

Raman and infrared spectra of m-fluoroaniline

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Raman spectrum of m-Fluoroaniline molecule has been recorded using Argon laser source. Infrared spectrum of the same molecule in the liquid state has been recorded on Perkin-Elmer 521 infrared spectrophotometer in the region 250-4000 cm^{-1} . Vibrational frequencies observed in both the spectra have been correlated and assigned to various probable modes of vibration assuming C_s symmetry for the molecule.

1. INTRODUCTION

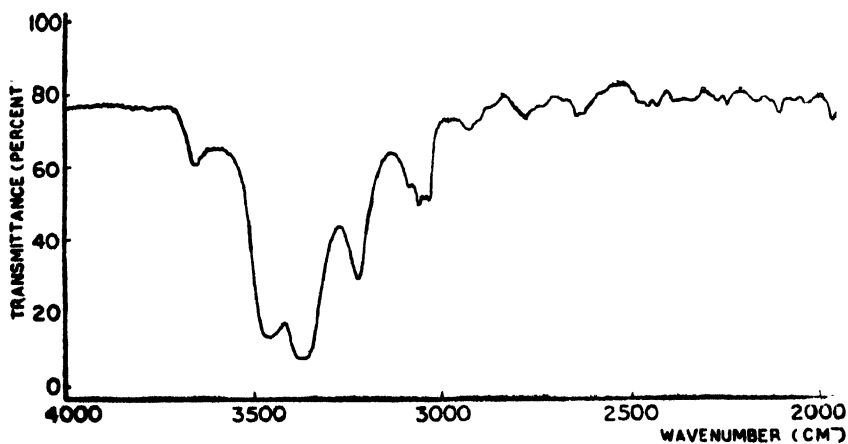
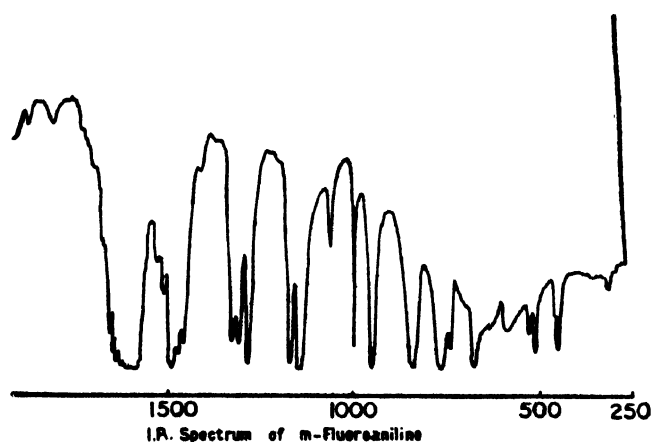
The ultra-violet absorption spectra of isomeric fluoroanilines in the vapour phase were studied by M. A. Shashidhar⁽¹⁾ and K. S. Rao. The ultraviolet absorption spectrum of m-fluoroaniline molecule in vapour was studied by us⁽²⁾ in detail. The emission spectrum of m-fluoroaniline in the vapour phase was recorded and studied for by us⁽³⁾. The infrared spectra of isomeric fluoroanilines in the liquid state were investigated by M. A. Shashidhar *et al*⁽⁴⁾ in the region 650-4000 cm^{-1} only. Interpolated Raman spectrum for m-fluoroaniline molecule has been reported by Kohlrausch *et al*⁽⁵⁾. In the present work Raman spectrum of m-Fluoroaniline has been recorded for using Argon laser source. Depolarization ratios of Raman lines have been calculated by the intensities of lines at perpendicular polarizations. With the help of the depolarization ratios we are able to confirm the exact symmetry of normal mode of vibration. Infrared spectrum of this molecule in liquid state has also been recorded in the region 250-4000 cm^{-1} vibrational frequencies on the basis of depolarization ratios of Raman lines.

2. EXPERIMENTAL PROCEDURE

The Raman spectrum of m-fluoroaniline was taken in the liquid state in a $1 \times 1 \times 5$ cm fused silica cell. The source was a CRL argon laser operating at 4880 Å with a power of about 700 mW. A Spex 1400 double monochromator and EMI 6256 photomultiplier were used with photoncounting detection. The two polarized components of the scattered light were measured by using a Polaroid HN-22 analyzer in the scattered beam and recording the spectra of the light polarised parallel and perpendicular to the polarization vector of the incident light, which was fixed perpendicular to the optical axis of the spectrometer.

Infrared spectrum of m-fluoroaniline molecule in liquid state was recorded on Perkin-Elmer 521 grating infrared spectrophotometer. Liquid was kept in a CSBr cell of thickness 0.025 mm. Scantime was 32 minutes.

Vibrational frequencies observed in Raman and Infrared spectra of m-fluoroaniline and their probable assignments have been given in table 1. Infrared spectrum of m-fluoroaniline has been shown in Figure I.



3. RESULTS AND DISCUSSION

m-fluoroaniline molecule belongs to C_s point group having the plane of the molecule as the only element of symmetry. In this case there are two types of probable vibrations namely a' and a'' . a' vibrations are totally symmetric

Table 1. Raman and infrared vibrational frequencies of m-fluoroaniline and their probable assignments

Raman frequencies in cm^{-1}	Depolarization ratio	Infrared frequencies in cm^{-1}	Intensity	Assignment
251.7	.73	—	—	a'' C-F bending o.p.
324.7	.85	315	3	a'' C-C bending o.p.
468.6	.71	452	5	a'' C-C bending o.p.
		460	sh	
518.4	.77	515	5	a'' C-C bending o.p.
538.9	.23	530	3	a' C-C- bending i.p.
610.5	.20	590	2.5 b	a' C-C bending i.p.
		640	2	A' 2 X 315
		675	5	
741.5	.03	740	3	a' C-F bending i.p.
765.9	dep	765	6 b	a'' C-H bending o.p.
859.2	dep	840	6 b	a'' C-H bending o.p.
952.7	polarized	950	7	a fundamental
998.8	.08	1000.0	1	a' C-C stretching
1064.5	.41	1060	4	a' C-H bending i.p.
1105.4	.80			a'' N-H bending o.p.
1146.6	.66	1145	7	a' C-H bending i.p.
1171.0	.20	1170	6	a' C-H bending i.p.
1285.1	.06	1284	7	a' C-F stretching
1316.1	.12	1310	4	a' C-N stretching
1330.3	.21	1328	4	a' C-H bending i.p.
1371.99(W)				a' C-C stretching
1409.8 (W)		1412	2	a' C1C stretching
1466.4 (W)		1460	5	A'' 1145 + 315
1477.4 (W)		1475	6	2 X 741.5 A'
1499.0 (W)		1490	6	a' C-C stretching
		1500	sh	
		1512	3	A'' 1000 + 515
		1530	2	A' 1000 + 530
1598.3	polarized	1590	7	a' N-H bending i.p.
		1610	W	

Table 1 (Contd.)

Raman frequencies in cm^{-1}	Depolarization ratio	Infrared frequencies in cm^{-1}	Intensity	Assignment	
1620.6	.54	1625	W	a' C-C stretching	
		1640	W		
		1650	W		
		1655	W		
		1670	sh		
		1675	Weak		1000 + 675
		1685	sh		A' 2 X 840
		1700	sh		
		1815	2		
		1885	2		A' 1145 + 740
		1920	3		A' 1170 + 740
		1950	1		A' 1000 + 950
		2095	1		A' 1145 + 950
		2232	1		A' 1284 + 950
		2425	1		A' 1598 + 840
		2450	1		A' 1284 + 1170
		2615	sh		
		2635	1		A' 2 X 1315
		2770	1		A' 1598 + 1170
		2925	2 b		A' 1598 + 1315
2986.9	polarized		A' 2 X 1490		
3035.6	.18	3030		a' C-H stretching	
		3045			
3067.2	.69	3060			
3086.6	.13	3088		a' C-H stretching	
3226.3	polarized	3222	5	A' 1620 + 1598	
3383.1	polarized	3375	7	a' N-H stretching	
		3468	5	a' N-H stretching	
		3655	strong		

s = shoulder
 W = Weak
 s = strong
 p = polarized
 dep = depolarized
 b = broad

and give rise to polarized Raman lines whereas a'' vibrations are antisymmetric and give rise to depolarized Raman lines. The analysis of the bands and the assignment of the fundamental frequencies have been done mainly on the basis of depolarization ratios of Raman lines which have been calculated with the help of the intensities of Raman lines in perpendicular directions.

C-H stretching Frequencies

There are six C-H stretching frequencies in benzene with the following modes of vibration 3062 (a_{1g}), 3060 (b_{1u}), 3047 (e_{2g}), and 3080 (e_{1u}): the last two frequencies are doubly degenerate. In the case of disubstituted benzenes only four C-H stretching frequencies are expected as the other two frequencies would depend upon the mass and nature of the substituents. Out of these four frequencies only two frequencies at 3030 & 3088 cm^{-1} have been assigned to C-H stretching mode of vibration. The values of these two frequencies are 3035 and 3086 cm^{-1} in Raman spectrum. Both Raman lines are polarized.

C-H bending modes

The C-H bendings modes in substituted benzenes occur in two different frequency ranges 1000–1300 cm^{-1} (in-plane bending modes) and 750–1000 cm^{-1} (out-of-plane bending modes). The six C-H in-plane bending modes are derived from a_{2g} (1340), b_{2u} (1152), e_{2g} (1178) and e_{1u} (1037) modes of benzene. Corresponding to these six C-H in-plane bending modes only four are expected to be observed in disubstituted benzenes. Four frequencies at 1060, 1145, 1170 and 1328 cm^{-1} are observed in the infrared spectrum of *m*-fluoroaniline. Corresponding Raman frequencies are 1064, 1146, 1171 and 1330 cm^{-1} . All the four Raman lines corresponding to C-H in-plane mode of vibration are polarized. This interpretation finds support from the infrared spectrum of *m*-chloroaniline in which 1978, 1166, and 1298 and 1314 cm^{-1} vibrations have been assigned to C-H in-plane bending mode by Singh⁽⁹⁾.

In the present case two bands at 765 and 840 cm^{-1} in the infrared spectrum have been assigned to C-H out-of plane bending mode of vibration. Its values in Raman spectrum are 765 and 859 cm^{-1} . Both these Raman lines are depolarized. One vibration 952 cm^{-1} in Raman spectrum and 950 cm^{-1} in infrared spectrum may be assigned to C-H out-of plane bending mode of vibration. But Raman line at 952 cm^{-1} is totally polarized. Therefore, this vibration at 950 cm^{-1} has not been assigned to C-H out-of plane antisymmetric mode of vibration. However, this vibration has been taken as a fundamental vibration.

Ring stretching modes

The four carbon stretching modes of benzene namely, e_2 (1956), e_{1u} (1485), b_{2u} (1310) and a_{1g} (992) are expected to give rise to six carbon stretching vibrations in disubstituted benzenes. In the present case the vibrational frequencies 1000, 1371, 1409, 1490 and 1620 cm^{-1} have been assigned to C-C stretching mode of vibration. The frequency at 1000 cm^{-1} is also called as a *ring breathing* vibration corresponding to a_{1g} (992) mode in benzene.

C-F stretching mode

The infrared spectra of a number of fluorinated benzenes have been studied by Ferguson *et al.*^(7,8). They have assigned the frequency 1250 cm^{-1} to C-F stretching mode of vibration. In analogy to these assignments, the strong band at 1284 cm^{-1} in infrared spectrum and 1286 cm^{-1} in Raman spectrum have been assigned to C-F stretching mode of vibration. This Raman line is completely polarized.

Vibrations of C-NH₂ group

The N-H stretching frequencies are generally observed in the region 3300–3500 cm^{-1} . Evans⁽⁹⁾ has assigned two intense bands at 3360 and 3440 cm^{-1} to the two N-H vibrations in NH₂ group. Therefore, the frequencies 3375 and 3468 cm^{-1} observed in the infrared spectrum of *m*-fluoroaniline have been attributed to the N-H stretching mode of vibration. In the Raman spectrum only one polarized Raman frequency of 3386 cm^{-1} corresponding to N-H stretching mode of vibration has been observed.

The infrared band at 1310 cm^{-1} has been taken to represent the C-N stretching mode of vibration corresponding to totally symmetric a' species. Corresponding Raman frequency is 1316 cm^{-1} and completely polarized.

The infrared band at 1590 cm^{-1} and Raman frequency 1598 cm^{-1} polarized have been assigned to N-H in-plane bending mode of vibration. The same mode of vibration in aniline molecule has been assigned at 1618 cm^{-1} .

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