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Vibrational studies of trifluoromethyl benzene derivatives I : 2-amino, 5-chloro and 2-amino, 5-bromo benzotrifluorides

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Abstract Polarized Raman spectra of 2-amino, 5-chloro and 2-amino, 5-bromo benzotrifluorides have been recorded in the liquid phase on a Yobin Yvon Raman HG 2S spectrometer and a 1403 Spex monochromator in the region 100–4000 cm $^{-1}$. Infrared spectra have been recorded on a Perkin-Elmer-783 and an FTIR-200 spectrometers in the region 200–4000 cm $^{-1}$. Vibrational assignments for the observed Raman and infrared bands have been made assuming C_s point group symmetry It could be possible to assign 43 normal modes for the two molecules on the basis of the observed bands directly. The remaining two modes that lie below 120 cm^{-1} could be assigned using combination and overtone bands.

Keywords IR and Raman spectra, vibrational spectra, fundamental frequencies

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1. Introduction

Vibrational spectra of mono-substituted trifluoromethyl benzene (≡ benzotrifluoride ≡ $C_6H_5.CF_3$) derivatives have been widely studied [1,2]. However, vibrational studies on di-substituted trifluoromethyl benzene derivatives have not been reported in literature so far. Hence, such studies are desirable on di-substituted trifluoromethyl benzene derivatives. The present article deals with the Raman and infrared spectral studies and vibrational assignments for 2-amino, 5-chloro and 2-amino, 5-bromo benzotrifluorides (hereafter referred to as 2-A, 5-CB and 2-A, 5-BB respectively). This work was undertaken to propose consistent vibrational assignments for the normal modes of these two molecules and to study the effects of the amino and Cl/Br groups on the phenyl ring modes and the CF_3 group modes and the effect of the CF_3 group on the NH_2 group modes.

2. Experimental

2-A, 5-CB and 2-A, 5-BB of specpure grade were purchased from the Sigma Chemical Co. (U.S.A.). These compounds form colourless liquid at room temperature and were distilled under vacuum prior to use.

Polarized Raman spectra of the two chemicals were recorded in the neat liquid phase in the region 100–4000 cm $^{-1}$ on a Yobin Yvon Raman HG.2S spectrometer and a Spex-1403 spectrometer using the 4880 A line of Ar^+ laser as the source of excitation. The spectra were calibrated with the spectra of $CHCl_3$ and CCl_4. The infrared spectra in the pure liquid state were recorded in the region 200–4000 cm $^{-1}$ on a Perkin-Elmer-783 spectrometer by placing the liquid between two CsI plates. The spectra were calibrated with the spectrum of a thin film of polystyrene. FTIR spectra of these compounds were recorded in the region 200–4000 cm^{-1} on a FTIR-200 spectrometer. The resolution

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of the Raman spectrometer was better than 2 cm^{-1} and that of the FTIR and the IR spectrometers was better than 3 cm^{-1}.

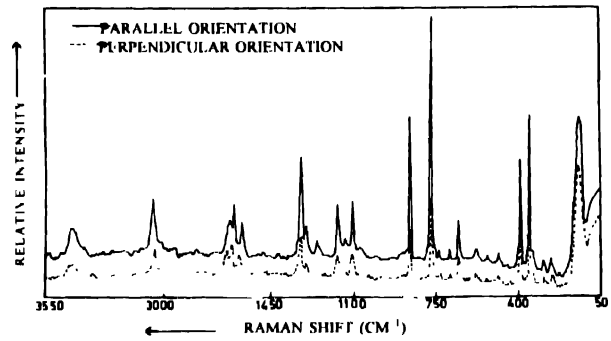

Figure 1. Polarised Raman spectrum of 2-amino-5-chloro benzotrifluoride.

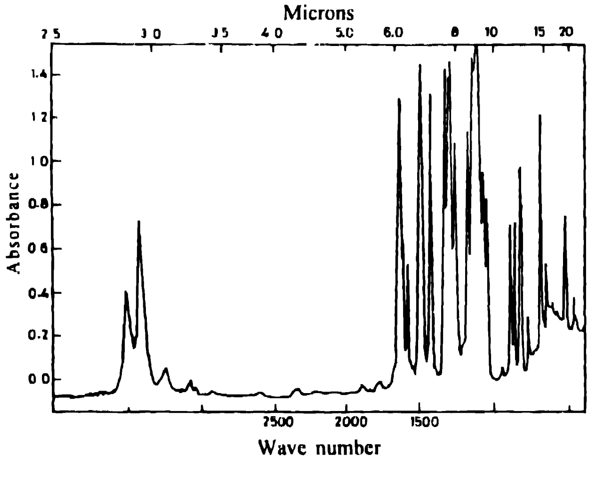

Figure 2. FTIR spectrum of 2-amino-5-chloro benzotrifluoride.

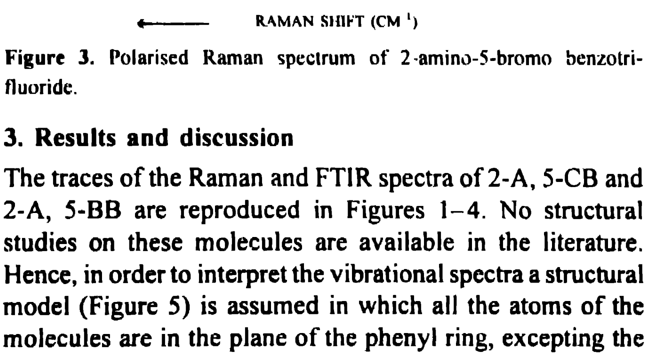

Figure 3. Polarised Raman spectrum of 2-amino-5-bromo benzotrifluoride.

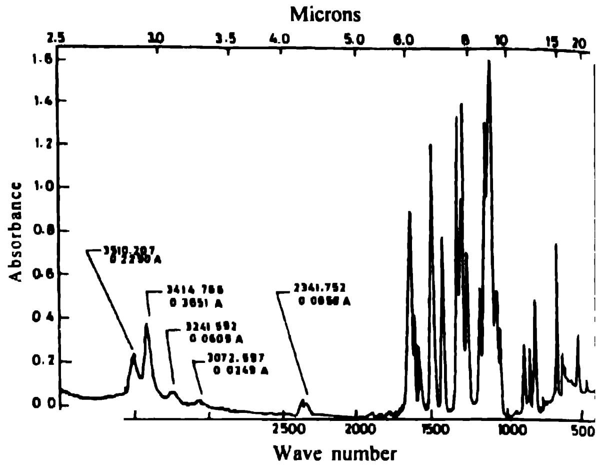

Figure 4. FTIR spectrum of 2-amino-5-bromo benzotrifluoride.

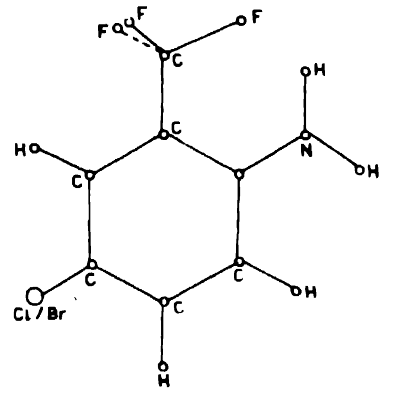

Figure 5. Structural model for 2-A 5-CB and 2-A 5-BB

3. Results and discussion

The traces of the Raman and FTIR spectra of 2-A, 5-CB and 2-A, 5-BB are reproduced in Figures 1–4. No structural studies on these molecules are available in the literature. Hence, in order to interpret the vibrational spectra a structural model (Figure 5) is assumed in which all the atoms of the molecules are in the plane of the phenyl ring, excepting the two F atoms of the CF_3 group, which are positioned symmetrically above and below the phenyl ring plane. Thus, these molecules belong to the C_s point group. The two molecules, being 17-atomic, have 45 normal modes of vibration, distributed between the two species a' and a'' of the C_s point group as : $30a + 15a''$. Out of these 45 modes, 30 belong to the phenyl ring ($21a' + 9a''$), 9 to the CF_3 group ($5a' + 4a''$) and 6 to the NH_2 group ($4a' + 2a''$). The distribution of the normal modes of the phenyl ring is well known and that of the CF_3 and the NH_2 groups is given in Table 1.

Table 1. Normal modes of CF_3 and NH_2 groups

C_s point group	a' species	a'' species
CF_3 group	$\nu_s(CF_3)$ = symmetric stretch	$\nu_{as}(CF_3)$ = antisymmetric stretch
	$\nu_{as}(CF_3)$ = antisymmetric stretch	$\delta_{as}(CF_3)$ = antisymmetric deformation
	$\delta_s(CF_3)$ = symmetric deformation	$\rho_\perp(CF_3)$ = perpendicular rocking
	$\delta_{as}(CF_3)$ = antisymmetric deformation	$\tau(CF_3)$ = torsion
	$\rho_\parallel(CF_3)$ = parallel rocking	
NH_2 group	$\nu_s(NH_2)$ = symmetric stretch	$\omega(NH_2)$ = wagging
	$\nu_{as}(NH_2)$ = antisymmetric stretch	$\tau(NH_2)$ = torsion
	$\beta(NH_2)$ = scissoring	
	$\rho(NH_2)$ = rocking	

Table 2. Vibrational assignments for 2-A 5-CB.

IR		FTIR	RAMAN		Proposed	Species
Pure liquid	CS$_2$ solution	Pure liquid	Pure liquid		Assignments	
cm^{-1}(Rel. Int.)	cm^{-1}(Rel Int)	cm^{-1}(Rel. Int.)	+(cm^{-1})	++(cm^{-1}) (Rel. Int.)		
			133 (s)	131 (66, 0.72)	β (C–CF$_3$)	a'
			159 (ms)	160 (30, 0.67)	γ (C–Cl)	a''
				221 (30, 0.67)	γ (C–NH$_2$)	a''
258 (5)			253 (w)	253 (6, 0.77)	^{5}FR between $\rho_{\parallel}$(CF$_3$) and	
290 (7)	285 (6)		287 (w)	287 (6, 0.67)	combination of γ (C–NH$_2$)	
					and τ (CF$_3$)	a'
304 (10)	303 (7)				0 + 2 × 160	
315 (11)					0 + 221 + 95	
340 (12)			337 (w)	338 (5, 0.91)	τ (NH$_2$)	a''
355 (17)	352 (12)		351 (s)	350 (61, 0.38)	δ_s (CF$_3$)	a'
375 (16)					β (C–NH$_2$)	a'
385 (18)	385 (13)		389 (ms)	387 (43, 0.50)	β (C–Cl)	a'
400 (14)	400 (11)				$\rho_{\perp}$ (CF$_3$)	a''
422 (15)	422 (10)			428 (2, –)	0 + 131 + 287	
464 (26)	461 (19)	466 (28)			ϕ (CCCC)	a''
			479 (w)	479 (5, 0.45)	δ_{as} (CF$_3$)	a'
525 (57)	525 (43)	528 (48)		528 (3, -)	δ_{as} (CF$_3$)	a''
555 (vw)				559 (1)		
580 (32)		577 (14)	577 (w)	577 (5, 0.60)	α (CCC)	a'
598 (33)	594 (24)				ϕ (CCCC)	a''
602 (19)		608 (22)			0 + 350 + 253	
620 (17)					0 + 525 + 95	
635 (18)					0 + 580 + 55	
647 (24)	648 (20)	651 (35)	651 (w)	651 (17, 0.60)	α (CCC)	a'
666 (17)	668 (15)				ϕ (CCCC)	a''
686 (51)	686 (39)	690 (84)	689 (w)	689 (6, 0.45)	ν (C–Cl)	a'
740 (6)			737 (w)	737 (5, 0.55)	ω (NH$_2$)	a''
752 (8)					0 + 160 + 598	
765 (12)	766 (12)	770 (20)	771 (vs)	769 (100, 0.32)	υ_s(CF$_3$)	a'
816 (44)	816 (32)	820 (70)		817 (1, -)	γ (C–H)	a''
860 (31)	859 (22)	862 (49)	861 (s)	860 (58, 0.40)	υ (C–C)	a'
888 (35)	887 (25)	890 (48)			γ (C–H)	a''
	930 (24)*				0 + 350 + 577	
945 (8)	943 (9)	948 (3)	936 (vw)		γ (C–H)	a''
	975 (25)*				0 + 577 + 400	
995 (14)	1002 (30)*			996 (1, –)	α (CCC)	a'
1044 (52)	1045 (36)	1047 (56)	1049 (vw)	1045 (2, –)	ρ (NH$_2$)	a'
1065 (60)	1066 (43)	1069 (63)	1062 (w)	1070 (3, 0.60)	β (C–H)	a'
1110 (100)	1112 (75)	1115 (100)	1109 (mw)	1109 (22, 0.41)	υ_{as} (CF$_3$)	a'
1142 (93)	1142 (70)	1145 (96)	1141 (w)	1141 (4, 0.75)	υ_{as} (CF$_3$)	a''
1170 (73)	1170 (57)	1173 (77)	1171 (mw)	1173 (20, 0.41)	β (C–H)	a'
1205 (38)	1205 (38)		1217 (w)	1211 (2, 0.60)	0 + 1112 + 95	
1255 (69)	1256 (53)	1260 (77)	1259 (w)	1259 (6, 0.73)	υ (C–NH$_2$)	a'
1290 (97)	1290 (72)	1292 (98)	1294 (w)		υ (C–C)	a'
1302 (84)	1302 (63)	1306 (92)	1305 (w)	1308 (8, 0.40)	β (C–H)	a'

Table 2. *(Cont'd.).*

IR		FTIR	RAMAN		Proposed	Species
Pure liquid	CS_2 solution	Pure liquid	Pure liquid		Assignments	
cm^{-1}(Rel. Int.)	cm^{-1}(Rel. Int)	cm^{-1}(Rel. Int.)	+(cm^{-1})	++(cm^{-1}) (Rel Int.)		
1325 (91)	1326 (67)	1327 (94)	1329 (ms)	1328 (37, 0.39)	υ (C–CF_3)	a'
1355 (35)	1355 (20)*		1360 (vw)		0 + 1302 + 55	
1390 (39)	1390 (18)*				0 + 737 + 651	
1415 (57)			1418 (w)		0 + 769 + 651	
1425 (82)	1425 (61)	1428 (91)	1429 (3, –1)		υ (C–C)	a'
1442 (34)			1446 (vw)		0 + 1110 + 338, 0 + 860 + 580	
1451 (35)	1452 (32)*				0 + 769 + 689, 0 + 1325 + 131	
1462 (34)	1465 (40)*				0 + 1302 + 160	
1470 (41)			1471 (w)		0 + 1142 + 338	
1491 (87)	1490 (60)	1493 (95)	1494 (w)	1498 (2, –)	υ (C–C)	a'
1500 (75)	1500 (56)				0 + 1110 + 387	
1535 (34)	1535 (32)		1541 (w)		0 + 2 × 769	
	1562 (46)*		1561 (w)		0 + 1425 + 132	
1576 (48)	1575 (40)	1578 (34)	1579 (w)	1579 (11, 0 54)	υ (C–C)	a'
1611 (58)	1612 (46)	1613 (42)	1611 (mw)	1611 (12, 0.57)	υ (C–C)	a'
1630 (84)	1630 (62)	1633 (90)	1629 (w)	1633 (7, 0 73)	ξFR between $\beta(NH_2)$ and combination of υ(C–NH_2) and β(C–NH_2)	a'
1640 (73)	1640 (56)	1640 (84)	1630 (w)			
1658 (38)	1658 (37)				0 + 1498 + 160	
1680 (35)	1677 (16)*		1684 (w)		0 + 1325 + 355	
1695 (33)	1693 (14)*				0 + 1044 + 651	
1712 (32)	1710 (10)*		1714 (vw)		0 + 1325 + 385	
1745 (29)	1750 (14)(w)				0 + 1611 + 131	
1766 (28)					0 + 1425 + 338	
1778 (25)	1776 (14)*	1776 (vvw)	1781	1772 (3, –)	0 + 1425 + 350	
1840 (24)		1841 (vvw)			0 + 1070 + 769	
1885 (25)	1885 (12)*	1891 (vw)			0 + 1498 + 387	
2330 (27)					0 + 1633 + 689	
2352 (28)		2343 (vw)			0 + 1576 + 769	
2590 (26)	2585 (6)*	2595 (vvw)			0 + 1328 + 1259	
2850 (47)	2850 (44)				2 × 1425	
2920 (65)	2920 (57)	2919 (vvw)	2920 (w)		0 + 1490 + 1429	
2950 (49)	2952 (45)		2950 (w)		1630 + 1325	
				2971 (3, 0.28)	2 × 1493	
3018 (25)					υ (C–H)	a'
3040 (26)			3042 (w)	3041 (w, –)	υ (C–H)	a'
			3050 (w)	3048 (w, –)	0 + 1630 + 1425	
3085 (28)		3077 (w)	3074 (mw)	3076 (22, 0.42)	υ (C–H)	a'
				3160 (2, –)	0 + 2 × 1579	
3230 (27)			3236 (vw)	3236 (w, –)	0 + 1611 + 1630, 0 + 3076 + 160	
		3250 (3)		3250 (w, –)	0+2 × 1630, 0+3076+160, 0+1633+1613	
3418 (63)	3420 (70)	3421 (49)	3418 (mw)	3421 (11, 0.41)	$\upsilon_s(NH_2)$	a'
3508 (50)	3510 (65)	3506 (28)	3506 (w)	3506 (2, –)	$\upsilon_{as}(NH_2)$	a'

* Frequencies observed in CCl_4 solution

\+ Recorded on Spex Raman spectrophotometer

Recorded on Jobin Yvon Ramanor HG.2S spectrophotometer

ξ FR = Fermi resonance.

Table 3. Vibrational assignments for 2-A 5-BB.

IR		FTIR	RAMAN		Proposed	Species
Pure liquid	CS_2 solution	Pure liquid	Pure liquid		Assignments	
cm^{-1}(Rel.Int.)	cm^{-1}(Rel.Int.)	cm^{-1}(Rel.Int.)	+(cm^{-1})	++(cm^{-1}) (Rel.Int)		
			132 (vs)	131 (80, 0 46)	β (C–CF_3)	a'
			219 (w)		γ (C–Br)	a''
			238 (w)	239 (7, 0 44)	γ (C–NH_2)	a''
262 (5)					0 + 2 × 131	
270 (2)			276 (s)	276 (75, 0 33)	β (C–Br)	a'
290 (4)					0 + 219 + 65	
304 (12)	305 (5)		304 (w)		$\rho_{\|\|}$(C–CF_3)	a'
316 (12)			318 (vw)		τ (NH_2)	a''
328 (15)			333 (ms)	333 (26, 0 47)	δ_s(CF_3)	a''
376 (15)					β (C–NH_2)	a'
385 (13)					0 + 131 + 239	
400 (14)	400 (8)		405 (w)	403 (2, –)	$\rho_\perp$(CF_3)	a''
463 (24)	462 (17)	465 (26)	474 (vw)		ϕ (CCCC)	a''
			482 (5, w)	480 (5, 0.57)	δ_{as}(CF_3)	a'
523 (53)	523 (41)	526 (45)			δ_{as}(CF_3)	a''
545 (29)					0 + 481 + 65	
574 (30)		575 (23)	574 (w)	577 (8, 0 36)	α (CCC)	a'
595 (29)	592 (19)				ϕ (CCCC)	a''
605 (20)			604 (w)		0 + 333 + 276	
630 (23)	630 (19)		631 (w)	631 (13, 0.33)	υ (C–Br)	a'
672 (44)	672 (44)	675 (42)	673 (w)		α (CCC)	a'
690 (11)			681 (w)	688 (4, –)	ϕ (CCCC)	a''
			733 (w)	732 (4, 0 60)	ω (NH_2)	a''
760 (12)	760 (2)	764 (14)	763 (vs)	763 (100, 0.23)	υ_s(CF_3)	a'
815 (35)	815 (34)	818 (70)	820 (w)		γ (C–H)	a''
850 (21)	850 (16)	853 (32)	850 (s)	850 (75, 0.23)	υ (C–C)	a'
888 (32)	888 (23)	891 (45)			γ (C–H)	a''
945 (21)	945 (2)	948 (10)	943 (w)		γ (C–H)	a''
998 (27)			998 (w)	996 (3, 0 50)	α (CCC)	a'
1042 (38)	1040 (39)	1044 (40)	1036 (w)		ρ (NH_2)	a'
1066 (49)	1065 (50)	1069 (51)	1070 (w)		β (C–H)	a'
1110 (100)	1110 (100)	1113 (100)	1090 (w)	1099 (27, 0.27)	υ_{as}(CF_3)	a'
			1120 (vw)		0 + 998 + 110	
1140 (89)	1140 (90)	1143 (91)	1143 (w)	1146 (6, 0.50)	υ_{as}(CF_3)	a''
1172 (58)	1170 (55)	1174 (60)	1170 (mw)	1171 (24, 0.24)	β (C–H)	a'
				1209 (5, 0.28)	0 + 1140 + 65	
	1255 (47)*		1256 (vw)		0 + 523 + 732	
1260 (62)	1258 (61)	1262 (70)	1259 (w)	1260 (6, 0 75)	υ (C–NH_2)	a'
1290 (93)	1290 (93)	1292 (93)	1288 (w)		υ (C–C)	a'
1302 (79)	1302 (72)	1306 (90)	1302 (w)	1305 (7, 0.38)	β (C–H)	a'
1325 (83)	1323 (82)	1327 (87)	1324 (ms)	1325 (38, 0.27)	υ (C–CF_3)	a'
1360 (w)			1359 (w)		0 + 1290 + 65	
1382 (w)					0 + 276 + 1110	
1392 (w)				1389 (3, 0.50)	0+763+633, 0+1070+318, 1110+290	
1420 (66)	1420 (65)	1422 (76)	1421 (w)		υ (C–C)	a'

Table 3. *(Cont'd.)*

IR		FTIR	RAMAN		Proposed Assignments	Species
Pure liquid cm^{-1}(Rel. Int.)	CS_2 solution cm^{-1}(Rel Int.)	Pure liquid cm^{-1}(Rel. Int.)	Pure liquid +(cm^{-1})	++(cm^{-1}) (Rel Int.)		
1452 (31)	1450 (w)*		1449 (w)		0 + 763 + 688	
1470 (38)	1468 (35)		1469 (vw)		0 + 333 + 1140	
1490 (72)	1490 (77)	1492 (80)	1488 (w)	1491 (5, p)	υ (C–C)	a'
1502 (46)					0 + 1110 + 400	
1520 (33)	1518 (24)				0 + 850 + 672, 0 + 2 × 763	
1552 (31)	1552 (22)	1559 (32)		1557 (5, 0.57)	0 + 1490 + 65	
1575 (41)	1576 (37)	1579 (w)	1575 (w)	1578 (15, 0.43)	υ (C–C)	a'
1605 (49)	1605 (45)	1607 (33)	1604 (mw)	1605 (23, 0.42)	υ (C–C)	a'
1632 (75)	1630 (72)	1632 (82)	1630 (mw)	1628 (15, 0.40)	$^{\xi}$FR between $\beta(NH_2)$ and combination of $\upsilon(C–NH_2)$ and $\beta(C–NH_2)$	a'
1640 (55)	1649 (51)					
				1661 (4, p)	0 + 2 × 850	
2350 (34)	2350 (22)	2342 (20)			0 + 1302 + 1042	
2860 (53)	2860 (59)				0 + 1605 + 1260	
2920 (60)					0 + 1490 + 1420	
3020 (36)			2998 (w)	2997 (3, p)	υ (C–H)	a'
3060 (34)			3066 (w)	3049 (5, 0.57)	υ (C–H)	a'
3090 (35)		3073 (30)	3083 (mw)	3075 (17, 0.47)	υ (C–H)	a'
3120 (35)			3125		0 + 2 × 1490	
				3196 (1, –)	0 + 1578 + 1605	
		3242 (5)			0+2 × 1628, 0+2997+239, 0+1632+1607	
				3310 (3, –)	0 + 2 × 1632	
3418 (67)	3418 (52)	3415 (50)		3411 (10, 0.35)	$\upsilon_s(NH_2)$	a'
			3476	3480 (3, 0.50)	0 + 3090 + 400	
			3497	3495 (4, p)	0 + 3020 + 480	
3510 (57)	3510 (43)	3510 (30)		3514 (1, –)	$\upsilon_{as}(NH_2)$	a'

*, +, ++, ξ as explained in Table 2

Vibrational assignments have been proposed with the help of vibrational studies dealing with the vibrational modes of the CF_3, NH_2 and mono-halogen substituted benzenes [3–11]. Assignments of the fundamentals, overtones and combination bands of 2-A, 5-CB and 2-A, 5-BB have been presented in Tables 2 and 3 respectively. Vibrational assignments in the present work are discussed under the following four heads : (i) Phenyl ring modes, (ii) C–X (X = Cl/Br, CF_3 and NH_2) group modes, (iii) CF_3 group modes and (iv) NH_2 group modes.

3.1. Phenyl ring modes

Assignments for many of the phenyl ring modes are straightforward and hence need no further discussion. In the following, only a few of the interesting modes are considered. In the Kekule vibrational mode, a ring carbon and the attached hydrogen atoms move in phase, opposite to the neighbouring carbon and the attached hydrogen atoms just like in a scissoring mode. Hence, the C–C bonds of the phenyl ring would be deformed to a very little extent upon substitution and there should be a relatively small change in the magnitude of this mode in substituted benzenes. In the case of 2-A, 5-CB and 2-A, 5-BB, the regions above and below 1300 cm^{-1} are over crowded due to appearance of the C–CF_3 and the C–NH_2 stretching and the C–H in-plane bending modes. Therefore, there is a possibility of interaction as well as overlapping amongst these modes [5]. We have assigned the Kekule mode at ~1290 cm^{-1} for both the molecules. The present assignment for the Kekule mode is in good agreement with earlier assignments proposed by several workers [2,12,13].

Assignment of the ring-breathing mode in benzene derivatives is controversial and has found some place for discussion in almost every article on the vibrational spectra of benzene derivatives. Because of its most symmetric nature, the ring-breathing mode should give rise to an intense

Raman line with a low depolarization ratio like the 992 cm^{-1} frequency of benzene [14]. For *p*-trifluoromethyl benzonitrile [15], *p*-trifluoromethyl benzaldehyde [16] and *p*-trifluoromethyl aniline [11] the ring-breathing mode has been assigned at 811 cm^{-1}, 843 cm^{-1} and 846 cm^{-1} respectively. In the present case for 2-A, 5-CB and 2-A, 5-BB, the frequencies 860 and 850 cm^{-1} are observed as the strongest Raman lines which are strongly polarized. These frequencies are assigned to the ring-breathing mode. The infrared bands corresponding to this mode are observed with medium intensities because under the C_s point group symmetry, the ring-breathing mode is allowed in both the Raman and the IR spectra. The lowering of the magnitude of the ring-breathing mode could be due to its interaction with the substituents modes. The above viewpoint is supported by the work of Shanker *et al* [17]. Assignment for this mode is also in agreement with the assignment of the ring-breathing mode for *p*-chloroaniline [7].

Similar to the ring breathing mode, the C-C-C in plane bending mode (C–C–C trigonal angle bending mode) is also one of the controversial modes in mono-, meta-di-, and 1, 3, 5- tri-substituted benzenes. It has been mentioned during the discussion of the assignment of the ring breathing mode [18] that a group of workers has assigned an intense and strongly polarized Raman line at ~1000 cm^{-1} to the trigonal angle bending mode irrespective of the nature of substituents. Similarly from the force field calculations, Yadav and Singh [11,15,16] have assigned the trigonal angle bending mode near 1000 cm^{-1} for para-substituted benzotrifluorides. In the present case, the frequencies ~1000 cm^{-1} are observed for 2-A, 5-CB and 2-A, 5-BB molecules. These frequencies are assigned to the trigonal angle bending mode.

3.2 C–X (X = Cl/Br, CF_3 and NH_2) group modes :

In benzene derivatives containing a Cl atom, the C–Cl stretching frequency appears in the region 600–800 cm^{-1} [3,5,8]. The frequency 689 cm^{-1} observed with medium strong intensity in the IR spectra and polarized in the Raman spectrum is assigned to the C–Cl stretching mode. The C–Br stretching modes are observed in the region 200–650 cm^{-1} [3,5,19–21]. The frequency at 633 cm^{-1} observed with moderate intensities in both the IR and the Raman spectra is assigned to the C–Br stretching mode. This assignment also finds support from the work of Shyampati *et al* [5].

The C–Cl deformation mode β(C–Cl), with wavenumbers expected below 400 cm^{-1} [8], is rather difficult to assign in 2-A, 5-CB; firstly, because the most Raman spectral lines are weak in the region and secondly, because the IR range does not go beyond 200 cm^{-1}. In the present case, a weak IR band at 385 cm^{-1} with the corresponding medium strong Raman line at 387 cm^{-1} is assigned to the β(C–Cl) mode. Assignment for the β(C–Br) mode is well within the expected range suggested by Varsanyi [20]. A strong frequency in the Raman spectrum at 276 cm^{-1} with weak IR counterpart at 270 cm^{-1} is assigned to the β(C–Br) mode. This assignment is in good agreement with the assignments proposed earlier [5].

For the 2-A, 5-CB molecule, the Raman frequency at the wavenumber 159 cm^{-1} is the only suitable candidate for the out-of-plane C–Cl bending mode. For 2-A, 5-BB, the frequency 219 cm^{-1} observed with weak intensity in the Raman spectrum has been assigned to the C–Br out-of-plane bending modes. These assignments for the C–Cl and C–Br out-of-plane bending modes are well within the expected ranges suggested by Varsanyi [20].

The C–CF_3 stretching mode has been assigned in the range 1300-1360 cm^{-1} in benzene derivatives containing a CF_3 group [1,2,4,9-11,15–18]. In the present case, strong IR bands at 1327 cm^{-1} with medium Raman lines at 1329 and 1324 cm^{-1} are assigned to the C–CF_3 stretching mode for 2-A, 5-CB and 2-A, 5-BB respectively. Force field calculations placed the planar and non-planar C–CF_3 bending modes at ~130 and 100 cm^{-1} [1,11,15,16]. In the present case, the β(C–CF_3) mode is assigned at 133 and 132 cm^{-1} for the two molecules 2-A, 5-CB and 2-A, 5-BB. The non-planar C–CF_3 bending mode could not be observed; however from combination bands, it is estimated to be at 95 and 110 cm^{-1} for both the molecules.

In the present case, the C–NH_2 stretching mode could be assigned at 1260 cm^{-1} whereas the β(C–NH_2) mode is observed at 375 cm^{-1} for both the molecules. The non-planar C–NH_2 bending mode is assigned at 221 and 238 cm^{-1} for 2-A, 5-CB and 2-A, 5-BB. The assignments for the C–NH_2 modes are in good agreement with the reported work [6,12].

3.3. CF_3 group modes :

Under the C_{3v} point group symmetry, the CF_3 group has 3 non-degenerate and 3 doubly-degenerate normal modes of vibration. On reducing the symmetry from C_{3v} to C_s, each of the doubly degenerate mode splits up into two, giving rise to total 9 normal modes of vibration of the CF_3 group in the two molecules under consideration (Table 1).

It has been argued in literature [1,2,11,15,16] that the symmetric CF_3 stretching mode $\nu_s(CF_3)$ appears at a lower magnitude, in the range 700–800 cm^{-1}, compared to its anti-symmetric counterparts - $\nu_{as}(CF_3)$ ($a' + a''$) which appear in the range 1100–1200 cm^{-1}. Moreover, the ν_s mode is observed as a strong Raman line and the ν_{as} modes are observed as strong IR bonds [1,2,11,15,16]. In the present case, the strongest Raman frequencies 770 and 763 cm^{-1} are assigned to the ν_s(CF$_3$) mode for the 2-A, 5-CB and 2-A, 5-BB molecules respectively. The ν_{as} modes are observed at 1115 and 1145 cm^{-1} for 2-A, 5-CB and at 1113 and 1143 cm^{-1} for 2-A, 5-BB. Usually, the two components of the ν_{as} modes ($a' + a''$) are observed to have nearly same magnitude [1]. A frequency different of 30 cm^{-1} between the a' and a'' components of the ν_{as}(CF$_3$) mode, could be correlated to the fact that in the configuration shown in Figure 5, the F atom in the plane of the ring might have intramolecular hydrogen bonding with the H atom of the NH$_2$ group.

Assignments for the symmetric and anti-symmetric ($a' + a''$) deformation modes (δ_s and δ_{as}) and the rocking modes $\rho_{\parallel}$ and $\rho_{\perp}$ in the present case, are in agreement with the assignments reported in literature [1,2,11,15,16]. The magnitude of the CF$_3$ torsional mode lies below the spectral range investigated presently and is estimated from the assignment of combination and overtone bands to be 55 cm^{-1} for 2-A, 5-CB and 65 cm^{-1} for 2-A, 5-BB.

For 2-A, 5-CB the Raman lines 253 and 287 cm^{-1} appears to be similar in all respect. The average 270 cm^{-1} of the two frequencies is assigned to the CF$_3$ rocking ($\rho_{\parallel}$) mode. The origin of the two component wavenumbers 253 and 287 cm^{-1} could be understood in terms of Fermi resonance between the CF$_3$ rocking ($\rho_{\parallel}$) mode and the combination of the γ(C–NH$_2$) and the τ(CF$_3$) modes as 221 + 55 = 276 cm^{-1}.

3.4. NH$_2$ group modes :

The symmetric and anti-symmetric NH$_2$ stretching modes can be easily assigned on account of their characteristic magnitudes. If the two NH bonds of the NH$_2$ group are identical these modes satisfy an empirical relation given by Bellamy and Williams [22] as,

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

where ν_s and ν_{as} are in wavenumber unit. In the present case, the frequencies 3420 and 3418 cm^{-1} are assigned to the ν_s mode and frequencies 3508 and 3510 cm^{-1} to the ν_{as} mode for 2-A, 5-CB and 2-A, 5-BB respectively. It is to be noted that the magnitudes of the ν_s and ν_{as} modes satisfy the above empirical relation suggesting equivalence of the two NH bonds of the NH$_2$ group.

The NH$_2$ scissoring mode appears in the region 1615–1650 cm^{-1} in benzene derivatives containing an NH$_2$ group. In the present case, two strong IR bands are observed at 1630 and 1640 cm^{-1} for both the molecules. These two bands could be correlated to the NH$_2$ scissoring mode. The appearance of doublet might be explained as arising due to a Fermi resonance between the NH$_2$ scissoring mode and the combination of the frequencies 1260 cm^{-1} [ν(C–NH$_2$)] and 375 cm^{-1} [β(C–NH$_2$)]. Assignments for the remaining 3 modes of the NH$_2$ group, namely, ω(NH$_2$), ρ(NH$_2$) and τ(NH$_2$) group are in agreement with the reported work [6,11–13,23] and are given in Tables 2 and 3.

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