

Vibrational studies of trifluoromethyl benzene derivatives : II 5-amino-2-fluoro and 5-amino-2-chloro benzotrifluorides

R K Yadav and N P Singh*

Department of Physics, Udai Pratap (Autonomous) College,
Varanasi-221 002, India

and

R A Yadav

Department of Physics, Banaras Hindu University,
Varanasi-221 005, India

E-mail : rayadav@banaras.ernet.in

Received 21 November 2002, accepted 3 June 2003

Abstract Raman spectra of 5-amino-2-fluoro and 5-amino-2-chloro benzotrifluorides have been recorded in the liquid phase on a Jobin Yvon Ramanor HG.2S and a Spex 1403 spectrometers in the spectral range 100-4000 cm^{-1} . Polarisation measurement for the observed Raman lines has also been carried out. Infrared spectra of these two compounds have been recorded in the spectral range 200-4000 cm^{-1} on a Perkin Elmer 783 and on an FTIR model Cygnus-100 (Mattson Co.) spectrometers. Assuming C_{2v} point group symmetry for these molecules, vibrational assignments for the observed frequencies have been proposed. Out of the 45 expected normal modes, 43 could be assigned on the basis of the observed frequencies directly and 2 are estimated from the assignments of overtone/combination bands.

Keywords : Raman and IR spectra, vibrational frequencies, normal modes, 5-amino-2-fluoro-and 5-amino-2-chloro benzotrifluorides

PACS Nos. : 33.20.Ea, 33.20.Fb, 33.20.Tp

1. Introduction

Some of the vibrational modes of benzene are substituent sensitive. To understand this, the vibrational study of substituted benzenes is desirable. Ample literature is available on mono and di-substituted benzenes [1,2]. However, on tri-substituted benzenes, such studies are limited. In an effort to study the vibrational spectra of tri-substituted benzenes, the vibrational spectra of 2-amino-5-chloro and 2-amino-5-bromo benzotrifluorides were reported [3]. The present work is in continuation of the above work and it deals with the recording of the Raman spectra together with the measurement of the depolarisation ratios of the Raman lines and infrared spectra and vibrational interpretation of the observed frequencies for 5-amino-2-fluoro and 5-amino-2-chloro benzotrifluorides (here after called as 5A2FB and 5A2CB). To the best of our information,

spectral studies on these molecules are not reported in the literature.

2. Experimental

5A2FB and 5A2CB were purchased from the Sigma Chemical Co. (U.S.A.). 5A2FB forms a colorless liquid at room temperature while 5A2CB compound is a colorless solid with melting point $\sim 70^\circ\text{C}$.

Polarized Raman spectrum of 5A2FB was recorded at room temperature in the range 100-4000 cm^{-1} in liquid phase on a Jobin Yvon Ramanor HG.2S spectrometer and on a Spex 1403 monochromator. To record the Raman spectrum of 5A2CB, the sample cell was placed on a metal plate and its temperature was raised till the sample had melted completely. The Raman spectrum of this molten sample was recorded. The 4880A⁰ line of an Ar⁺ laser was used as the source of excitation. The Raman

*Corresponding Author

spectrometers were calibrated with the Raman spectra of CHCl_3 and CCl_4 .

Infrared spectrum of 5A2FB has been recorded in the liquid phase in the range 200-4000 cm^{-1} on a Perkin-Elmer 783 spectrometer by placing the liquid between two CsI plates. IR spectrum of 5A2CB was recorded in nujol mull. FTIR spectra of the two compounds have been recorded in the range 400-4000 cm^{-1} on an FTIR spectrometer model Cygnus-100 (Mattson Co.). The IR spectrometers were calibrated with the spectrum of a thin film of polystyrene. The accuracy of the measurements was estimated to be within $\pm 3 \text{ cm}^{-1}$ and the resolution was better than 2 cm^{-1} throughout the entire range for both the spectra.

3. Results and discussion

Raman (Figures 1 and 2) and infrared (Figures 3 and 4) spectra of 5A2FB and 5A2CB have been reproduced here. In the absence of any structural information for these molecules, C_s point group symmetry has been assumed to interpret the vibrational spectra. All the atoms excepting the two F atoms, are taken to be coplanar while the two F atoms are taken to be symmetrically below and above the plane of all other atoms. 5A2FB and 5A2CB are 17 atomic molecules and hence, these have 45 normal modes of vibrations distributed between the two species a' and a'' as,

Phenyl ring	$21a' + 9a''$
CF_3 group	$5a' + 4a''$
NH_3 group	$4a' + 2a''$

The detailed description of the phenyl ring modes is well known and that of the CF_3 and NH_3 groups modes is given earlier [3]. The observed Raman and IR frequencies, their relative intensities and depolarization ratios of the Raman lines and assignments of the fundamental, overtone and combination bands for 5A2FB and 5A2CB have been collected in Tables 1 and 2 respectively. The discussion has been divided into four parts as :

Table 1. Vibrational assignments of IR and Raman bands for 5A2FB.

IR bands	FTIR bands	Raman lines		Proposed assignments	Species
		Pure liquid	Pure liquid		
			a		
			b		
				130 (100, 0.26)	β (C- CF_3) (9b) a'
				167 (11, 0.46)	2×90 A'
					γ (C- NH_2) (10a) a''
260 (2)	260 (5)		278 (mw)	276 (26, 0.23)	τ (NH_2) a''
	270 (8)				$130 + 2 \times 90$ A'
290 (2)	290 (11)				γ (CF) (17b) a''
318 (6)	315 (17)		322 (w)	315 (10, 0.46)	δ_s (CF_3) a'
330 (11)	331 (20)		335 (w)	336 (9, 0.41)	ρ_1 (CF_3) a'
355 (13)	355 (17)				β (C- NH_2) (15) a'
376 (10)	375 (15)		379 (mw)	377 (26, 0.31)	ρ_2 (CF_3) a''
402 (11)	400 (12)				ϕ (CCCC) (16b) a''
424 (8)	422 (13)				β (C-F) (18b) a'
470 (30)	470 (29)	469 (32)	470 (s)	469 (67, 0.20)	δ_{as} (CF_3) a'
505 (50)	495 (36)	493 (40)	493 (W)	492 (9, 0.41)	δ_{as} (CF_3) a''
530 (54)	532 (47)	534 (50)			α (CCC) (6b) a'
585 (37)	580 (31)	585 (30)	587 (w)	584 (7, 0.30)	ϕ (CCCC) (16a) a''
608 (23)	610 (32)				$530 + 90$ A'
	625 (34)	626 (32)			α (CCC) (6a) a'
664 (23)	665 (34)	667 (20)	667 (w)	666 (14, 0.21)	ϕ (CCCC) (4) a''
690 (16)	690 (27)				ω (NH_2) a''
	720 (25)	712 (20)	723 (w)	722 (4, 0.66)	ν_s (CF_3) a'
742 (18)	745 (27)	748 (20)	750 (vs)	749 (95, 0.17)	α (C-C-C) (12) a'
780 (24)	780 (37)	754 (22)	785 (ms)	781 (41, 0.15)	γ (CH) (11) a''
821 (34)	822 (37)	824 (32)			γ (CH) (17a) a''
870 (28)	870 (40)	872 (27)			ν (C-C) (1) a'
905 (25)	905 (39)	908 (26)	910 (s)	906 (69, 0.17)	γ (CH) (5) a''
940 (17)	940 (5)	940 (18)			ρ (NH_2) a'
1027	1015 (8)				β (CH) (18a) a'
1047 (70)	1046 (48)	1050 (65)	1050 (w)	1047 (16, 0.13)	ν_{as} (CF_3) a'
1125 (100)	1125 (100)	1126 (98)	1120 (w)	1125 (4, 0.51)	β (CH) (9a) a'
		1140 (100)	1139 (w)	1143 (4, 0.51)	ν_{as} (CF_3) a''
1160 (87)	1158 (76)	1159 (80)	1170 (w)	1170 (7, 0.22)	ν (C-F) (7b) a'
1225 (91)	1225 (81)	1229 (85)	1228 (w)	1226 (7, 0.33)	γ (C- NH_2) (13) a'
1258 (91)	1258 (81)	1261 (87)	1271 (mw)	1270 (21, 0.17)	ν (C=C) (14) a'
	1269* (52)	1269 (45)			β (CH) (3) a'
1310 (66)	1308 (41)	1312 (50)			ν (C- CF_3) (7a) a'
1340 (100)	1340 (66)	1337 (80)	1344 (s)	1341 (55, 0.16)	

Table 1. Contd...

IR bands		FTIR bands	Raman lines	Proposed	Species
Pure liquid	CS ₂ solution	Pure liquid	Pure liquid	assignments	
1370 (53)	1370 (40)			781 + 584	A'
1390 (53)	1390 (35)			610 + 780	A"
1400 (47)	1400 (12)			130 + 1270, 1125 + 377	A'
1412 (49)	1410 (14)			1340 + 70	A"
1452 (77)	1450 (57)	1454 (65)	1455 (6, 0.37)	v (C-C) (19b)	a'
1505 (90)	1502 (63)	1503 (85)		v (C-C) (19a)	a'
1512 (94)	1512 (65)	1514 (87)		1140 + 377	A'
1538 (51)	1535 (26)			749 + 781	A"
1552 (49)	1550 (29)			1270 + 276, 1170+377	A'
1572 (45)	1570 (21)			v (C-C) (8b)	a'
1620 (66)	1620 (40)	1621 (67)	1610 (9, 0.33)	v (C-C) (8b)	a'
1632 (67)	1630 (32)	1633 (65)	{ 1630 (13, 0.33) 1658 (3, 0.50) }	FPR between β (NH ₂) and 1260 + 377	a'
1642 (61)	1640 (24)				
1660 (47)				1170 + 492	A"
1668 (49)	1665 (14)			1340 + 330	A'
1680 (49)	1680 (11)			1610 + 70	A"
1695 (53)	1693 (11)			1226 + 469	A'
1712 (50)	1712 (12)			1341 + 377, 1226 + 492, 1125 + 584	A'
1730 (51)	1728 (19)			1143 + 584	A'
1745 (47)	1745 (17)	1737 (40)		720 + 1027	A"
1790 (43)	1790 (11)			1455 + 336	A'
1865 (41)	1836 (12)			1143 + 722	A"
2340 (51)		2341 (50)		1340 + 1027	A'
2850 (63)	2850 (26)			1505 + 1340	A'
2920 (78)	2920 (37)			2 x 1455	A'
2950 (64)	2950 (26)		2960 (7, p)	1340 + 1610	A'
2990 (44)	2990 (12)			2 x 1502	A'
3020 (41)	3021 (11)		3026 (8, 0.36)	v (C-H) (20b)	a'
	3050 (17)	3055 (15)	3047 (11, 0.3)	v (C-H) (20a)	a'
3070 (44)	3070 (16)		3078 (20, 0.29)	v (C-H) (2)	a'
3106 (43)	3090 (15)		3118 (5, 0.43)	1620 + 1505	A'
3218 (50)	3225 (19)	3220 (20)		3078 + 130	A'
			3362 (8)	3026 + 336	A'
3380 (67)				3047 + 336	A'
	3390 (51)	3390 (47)	3393 (7, p)	ν_s (NH ₂)	a'
3480 (66)	3480 (47)	3478 (42)	3488 (s, p)	ν_{as} (NH ₂)	a'
3610 (53)				130 + 3488	A'
3642 (35)				3390 + 260	A"
3670 (51)				3393 + 276	A"
3730 (51)				3393 + 336	A'

 Frequency observed in CCl₄ solution

 Recorded on Spex Raman Spectrometer, due to high level of fluorescence no Raman bands could be recorded above 1350 cm⁻¹.

Recorded on Jobin Yvon Ramanor HG.2S spectrometer

FR : Fermi Resonance

- (i) NH₂ group modes,
- (ii) CF₃ group modes,
- (iii) ring-substituents modes,
- (iv) benzene ring modes.

 (i) NH₂ group modes

Out of the 6 NH₂ group modes, the 4 modes, namely, the two NH₂ stretching (symmetric and anti-symmetric) modes (a'), the NH₂ wagging and the NH₂ torsional modes (a'') are pure group modes and are localized within the NH₂ group. However, the NH₂ scissoring and the NH₂ rocking modes (a') are the modes which interact with the ring modes to some extent. The NH₂ stretching modes have a characteristic spectral range 3200-3500 cm⁻¹ and for the identical NH bonds have magnitudes which satisfy an empirical relation [4]:

$$\nu_s = 345.5 + 0.876 \nu_{as}$$

For the two molecules 5A2FB and 5A2CB, three bands appear in the region 3200-3500 cm⁻¹ around 3200, 3400 and 3500 cm⁻¹, all of which appear to be characteristic of the NH₂ group as these are also present in the IR spectra of 2A5CB and 2A5BB [3].

The frequencies 3390 and 3480 cm⁻¹ of 5A2FB and 3400 and 3490 cm⁻¹ of 5A2CB nicely fit the above relationship and hence, the frequencies 3390 and 3400 cm⁻¹ are assigned to the ν_s mode (a') and 3480 and 3490 cm⁻¹ to the ν_{as} mode (a'). The NH₂ scissoring mode (a') is a mixed mode, although it has a characteristic magnitude in the region 1600-1700 cm⁻¹. In the IR spectra of 5A2FB and 5A2CB, two bands of nearly equal intensities are observed at ~ 1630 and ~ 1640 cm⁻¹ which could be explained to arise due to Fermi resonance between the NH₂ scissoring fundamental (a') and the combination band of the C-NH₂ stretching and the planar C-NH₂ bending modes (a'). The band around 3200 cm⁻¹ could be explained as an overtone band of the NH₂ scissoring fundamental. The remaining 3 modes of the NH₂ group lie

Table 2. Vibrational assignments of IR and Raman bands for 5A2CB.

IR bands		FTIR bands		Raman lines		Proposed assignments	Species
Pure liquid	CS ₂ solution	Pure liquid	Pure liquid	Pure liquid			
				a	b		
				122 (vs)	123 (76, 0.94)	β (C-CF ₃) (9b)	a'
				147 (s)	149 (51, 0.93)	γ (C-Cl) (17b)	a''
					221 (7, 0.81)	γ (C-NH ₂) (10a)	a''
				234 (w)	239 (7, 0.81)	τ (NH ₂)	a''
275 (2)	270(3)					122 + 147	A''
285 (2)						221 + 65	A'
305 (22)	300 (11)				305 (24, 0.92)	δ_s (CF ₃)	a'
328 (13)	320 (9)					221 + 100	A''
				342 (vw)		ρ_1 (CF ₃)	a'
352 (21)	355 (12)				350 (10, 0.68)	ρ_{\perp} (CF ₃)	a''
				366 (w)	368 (6, 1.00)	ϕ (CCCC) (16a)	a''
385 (29)	385 (12)					β (C-NH ₂) (15)	a'
402 (43)	400 (17)			403 (vs)	405 (100, 0.41)	β (C-Cl) (18b)	a'
465 (43)		465 (38)			468 (5, 0.87)	δ_{as} (CF ₃)	a'
523 (57)		534 (50)			530 (13, 0.57)	δ_{as} (CF ₃)	a''
				547 (vw)		402 + 147	A''
570 (46)		569 (46)	564 (w)	563 (8, 0.71)		α (CCC) (6b)	a'
595 (50)	595 (30)					ϕ (CCCC) (16b)	a''
605 (55)						465 + 147	A''
625 (59)		627 (53)	631 (w)	626 (3, 0.60)		α (CCC) (6a)	a'
655 (64)						595 + 65	A'
665 (71)	665 (26)	669 (55)	667 (mw)	668 (24, 0.46)		ν (C-Cl) (76)	a'
690 (39)						ϕ (CCCC) (4)	a''
720 (46)		721 (44)			739 (11, 0.50)	ω (NH ₂)	a''
745 (40)		750 (40)	748 (s)	748 (89, 0.33)		ν_s (CF ₃)	a'
765 (27)						625 + 147	A''
815 (32)						750 + 65	A''
828 (57)						γ (CH) (11)	a''
870 (61)	868 (28)*	871 (45)	870 (vw)			γ (CH) (17a)	a''
898 (49)	900 (13)**	902 (36)	900 (mw)	904 (26, 0.37)		α (CCC) (12)	a'
			917 (w)	918 (12, 0.35)		402 + 523	A''
	930 (3)*						
950 (28)		953 (25)				385 + 570	A'
			964 (6, P)			402 + 570	A'
			1011 (vw)	1005 (3)		γ (CH) (5)	a''
1025 (65)	1030 (31)*	1029 (50)	1026 (ms)	1027 (47, 0.36)		ν (C-C) (1)	a'
			1057 (w)	1057 (7, 0.83)		ρ (NH ₂)	a'
1090 (71)			1086 (w)			β (CH) (18a)	a'
1113 (89)	1115 (49)*	1116 (60)	1113 (mw)	1115 (33, 0.34)		ν_{as} (CF ₃)	a'
1145 (100)	1145 (80)*	1147 (85)	1146 (vw)	1140 (7, p)		β (CH) (9a)	a'

in the spectral region crowded with other modes. The assignments for these modes are presented in Tables 1 and 2.

(ii) CF₃ group modes

The CF₃ group gives rise to a strong characteristic Raman line in the range 700-760 cm⁻¹ and this is assigned to the symmetric CF₃ stretching mode (a') by a number of workers [1-3, 5]. In the present case, strongly polarized Raman lines 750 cm⁻¹ for 5A2FB and 748 cm⁻¹ for 5A2CB observed with strong intensities are assigned to the ν_s (CF₃) mode (a'). The anti-symmetric stretching modes ν_{as} (CF₃) (a' + a'') appear in the region 1100-1200 cm⁻¹. Theoretical calculations [1] place the a'' mode at a higher magnitude than the a' mode. For 5A2FB, two broad bands 1125 and 1160 cm⁻¹ appear strongly in the IR spectra which appear to contain 3 frequencies in the FTIR spectrum as 1126, 1140 and 1159 cm⁻¹. The frequency 1140 cm⁻¹ appears to be a better candidate for the C-H planar bending mode and hence, the frequencies 1126 (a') and 1159 cm⁻¹ (a'') are assigned to the CF₃ anti-symmetric stretching modes. For 5A2CB, these modes are correlated to strong IR bands at 1113 and 1172 cm⁻¹. The C-H planar bending mode (a') in this case is observed at 1145 cm⁻¹ as the strongest IR band. The Raman lines corresponding to all the 3 C-H planar bending modes (a') appear with weak intensities for both the molecules.

The CF₃ deformation (symmetric (a') and anti-symmetric (a'')) and rocking (parallel (a') and perpendicular (a'')) are assigned in the region 200-600 wavenumber [6-11]. A Raman frequency with good intensity is observed in the spectra of CF₃ containing benzene derivatives in the region 300-400 cm⁻¹ which appears to be characteristic frequency of the CF₃ group. This frequency is correlated to the δ_s (CF₃) mode (a') of the CF₃ group by a number of workers [1-3, 8-11]. For 5A2FB and 5A2CB, the frequencies 330 and 305 cm⁻¹ are observed with appreciable intensity and are polarised. These frequencies are assigned to the δ_s (CF₃)

Table 2. Contd..

IR bands Pure liquid	CS ₂ solution	FTIR bands Pure liquid	Raman lines		Proposed assignments	Species					
			Pure liquid								
			a	b							
72 (90)	1172 (74)	1175 (75)	1174 (w) 1232 (vw)	1174 (5, 0.6)	ν_{as} (CF ₃) 1115 + 123	a" A'					
152 (92)	1252 (77)	1256 (75)	1255 (mw) 1282 (vw)	1259 (20, 0.38)	ν (C-NH ₂) (13) ν (C-C) (14)	a' a'					
185 (47)			1305 (vw)		β (CH) (3)	a'					
105 (50)	1302 (29)*				ν (C-CF ₃) (7a)	a'					
132 (91)	1335 (70)	1336 (70)	1334 (mw)	1338 (39, 0.44)	1395 + 65, 1255 + 123	A" A'					
172 (65)	1372 (40)*	1377 (50)	1375 (w) 1404 (w)		1282 + 123, 1255+149, 1172+239	A" A'					
442 (96)	1445 (60)*	1446 (80)	1441 (w)	1443 (7, 0.63)	ν (C-C) (19a)	A'					
460 (45)			1460 (w)		1335 + 123, 1305+149, 1115+350	A' A"					
482 (85)	1483 (76)	1486 (70)	1486 (w)	1488 (10, 0.70)	ν (C-C) (19b)	a'					
500 (27)	1500 (40)				1255+239, 1442+65	A"					
515 (23)	1515 (42)				1145 + 368	A"					
535 (21)	1535 (38)		1538 (vw)		1442 + 100	A"					
550 (22)		1550 (24)	1549 (w) 1568 (w)	1568 (7, p)	1486+65 1443+123, 1255+305	A" A'					
585 (39)		1588 (35)	1584 (W)	1589 (13, 0.66)	ν (C-C) (8a)	a'					
608 (48)		1608 (40)	1067 (mw)	1610 (27, 0.72)	ν (C-C) (8b)	a'					
625 (67)	1622 (52)*	1626 (55)	1623 (mw) 1655 (w) 1664 (w)	1628 (25, 0.66)	Φ FR between β (NH ₂) and 1252+385 1255+405	a' A' A'					
1658 (21)											
1680 (13)							1680 (9)*	1675 (w)	1681 (6, 0.50)	1443+239, 1335+350	A"
1692 (10)	1691 (9)*				1625+65	A"					
1712 (11)	1710 (20)				1588+123, 1305+405, 1255+468	A'					
1743 (12)			1743 (w)		1625+123, 1443+305 1335+405	A'					
			1777 (w)		1625+149, 1335+239	A"					
			1826 (w)		1588+239	A"					
1900 (8)			1901 (w)		1588+305	A'					
2846 (88)	2845 (51)		2840 (w)		1255 + 1588	A'					
2920 (90)	2920 (67)		2926 (w)		1335 + 1588	A'					
				2996 (7, p)	2 x 1488	A'					
				3030 (11, 0.16)	ν (C-H) (20b)	a'					
3052 (30)			3041 (w)	3064 (19, 0.67)	ν (C-H) (20a)	a'					
				3070 (24, 0.39)	ν (C-H) (2)	a'					
3220 (39)		3226 (30)	3225 (w)		3030+2 x 100	A'					
				3243 (5, 1.1)	3490-234	A"					
3340		3350 (2)	3351 (s)		3052 + 305	A'					
				3388 (13, p)	3052 + 342	A'					
3400 (44)	3400 (29)		3395 (w)	3396 (19, p)	ν_s (NH ₂)	a'					
3440 (55)					3030 + 405	A'					
3490 (33)	3490				ν_{as} (NH ₂)	a'					

 Frequency observed in CCl₄ solution

 Recorded on Spex Raman Spectrometer, due to high level of fluorescence no Raman bands could be recorded above 1350 cm⁻¹.

Recorded on Jobin Yvon Ramanor HG.2S spectrometer

FR : Fermi Resonance

mode (a'). The anti-symmetric deformation modes (a' + a'') appear near 500 cm⁻¹; however, $\rho_{||}$ (a') and ρ_{\perp} (a'') appear to have variable magnitudes in CF₃ containing benzenes. In the present case, the mode $\rho_{||}$ is assigned at 355 and 342 cm⁻¹ and the mode ρ_{\perp} is assigned at 402 and 352 cm⁻¹ for 5A2FB and 5A2CB. The torsional mode (a'') of the CF₃ group lies below the spectral ranges presently investigated. It is estimated to be 70 and 65 cm⁻¹ for the molecules 5A2FB and 5A2CB from the assignments of combination bands.

(iii) Ring-substituent modes

There are 9 ring-substituent modes in the present case, namely, the 3 C-NH₂ modes, the 3 C-CF₃ modes and the 3 C-F (Cl) modes. In aniline and its derivatives, the C-NH₂ stretching mode (a') is observed in the range 1150-1300 wavenumber [10, 12]. for 2A5CB and 2A5BB, this mode is observed at ~ 1260 wavenumber [3]. In the present case, the frequencies 1258 and 1252 cm⁻¹ are observed as strong IR bands for 5A2FB and 5A2CB and these have good Raman intensities and are polarised. We assign these frequencies to the C-NH₂ stretching mode (a'). The assignments for the modes γ (C-NH₂) (a'') and β (C-NH₂) (a') are similar to those for 2A5CB and 2A5BB [3] and are given in Tables 1 and 2.

In all compounds with a CF₃ group, a strong IR band is observed in the region 1300-1350 cm⁻¹, the corresponding Raman line being polarised and appearing with good intensity. In a number of cases, this is assigned to the ν (C-CF₃) mode (a'). For 5A2FB, 1340 cm⁻¹ and for 5A2CB, 1332 cm⁻¹ are the frequencies with the above features and hence, these are assigned to the ν (C-CF₃) mode (a'). The planar C-CF₃ bending mode (a') has lowest magnitude amongst the observed modes and is assigned at 131 and 122 cm⁻¹ for 5A2FB and 5A2CB respectively. The γ (C-CF₃) mode (a'') is expected to appear below 100 cm⁻¹, beyond the presently

investigated range. The analysis of the combination bands places this mode at 90 and 100 cm^{-1} for 5A2FB and 5A2CB.

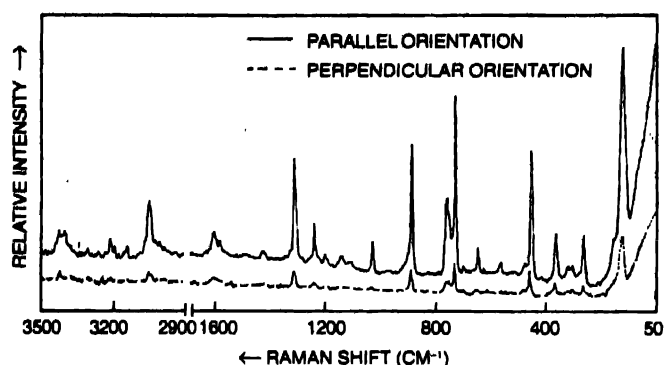


Figure 1. Polarised Raman spectrum of 5-amino-2-fluorobenzotrifluoride.

In benzene derivatives containing F atom(s) on the ring, the C-F stretching frequencies appear in the range of 1000-1400 wavenumber [6-9, 13-15]. The C-F stretching frequency usually appears with strong IR intensity. In the IR spectrum of 5A2FB, the frequency 1225 cm^{-1} appears strongly. The Raman line corresponding to this band at 1226 cm^{-1} is weak and polarised. We assign this frequency to the C-F stretching mode (α'). The planar (α') and non-planar (α'') C-F bending modes are assigned at 470 cm^{-1} and 318 cm^{-1} respectively in agreement with the earlier assignments [6, 7, 13, 15].

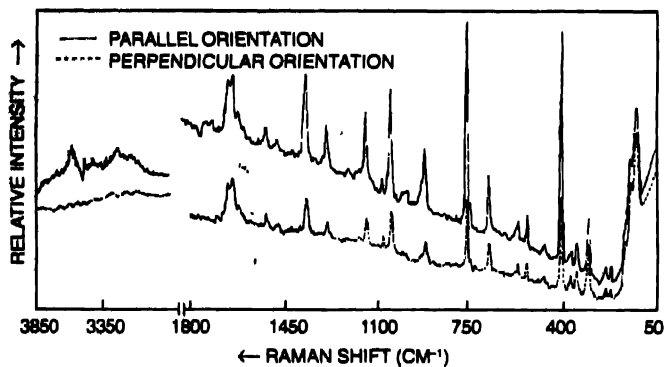


Figure 2. Polarised Raman spectrum of 5-amino-2-chlorobenzotrifluoride.

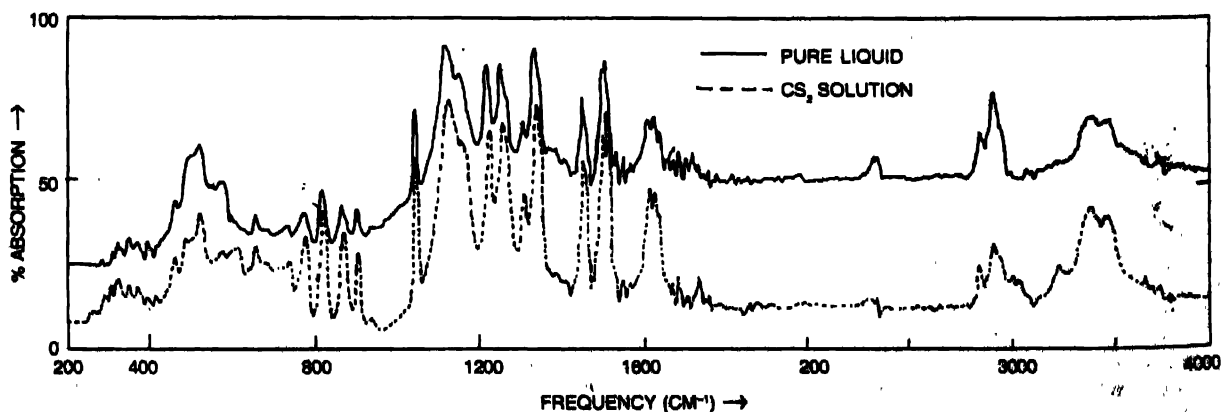


Figure 3. Infrared spectrum of 5-amino-2-fluorobenzotrifluoride.

The C-Cl stretching in Cl containing benzenes on the phenyl carbon is assigned in the region 650-800 cm^{-1} by a number of workers [6, 7, 12, 15, 16]. The frequency 665 cm^{-1} , strongly observed in the IR spectra of 5A2CB is a suitable candidate for the C-Cl stretching mode (α). The planar C-Cl bending (α') is assigned in the region 200-450 cm^{-1} by earlier workers [6,7,12,15,16]. The 402 cm^{-1} frequency appearing with strongest intensity in the Raman spectrum is assigned to the β (C-Cl) mode (α'). The assignment of the out-of-plane C-Cl bending mode (α'') at 147 cm^{-1} is also in agreement with the work reported in literature [6,7,12,15,16].

(iv) Phenyl ring modes

Most of the phenyl ring modes are well-discussed in literature and need no further discussion. However, some of the ring modes are substituent-sensitive and hence, need to be discussed. The ring breathing, the trigonal planar ring bending, the Kekule C-C stretching and the C-H umbrella wagging modes are some of such modes. The ring breathing and trigonal ring bending modes are affected significantly upon substitution for some benzene derivatives. For 2-amino-5-chloro/bromobenzotrifluorides [3], the breathing mode is assigned at ~ 850 cm^{-1} with very good Raman intensity. For a number of benzene derivatives, this mode is observed in the region 1000-1150 cm^{-1} [1,2,5,17-19]. In the present case for 5A2FB, two frequencies namely, 781 and 906 cm^{-1} are observed in the region 700-1100 cm^{-1} which have good Raman intensities and could be assigned to the ring breathing mode. For another set of molecules [3,9-11], this mode is assigned in the region 800-900 cm^{-1} . Varsanyi [17] has proposed the frequency ranges 600-700 and 1020-1110 cm^{-1} for this mode for the classes of molecules to which 5A2FB and 5A2CB belong. For 5A2CB, the two frequencies 904 and 1026 cm^{-1} have good Raman intensities and are polarised. We assign the stronger Raman frequencies i.e. the frequency 906 and 1026 cm^{-1} for the molecules 5A2FB and 5A2CB to the ring breathing mode (α'). The weaker frequencies 781 and 904 cm^{-1} are suitable candidates for the trigonal C-C-C angle bending mode (α').

The Kekule C-C stretching mode (α) which was assigned at $\sim 1290\text{ cm}^{-1}$ earlier [3], is observed to appear at 1269 cm^{-1} for 5A2FB and at 1282 cm^{-1} for 5A2CB. The C-H umbrella wagging mode (α'') in substituted benzenes, corresponds to the mode 11 (673 cm^{-1}) of benzene. For 2A5CB and 2A5BB [3], this mode

Acknowledgment

The authors are grateful to Dr. T. K. Gundoo Rao, RSIC, IIT, Mumbai, for the Raman spectra, the Head, Chemistry Deptt, BHU for the IR spectra and Dr. G. D. Saksena, Spectroscopy Division, BARC, Mumbai for the FTIR spectra.

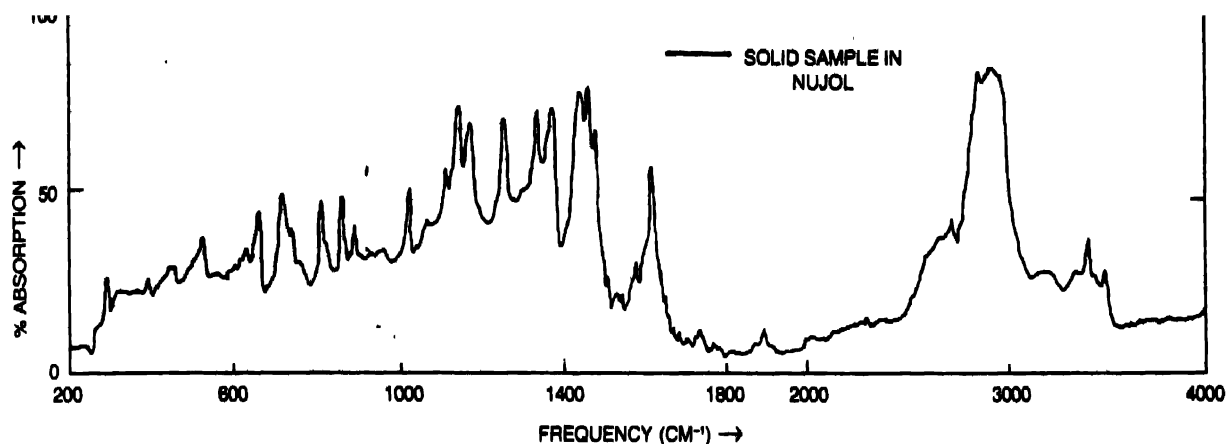


Figure 4. Infrared spectrum of 5 Amino-2chloro benzotrifluoride.

was assigned at $\sim 820\text{ cm}^{-1}$. In the present case, this mode is assigned at ~ 820 and $\sim 830\text{ cm}^{-1}$ for 5A2FB and 5A2CB.

4. Conclusions

All the 45 normal modes could be assigned for both the molecules. The ring breathing mode for 5A2FB is observed to have reduced magnitude (906 cm^{-1}), compared to that for benzene (993 cm^{-1}), whereas for 5A2CB, it is observed to have slightly higher magnitude (1026 cm^{-1}). The trigonal ring bending mode for the two molecules is assigned in the range $700\text{-}900\text{ cm}^{-1}$. The Kekule C = C ring stretching mode and the C-H non-planar umbrella wagging modes are observed in very narrow frequency ranges $1265\text{-}1285\text{ cm}^{-1}$ and $820\text{-}830\text{ cm}^{-1}$. The ν_{as} and ν_s modes of the NH_2 group satisfy the empirical relationship of Bellamy and Williams [4] suggesting the equivalence of two NH bonds. Hence, either the H atoms of the NH_2 group are not involved in the hydrogen bonding or their hydrogen bonding strength is nearly same if these are involved in hydrogen bonding. The scissoring mode of NH_2 group appears to be involved in Fermi resonance for both the molecules and the resonating candidates in two cases are the same i.e. the combination band of the C-NH₂ stretching and the C-NH₂ planar bending modes. The CF_3 group appears to have its characteristics frequencies at ~ 300 , ~ 745 , ~ 1120 , ~ 1170 and $\sim 1335\text{ cm}^{-1}$ which are assigned to the modes δ_s , ν_s , ν_{as} , and $\nu\text{-C-CF}_3$ modes respectively in agreement with the earlier work [1,5,8-12].

References

- [1] R A Yadav *Ph.D. Thesis* (Banaras Hindu University, Varanasi, India) (1983)
- [2] R Shanker *Ph.D. Thesis* (Banaras Hindu University, Varanasi, India) (1991)
- [3] N P Singh and R A Yadav *Indian J. Phys.* **75B** 347 (2001)
- [4] L J Bellamy and R L Williams *Spectrochim. Acta.* **9** 341 (1957)
- [5] N P Singh *Ph.D. Thesis* (Purvanchal University, India) (1994)
- [6] R D 'Cunha and V B Kartha *Can. J. Spectrosc.* **20** 18 (1975)
- [7] J H S Green and D J Harrison *Spectrochim. Acta* **33A** 837 (1977)
- [8] R A Yadav and I S Singh *Indian J. Pure Appl. Phys.* **20** 677 (1982)
- [9] R A Yadav and I S Singh *Indian J. Phys.* **58B** 536 (1984)
- [10] R A Yadav and I S Singh *Spectrochim. Acta* **41A** 191 (1985)
- [11] R A Yadav and I S Singh *Proc. Indian Acad. Sci. (Chem. Sci.)* **95** 47 (1985)
- [12] G N R Tripathi and J E Katan *J. Chem. Phys.* **20** 1383 (1979)
- [13] B B Lal, K Singh and I S Singh *Curr. Sci.* **42** 627 (1973)
- [14] R A Yadav, I S Singh and O Sala *J. Raman Spectrosc.* **14** 353 (1983)
- [15] P M Rao and G R Rao *J. Raman Spectrosc.* **20** 529 (1989)
- [16] Shyampati, I S Singh and J Shamir *Indian J. Phys.* **51B** 50 (1977)
- [17] G Varsanyi *Vibrational Spectra of Benzene Derivatives* (New York : Wiley) (1969)
- [18] M M Szostak *J. Raman Spectrosc.* **8** 43 (1979)
- [19] J E Katan, K Hanoi and G N R Tripathi *J. Chem. Phys.* **73** 697 (1980)