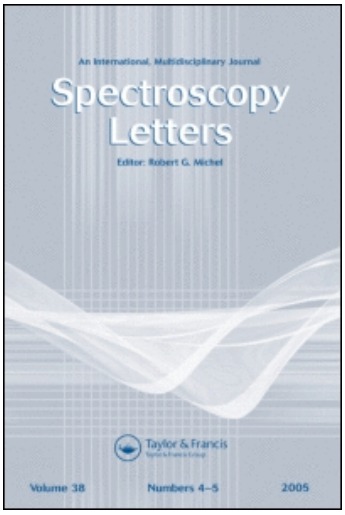

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Electronic Absorption Spectra of Some Fluoroaminotoluenes

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To cite this Article Singh, S. J.(1976) 'Electronic Absorption Spectra of Some Fluoroaminotoluenes', Spectroscopy Letters, 9: 6, 377 — 390
To link to this Article: DOI: 10.1080/00387017608067447
URL: http://dx.doi.org/10.1080/00387017608067447

SPECTROSCOPY LETTERS, 9(6), 377-390 (1976)

ELECTRONIC ABSORPTION SPECTRA OF SOME FLUOROAMINOTOLUENES

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Abstract

The near ultraviolet absorption spectra of 2-fluoro-5-amino-; 3-fluoro-4-amino-, 3-fluoro-6-amino- and 4-fluoro-2-aminotoluene have been investigated in vapour phase. The strongest band appearing at 2887.5 Å (34621 cm^{-1}), 2966.1 Å (33704 cm^{-1}), 3026.7 Å (33029 cm^{-1}) and 2891.4 Å (34575 cm^{-1}) in the respective molecules has been identified as the 0,0 band. All the bands have been analysed in terms of some ground and excited state fundamentals. The assignment of the fundamental frequencies to the probable modes of vibration have also been discussed.

Introduction

It has been established that 2880 Å band system of aniline is a bathochromically shifted secondary band system of benzene (around 2600 Å) and not due to a conjugation as suggested by Klevens and Platt[1].

The further substitution of CH_3 group in the ring would again modify the effect of NH_2 group substitution on the benzene spectra. Spectral studies of such types of molecules in which CH_3 and NH_2 both groups are present together (toluidine) have been done by a number of workers[2,3,4]. Biswas[5] has studied the change in absorption spectra from vapour to liquid to solid at 90°K, of the three isomers of toluidine. When the substances were liquified the narrow bands obtained in the vapour phase were replaced by the extended broad bands. These broad bands persists down to 90°K when the liquid were solidified. Recently the study of the electronic absorption spectra of o-toluidine in vapour phase has been done by D.K. Ghose[6].

However, no detailed study of the absorption spectra of halogenated toluidines seems to have been made. With the view of studying 0,0 band shift and the modification of the vibrational frequencies in such molecules the present work has been under taken. This

paper comprises work of the investigation of the electronic absorption spectrum of 2-fluoro-5-amino-; 3-fluoro-4-amino-; 3-fluoro-6-amino- and 4-fluoro-2-aminotoluene (hereafter referred as 2F5AT, 3F4AT, 3F6AT and 4F2AT respectively) in vapour phase.

Experimental Procedure

The spectra of these molecules have been photographed on medium quartz spectrograph on Kodak B10 and Illford N30 plates using slit width of 30 . The absorption column of length 100, 150 and 200 cm were used over a varying temperature ranging from 20 to 100°C. Hydrogen discharge lamp was used as source of contineous radiation. Iron arc spectrum has been used as the standard spectrum for comparison. The observed bands have been measured on Hilger's comparator having least count of .001 mm. Pure chemicals obtained from M/S K. Light Laboratories, England were used as such.

Results

The general range of absorption in the molecules of present study lies in the region 2700 - 3000 Å. The bands are in general diffuse and are correct to a measurement of 10 cm^{-1}. The strongest band at 2887.5 Å (34621 cm^{-1}) in 2F5AT, 2966.1 Å (33704 cm^{-1}) in 3F4AT,

3026.7 Å (33029 cm^{-1}) in 3F6AT and 2891.4 Å (34575 cm^{-1}) in 4F2AT has been identified as the 0,0 band. Separations of the some of the intense bands from 0,0 band on both side of it agree with the frequencies of the infrared[7]. These have been taken as the ground and excited state fundamental frequencies. The entire spectrum have been explained on the basis of the these ground and excited state fundamentals (Table 1-4). The assignment of these fundamental to the probable modes of vibration has been presented in table 5.

Discussions

Assuming NH_2 and CH_3 group each as single mass points C_s point group may be ascribed to all these molecules. This point group having only one element of symmetry, i.e. molecular plane, contains two types of vibrations (i) symmetric and (ii) antisymmetric to it. The A_{1g} — B_{2u} forbidden transition of benzene will transform to an allowed transition[13] A' - A' with the transition moment lying in the plane of the molecule. It is, therefore, expected that the strongest band on the longer wavelength side will be 0-0 band in each molecule. On both side of the 0-0 band a number of bands have appeared under different condition of temperature and pressure due to their different Boltzman factors. These have been

explained in terms of fundamentals, their combination and overtones.

Carbon Vibration: In the spectrum of benzene there are only two totally symmetric vibrations. But in the present case their number has increased to 21. This means that only totally symmetric vibration will mostly appear in the spectrum. The results of infrared spectra have been used to facilitate the analysis of ultraviolet absorption spectrum.

Excited state fundamental vibrations 750, 680, 786 768 and 727 cm^{-1} appear strongly in the electronic spectra of 2F5AT, 3F4AT, 3F6AT and 4F2AT respectively. Most of these are traced upto two quantas. Combinations of these excited state fundamentals are also found in their respective spectrograms. In the absence of the corresponding ground state values in the ultraviolet these excited state vibrations have been correlated with infrared[7] frequencies of the respective molecules. In view of the intensity, combinability and available literature[8-10] these vibrations have been assigned to the ring breathing mode corresponding to A_{1g} (992 cm^{-1}) of benzene.

In the spectrum of 2F5AT the weak band at 33578 cm^{-1} is due to fundamental frequency of 1043 cm^{-1} in ground state. A few combination of this with other ground state fundamentals have also been observed. Corresponding to this vibration no band on the shorter wavelength side of the 0-0

TABLE 1 ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF 2-FLUORO-5-AMINOTOLUENE

Band position cm^{-1}	Intensity*	Shift from 0,0 band cm^{-1}	Assignment
32311	vw	0-2310	0-1258-1043
32559	vw	0-2062	0-804-1258
32792	vw	0-1829	0-571-1258
32935	vw	0-1686	0-429-1258
33011	vw	0-1610	0-2x804
33144	w	0-1477	0-429-1043
33363	mb	0-1258	0-1258
33403	vw	0-1218	0-1258+36
33578	wb	0-1043	0-1043
33761	w	0-860	0-804-50
33817	mb	0-804	0-804
33861	vw	0-760	0-804+36
33996	w	0-625	0-571-50
34050	wb	0-571	0-571
34192	vw	0-429	0-429
34281	vw	0-340	0-293-50
34328	w	0-293	0-293
34383	w	0-238	0-238
34423	vw	0-198	0-238+36
34515	w	0-100	0-2x50
34571	w	0-50	0-50 (0-804+750)
34621	vs	0-0	0-0
34657	wb	0+36	0+36
34692	w	0+71	0+71, 0+2x36
34733	w	0+112	0+71+36
34797	w	0+176	0+282-2x50
34858	m	0+237	0+282-50
34903	s	0+282	0+282
34947	w	0+326	0+282+36
35006	w	0+385	0+489-2x50
35054	m	0+433	0+489-50
35110	s	0+489	0+489
35147	w	0+526	0+489+36
35186	wb	0+565	0+489+71
35279	wb	0+658	0+750-2x50
35330	msd	0+709	0+750-50
35371	s	0+750	0+750
35411	w	0+790	0+750+36
35443	w	0+822	0+750+71
35482	wd	0+861	0+750+36+71
35583	w	0+932	0+2x489-50
35598	m	0+977	0+489x2

Continued...

Table 1 Continued

Band Position cm^{-1}	Intensity*	Shift from 0,0 band cm^{-1}	Assignment
35637	w	0+1016	0+2x489+36
35670	w	0+1049	0+2x489+71
35708	w	0+1087	0+2x489+36+71
35766	m	0+1145	0+489+750-2x50
35806	m	0+1185	0+489+750-50
35860	m	0+1239	0+489+750
35937	w	0+1316	0+489+750+71
36016	wb	0+1395	0+2x750-2x50
36064	wb	0+1443	0+2x750-50
36123	md	0+1502	0+2x750
36157	w	0+1536	0+2x750+36
36349	w	0+1728	0+2x489+750
36610	w	0+1989	0+2x750+489

TABLE 2 ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF 3-FLUORO-4-AMINOTOLUENE.

Band Position cm^{-1}	Intensity*	Shift from 0,0 band cm^{-1}	Assignment
33465	wb	0-239	0-2x116
33588	mb	0-116	0-116
33666	sb	0-38	0-38
33704	sb	0-0	0-0
33768	mb	0+64	0+64
33822	mb	0+118	0+2x64
33885	mb	0+181	0+181
33967	msb	0+263	0+263
34085	mb	0+381	0+381
34154	wb	0+450	0+381+64
34209	wb	0+505	0+381+2x64
34260	wb	0+556	0+556
34334	mb	0+680	0+680
34564	wb	0+860	0+680+181
34654	msb	0+950	0+680+263
34765	msb	0+1061	0+381+680
34936	mb	0+1232	0+1232
35057	wb	0+1353	0+2x680
35308	wb	0+1604	0+381+1232
35495	wb	0+1799	0+556+1232

TABLE 3 ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF 3-FLUORO-6-AMINOTOLUENE.

Band position cm^{-1}	Intensity*	Shift from 0,0 band cm^{-1}	Assignment
32881	w	0-148	0-96-2x26
32933	m	0-96	0-96
33003	ms	0-26	0-26
33029	vs	0-0	0-0
33079	ms	0+50	0+50
33131	w	0+102	0+2x50
33224	vw	0+195	0+222-26
33251	ms	0+222	0+222
33333	m	0+304	0+304
33386	w	0+356	0+304+50
33446	m	0+417	0+446-26
33475	m	0+446	0+446
33644	w	0+615	0+2x304
33704	vw	0+675	0+768-96
33768	vw	0+739	0+768-26
33796	m	0+768	0+768
34026	w	0+997	0+768+222
34137	w	0+1108	0+1213-96
34242	m	0+1213	0+1213
34294	vw	0+1265	0+1213+50
34339	vw	0+1310	0+1213+2x50
34458	vw	0+1429	0+1213+222

band has been observed. This vibration, correlated with infrared[7] value at 1035 cm^{-1} has been assigned to the carbon trigonal bending mode.

Under C_s symmetry the two component of doubly degenerate vibration e_{2g} (608 cm^{-1}) of benzene will appear separately. In the present investigation the pair of intense excited state vibrations at (282 and 489 cm^{-1}),

TABLE 4 ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF 4-FLUORO-2-AMINOTOLUENE.

Band position cm^{-1}	Intensity*	Shift from 0,0 band cm^{-1}	Assignment
34206	w	0-369	0-369
34309	w	0-266	0-266
34365	vw	0-210	0-266+64
34392	vw	0-183	0-2x91
34437	w	0-138	0-2x65
34484	vw	0-91	0-91 (0-825+727)
34510	w	0-65	0-65
34526	m	0-49	0-49
34575	vs	0-0	0-0
34597	ms	0+22	0+22 (0+288-266)
34619	ms	0+44	0+2x22
34639	mw	0+64	0+64
34735	vw	0+160	0+288-2x65
34768	vw	0+193	0+288-91
34805	vw	0+230	0+288-65
34823	w	0+248	0+288-49
34863	ms	0+288	0+288
34909	vw	0+334	0+456-2x65
34965	vw	0+390	0+456-65
35031	ms	0+456	0+456
35055	vw	0+480	0+456+22
35077	vw	0+502	0+456+2x22
35100	vw	0+525	0+456+64
35167	vw	0+592	0+727-2x65
35228	mw	0+653	0+727-65
35302	ms	0+727	0+727
35747	vw	0+1175	0+727+456
36025	mw	0+1450	0+2x727

(381 and 556 cm^{-1}), (304 and 446 cm^{-1}) and (288 and 456 cm^{-1}) in 2F5AT.

3F4AT, 3F6AT and 4F2AT respectively are found to account for large number of bands. These vibrations are in good agreement with the observed infrared frequencies.

TABLE 5 CORRELATION OF THE FUNDAMENTAL VIBRATIONAL FREQUENCIES OF FLUOROAMINOTOLUENES IN INFRARED AND ULTRAVIOLET SPECTRA AND THEIR ASSIGNMENT TO THE PROBABLE MODES OF VIBRATION

2F5AT			3F4AT			3F6AT			4F2AT			Modes of vibration
I.R.	G.S.	E.S.	I.R.	G.S.	E.S.	I.R.	G.S.	E.S.	I.R.	G.S.	E.S.	
-	-	-	-	-	-	-	148	-	-	-	-	C-CH_3 o.p. bending
-	238	-	-	239	181	-	-	222	-	266	-	C-F o.p. pending
-	293	-	-	-	263	-	-	-	-	-	-	
415	429	282	-	-	381	-	-	304	-	369	288)	Component of e_{2g}(608 cm^{-1})
560	571	489	570	-	556	555	-	446	535	-	456)	
800	804	750	805	-	680	805	-	768	825	-	727	Ring breathing
1035	1043	-	-	-	-	-	-	-	-	-	-	C-C-C trigonal bending
1250	1258	-	1270	-	1232	1270	-	1213	-	-	-	C-F stretching

G.S = Ground State, E.S. = Excited State.

The correlation of these frequencies with the infrared value is only tentative. The assignment of these vibrations to the components of e_{2g} (608 cm^{-1}) is in fair agreement with those made in case of other trisubstituted benzenes.[11,12,14]

Substituent Vibrations: The ground and excited state bands at 0,0 - 1258 cm^{-1} in 2F5AT and at 0,0 1232 cm^{-1} in 3F4AT and 0,0 1213 cm^{-1} in 3F6AT combine with other vibrational frequencies to explain large number of bands of the system. These bands have been assigned to C-F stretching mode in accordance with the previous literature on fluorinated aromatics.[12,15,22]

Similarly on the basis of the available data on fluorinated benzenes[19-22] ground state fundamental at 238 cm^{-1} in 2F5AT and at 266 cm^{-1} in 4F2AT, excited state fundamental 181 cm^{-1} with its ground state counterpart at 239 cm^{-1} in 3F4AT and excited state fundamental at 222 cm^{-1} in 3F6AT have been assigned as C-F nonplanar bending vibrations. The bands at 50 cm^{-1} in 2F5AT, 38 cm^{-1} in 3F6AT and 49 and 65 cm^{-1} in 4F2AT involving small shifts towards the longer wavelength side of the 0,0 band have been identified to represent 'v-v transition' where as the band at 36, 64, 50 and 22 cm^{-1} towards the shorter wavelength side of 0,0 band in the respective molecules have been assigned as due to 'v-v' transition'.

The comparison of 0,0 band of the molecules of present study with aniline[23], o-m-p-fluoroanilines[26], toluene[24] o-m-p-fluorotoluenes[25] (Table 6) shows that band system of anilines have appreciably been shifted by the substitution of CH_3 group in the ring.

TABLE 6 COMPARISON OF 0,0 BAND OF THE MOLECULES OF PRESENT STUDY WITH FLUORINATED ANILINES AND TOLUENES

Molecules	Position of 0,0 band cm^{-1}	Reference
Toluene	37480	24
o-fluorotoluene	37576	25
m-fluorotoluene	37398	
p-fluorotoluene	36876	
Aniline	34032	23
o-fluoroaniline	34586	
m-fluoroaniline	34615	
p-fluoroaniline	32654	
2-fluoro-5-aminotoluene	34621	Present work
3-fluoro-4-aminotoluene	33704	
3-fluoro-6-aminotoluene	33029	
4-fluoro-2-aminotoluene	34575	

Acknowledgement: The author is very much thankful to Prof. Nitish K. Sanyal for providing necessary facilities and to Dr. S.M. Pandey for helpful discussions.

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Received: 8-25-75

Accepted: 4-21-76