		w	+2557	0+2(1277)
39264		vw	+2600	0+2(691)+1277-70;0+3(838)
39321		w	+2657	0+2(691)+1277
39354		vvw	+2690	0+3(964)-2(96)
39394		vvw	+2730	0+4(691)-43
39428		w	+2764	0+4(691);0+2(964)+838; 0+2(1277)+217
39462		vvw	+2798	0+3(964)-96
39562		mw	+2898	0+3(964);0+3(691)+838
39586		wbd	+2922	0+691+964+1277
39721		mw	+3057	0+2(691)+2(838); 0+2(1277)+691-2(96)
39818		w	+3154	0+2(1277)+691-96
39849		vw	+3185	0+2(1277)+691-70
39910		w	+3246	0+2(1277)+691
39967		vvw	+3303	0+2(691)+2(964)

Notations used are: vvs = very very strong, vs = very strong, s = strong, ms = medium strong, w = weak, mw = medium weak, vw = very weak, vvw = very very weak, b = broad and d = diffuse.

TABLE 2

Value of Carbon ring vibration in meta-disubstituted benzenes.

Molecule	Ground State (cm^{-1})	Excited State (cm^{-1})	Reference
m - Chloroanisole	996	950	11
m - Chlorobenzonitrile	995(IR)	966	11
m - Fluorophenol	-	976	12
m - Difluorobenzene	1014	967	13
m - Fluorochlorobenzene	1007	966	9
m - Bromophenol	995	969	14
m - Fluoroanisole	1000(IR)	964	This work

IR = infrared

metric nature. A frequency of this order in the ground state has been found in the spectra of para-fluoroanisole - 244 cm^{-1} ($p = 0.6$) in Raman[3], 236 cm^{-1} in absorption[5] and 220 cm^{-1} in fluorescence[4] and emission[4]. Similar frequencies in the ground electronic state at 222 cm^{-1} (E.S. = 185 cm^{-1}) and 228 cm^{-1} (E.S. = 158 cm^{-1}) in the absorption spectra of meta-chloroanisole[11] and meta-bromoanisole[11] have also been observed and, in each case, it has been attributed to $C-OCH_3$ out of plane bending vibration.

Close to the 0-0 transition, satellite bands at separations of 43, 70, 80 and 96 cm^{-1} towards red of the 0,0 band have also been observed. Of these, the last three occur as 1x70, 2x70; 1x80, 2x80; 1x96 and 2x96 with many of the prominent bands. Each of these satellite bands can be ascribed to a difference frequency which occurs between the ground state vibration and the same vibration in the excited state i.e. 1-1 type transition (Table 1).

The shifts in benzene transition on substitution of -F and $-OCH_3$ groups are -1473, 1425 and 2930 cm^{-1} for o-, m- and p- fluoroanisoles which is in the order p - > o- >m-. A similar observation was also reported in the case of chloroanilines[10] and fluoroanilines[15]. Regarding the relative positions of origins of the electronic transitions in ortho and meta isomers, the fluoroanilines and fluoroanisoles exhibit, closely, similar behaviour. The shifts of the 0,0 band observed in anisole upon substitution of the fluorine atom in ortho-, meta- and para positions are towards the violet for both the ortho and meta compounds in the order m- > o- and towards the red for the para compound. This feature, observed also in fluoroanilines, is attributed to the high electronegative nature of fluorine atom.

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