

Force Field Calculations for 5-Amino-2- Fluoro- and 5-Amino-2- Chloro Benzotrifluorides

R K Yadav^{a *}, N P Singh^b and R A Yadav^c

^aDepartment of Physics, CMP Degree College, University of Allahabad, Prayagraj - 211004 India

^bDepartment of Physics, Udai Pratap (Autonomous) College, Varanasi - 221002 India

^cDepartment of Physics, Banaras Hindu University, Varanasi - 221005 India

Abstract

Force field calculations have been carried out for 5-amino-2-chloro and 5-amino-2-fluoro benzotrifluorides. As the frequencies of the corresponding modes for the C-Cl and C-F groups do not differ widely the two molecules are assumed to be isotopomers for the purpose of the force field calculations. The calculated and the observed frequencies match nicely for both the molecules. Consistent vibrational assignments have been proposed for the ring modes and the internal modes of the CF₃ and NH₂ groups, based on the potential energy distributions (PEDs), the IR and the Raman intensities and depolarization ratios of the Raman lines.

Key Word : Vibrational frequencies, normal modes, force fields, 5-amino-2-fluoro- and 5-amino-2-chloro-benzotrifluorides

PACS Nos. : 33.2.Ea, 33.20.Fb, 33.20.Tp

Date of Submission: 07-09.2023

Date of acceptance: 20-09-2023

I. Introduction

Vibrational spectra of CF₃-substituted compounds have been extensively studied in the past [1-23]. Vibrational analysis for benzotrifluoride (C₆H₅-CF₃) has been proposed in details by a number of workers [2, 4, 9, 11, 13, 16, 17], D Cunha and Kartha [13] were the first to study the polarized Raman spectrum, liquid and gas-phase IR spectra and the force field calculations for benzotrifluoride and its deuterated derivatives. Green and Harrison [16] have reported the IR (liquid-gas-phase) and Raman (solid-, liquid-and gas-phase) spectra of benzotrifluoride and the polarized Raman and IR spectra of its 9 derivatives (o-, m- and p-X-C₆H₄-CF₃; X = F, Cl and Br) and proposed the vibrational analysis for these molecules. Yadav and Singh studied the IR and Raman spectra and carried out the forced field calculations for p-CF₃-C₆H₄-NH₂ [23], o-, m- and p-CF₃-C₆H₄-CHO [21] and o-, m- and p-CF₃-C₆H₄-CN [22]. These studies provide better understanding regarding the C-CF₃ stretching mode and the internal modes of the CF₃ group.

The vibrational spectra of benzene derivatives containing the NH₂ group have also been studied by a number of workers [16, 24-41]. Studies of the vibrational spectra and force fields of 9 derivatives of aniline (o-, m- and -p-X-C₆H₄-NH₂; X = F, Cl and Br) by Kumpawat *et al.* [36] are helpful in understanding the effect of NH₂ group on the modes of the phenyl ring. Studies made by several other workers [25-29] deal with the vibrational spectra of primary aromatic amines. Bellamy and Williams [24], have carried out a thorough study of the characteristics of the NH₂ group. The earlier studies [25-29] provide information regarding the vibrational frequencies of NH₂ group. Several workers [42-44] have made thorough studies of mono-halogenated benzene compounds. These studies provide good information regarding the vibrational frequencies of C-Cl and C-F groups. From the survey of the literature it appears that work on the vibrational spectra of di-substituted benzotrifluorides is limited to only a few publications [45,46]. However, to the best of our information the force field calculations for di-substituted benzotrifluorides have not been carried out so far.

In the present work the force field calculations have been carried out for 5-amino-2-chloro-and-5-amino-2-fluoro benzotrifluorides (here after called as 5A2CB and 5A2FB respectively) based on the IR and Raman spectra reported earlier [47-53]. The aim of the present study is to (i) make consistent assignment for the ring modes, (ii) study the effect of the positions of the substituents CF₃, NH₂, Cl and F on the ring modes and the internal modes of the substituents themselves, (iii) propose consistent assignments for the internal modes of the CF₃ and NH₂ groups and (iv) determine the force fields for these two molecules.

II. Normal Co-ordinate Calculations

Molecular structures of 5A2CB and 5A2FB are not available in literature and therefore, model structures for these molecules were assumed. In these structures the phenyl ring, the NH₂ group and C and one F atoms of the CF₃ are taken to be co-planar. A local C_{2v} point group symmetry is assumed for the NH₂ group and

similarly, a local C_{3v} point group symmetry is assumed for the CF_3 group. Hence, the remaining two of the three F atoms are placed symmetrically above and below the plane of the ring. The bond length and bond angles are as follows:

$r(CC) = 1.397 \text{ \AA}$, $r(CH) = 1.084 \text{ \AA}$, $r(C-Cl) = 1.750 \text{ \AA}$, $r(C-F) = 1.35 \text{ \AA}$, $r(N-H) = 0.990 \text{ \AA}$, $r(C-CF_3) = 1.481 \text{ \AA}$, $r(C-NH_2) = 1.450 \text{ \AA}$, $\angle CCC = 120^\circ$, $\angle CCX$, $N = H$, Cl , F , NH_2 and $CF_3 = 120^\circ$, $\angle CNH = 119^\circ$, $\angle CCF = \angle CFC = 109^\circ 28'$

The symmetry co-ordinates for the purpose of the force field calculations are constructed from the internal co-ordinates. The symmetry co-ordinates for the phenyl ring part were constructed in the same way as suggested by Whiffen [52], for the CF_3 group as given by Hollestein and Günthard [53] and for the NH_2 group as suggested by Yamaguchi *et al.* [54]. The torsion symmetry co-ordinates for the CF_3 groups were formed by taking average of all the six dihedral angle deformations and similarly, for the NH_2 group by taking average of all the four dihedral angle deformations. To calculate the F- and G-matrices and to perform the normal co-ordinate analysis computer program written by schhatschneider [55] was used.

The frequencies for the C-Cl and C-F groups for the corresponding modes are observed to be quite close. Therefore, in the present calculations the molecules 5A2CB and 5A2FB are assumed to be isotopomers. By doing so, one can determine more force constants. The principal force constants were taken from the work of Kydd [56] for Benzene, Bürger *et al.* [57] for $CF_3-CH=CH-CF_3$, D’Cunha and Kartha [13] for benzotrifluorides, Yamaguchi *et al.* [54] for $NH_2-CO-NH_2$ and Rastogi *et al.* [58] for 2,4-dichlorobenzonitrile. A 70 parameters force field was constructed to calculate the F-matrix of the molecules. The non-diagonal force constants were adjusted by hit and trial method keeping in view the potential energy distributions (PEDs) and agreement between the experimental and calculated frequencies. The diagonal and non-diagonal force constants for the two molecules 5A2FB and 5A2CB are collected in Tables-1 and 2.

Table 1: Valance force constants for 5A2FB

Force Constant No.	Description	Notation [®]	Value [#]	Dispersion [*]
1	C-C stretching	(R)	6.0209	0.0
2	C-CF ₃ stretching	(t ₁)	4.0046	0.0
3	C-H stretching	(s)	5.0488	0.0
4	C-NH ₂ stretching	(t ₂)	5.6099	0.0
5	C-F stretching	(t ₃)	5.5351	0.0
6	C-F(CF ₃) stretching	u	5.0515	0.0
7	N-H stretching	v	6.7458	0.0
8	C-C-C angle bending	α	0.9866	0.0
9	F-C-F angle bending	(α_1)	1.6388	0.0
10	F-C-C angle bending	(α_2)	1.2489	0.0
11	H-N-H angle bending	(α_3)	0.7622	0.0
12	C-N-H angle bending	(α_4)	0.4508	0.0
13	C-CF ₃ o.p.b.	(γ_1)	0.2067	0.0
14	C-H o.p.b.	γ	0.2602	0.0
15	C-NH ₂ o.p.b.	(γ_2)	0.1456	0.0
16	C-F o.p.b.	γ_3	0.3394	0.0
17	NH ₂ wagging	Ω	0.1121	0.0
18	C-C-C-C torsion	Φ	0.1012	0.0
19	CF ₃ torsion	τ_1	0.0055	0.0
20	NH ₂ torsion	τ_2	0.0074	0.0
21	C-CF ₃ i.p.b.	β_1	2.0806	0.0
22	C-H i.p.b.	B	0.9500	0.0
23	C-NH ₂ i.p.b.	β_2	1.5414	0.0
24	C-F i.p.b.	β_3	1.4767	0.0
25	(RR) ^o		0.7080	0.0
26	(RR) ^m		-0.3139	0.0
27	(RR) ^p		0.3405	0.0
28	(SS) ^p		0.0109	0.0
29	(SS) ^m		-0.0010	0.0
30	(SS) ^p		0.0006	0.0
31	t ₁ t ₂		0.0000	0.0
32	t ₁ t ₃		0.0000	0.0
33	t ₂ t ₃		0.0000	0.0
34	uu		2.1186	0.3480
35	vv		-0.0554	0.0
36	($\alpha\alpha$) ^p		-0.0226	0.0
37	($\alpha_1\alpha_1$)		-0.2584	0.2534
38	($\alpha_2\alpha_2$)		0.2704	0.2153
39	($\alpha_3\alpha_4$)		0.1044	0.0

40	$(\alpha_i\alpha_i)$		-0.1343	0.0
41	$(\gamma_1\gamma_2)$		-0.0121	0.0
42	$(\gamma_1\gamma_3)$		0.0094	0.0
43	$(\gamma_2\gamma_3)$		-0.0076	0.0301
44	$(\gamma\gamma)^o$		0.2454	0.0094
45	$(\gamma\gamma)^m$		0.0220	0.0
46	$(\gamma\gamma)^p$		-0.0181	0.0123
47	$(\Phi\Phi)^o$		-0.0200	0.0
48	$\beta_1\beta_2$		0.0261	0.7478
49	$\beta_1\beta_3$		0.5239	0.4319
50	$\beta_2\beta_3$		-0.1078	0.3088
51	$(\beta\beta)^o$		-0.0642	0.0545
52	$(\beta\beta)^m$		0.0152	0.0
53	$(\beta\beta)^p$		-0.0172	0.0854
54	$R_i\alpha_i = R_i\alpha_{i+1}$		-0.0358	0.1573
55	$R_{i+1}\beta_{i+1} = -R_{i+2}\beta_i$		-0.0453	0.0724
56	$R_{i+2}\beta_{i+2} = -R_{i+3}\beta_i$		0.1551	0.0724
57	$R_i\beta_{i+1} = -R_{i+1}\beta_i$		-0.0038	0.0
58	$\alpha_i\beta_{i+1} = -\alpha_i\beta_{i-1}$	$(\beta\equiv\beta)$	-0.2388	0.1426
59	$\alpha_i\beta_{i+1} = -\alpha_i\beta_{i-1}$	$(\beta\equiv\beta_2)$	-0.0405	0.4432
60	$\alpha_i\beta_{i+1} = -\alpha_i\beta_{i-1}$	$(\beta\equiv\beta_3)$	-0.1920	0.4321
61	$\gamma_i\Phi_i = -\gamma_i\Phi_{i+1}$	$(\gamma\equiv\gamma)$	0.0163	0.0
62	$\gamma_i\Phi_i = -\gamma_i\Phi_{i-1}$	$(\gamma\equiv\gamma_2)$	-0.0137	0.0
63	$\gamma_i\Phi_i = -\gamma_i\Phi_{i+1}$	$(\gamma\equiv\gamma_3)$	0.0103	0.0206
64	$(Rt_1)^o$		0.5886	0.4679
65	$(Rt_2)^o$		0.7492	0.4614
66	$(Rt_3)^o$		0.3980	0.4691
67	t_1u		0.3469	0.2422
68	$\alpha_1\alpha_2$		-0.0474	0.1000
69	$\alpha_i\beta_{i+1} = -\alpha_i\beta_{i-1}$	$(\beta\equiv\beta_1)$	0.1334	0.2354
70	$\gamma_i\Phi_{i+1} = -\gamma_i\Phi_{i-1}$	$(\gamma\equiv\gamma_1)$	-0.0003	0.0

@ abbreviations used : o.p.b. – out-of- plane bending; i.p.b – in-plane bending; o, m, p stand for ortho, meta and para interactions, respectively. R_i and α_i stand for R and α , respectively and subscript i represents the position R and α in the ring . The subscript i in β_i represents the position of β in the ring. Similar conditions are applicable to γ_i also.

#The units for force constants are as follows: stretch = m dyn/A°; stretch/ stretch = m dyn /A°; stretch / bend = m dyn; bend = m dyn/A°; bend/bend = m dyn /A°

*The force constants with zero dispersion were kept constants during the final calculation.

Table 2: Valance force constants for 5A2CB

Force Constant No.	Description	Notation [@]	Value [#]	Dispersion [*]
1	C-C stretching	(R)	6.0868	0.0
2	C-CF ₃ stretching	(t ₁)	4.0242	0.0
3	C-H stretching	(s)	5.0353	0.0
4	C-NH ₂ stretching	(t ₂)	5.5887	0.0
5	C-Cl stretching	(t ₃)	3.7457	0.0
6	C-F stretching (CF ₃)	(u)	4.8684	0.0
7	C-F stretching	(v)	6.5365	0.0
8	C-C-C angle bending	α	0.9922	0.0
9	F-C-F angle bending	(α_1)	1.2712	0.0
10	F-C-C angle bending	(α_2)	0.7527	0.0
11	H-N-H angle bending	(α_3)	0.7020	0.0
12	C-N-H angle bending	(α_4)	0.4198	0.0
13	C-CF ₃ o.p.b.	(γ_1)	0.3016	0.0
14	C-H o.p.b.	γ	0.2632	0.0
15	C-NH ₂ o.p.b.	(γ_2)	0.1823	0.0
16	C-Cl o.p.b.	(γ_3)	0.1886	0.0
17	NH ₂ wagging	ω	0.1067	0.0
18	C-C-C-C torsion	Φ	0.0744	0.0
19	CF ₃ torsion	τ_1	0.0038	0.0
20	NH ₂ torsion	τ_2	0.0064	0.0
21	C-CF ₃ i.p.b.	β_1	2.2173	0.0
22	C-H i.p.b.	β	0.9700	0.0
23	C-NH ₂ i.p.b.	β_2	1.6574	0.0
24	C-Cl i.p.b.	β_3	1.2767	0.0
25	(RR) ^o		0.9619	0.0
26	(RR) ^m		-0.3167	0.0
27	(RR) ^p		0.4360	0.0

28	(SS) ^o		0.0154	0.0
29	(SS) ^m		0.0017	0.0
30	(SS) ^p		0.0124	0.0
31	(t ₁ t ₂)		0.0000	0.0
32	(t ₁ t ₃)		0.0000	0.0
33	(t ₂ t ₃)		2.1186	0.0
34	uu		2.1186	0.3480
35	vv		0.0594	0.0
36	(αα) ^o		-0.2389	0.0
37	α ₁ α ₁		0.1364	0.1563
38	α ₂ α ₂		0.6864	0.2403
39	α ₃ α ₄		0.8200	0.0
40	α ₄ α ₄		0.12.90	0.0
41	γ ₁ γ ₂		0.0000	0.0
42	γ ₁ γ ₃		0.0252	0.0
43	γ ₂ γ ₃		0.0000	0.0
44	(γγ) ^o		0.0678	0.1189
45	(γγ) ^m		0.0426	0.4489
46	(γγ) ^p		-0.0619	0.3340
47	(ΦΦ) ^o		0.0000	0.0
48	(β ₁ β ₂)		0.2059	0.5168
49	β ₁ β ₃		0.1723	0.5210
50	β ₂ β ₃		0.1345	0.4446
51	(ββ) ^o		-0.0906	0.1661
52	(β β) ^m		0.0359	0.0
53	(β β) ^p		-0.1190	0.1074
54	R _i α _i = R _i α _{i+1}		0.3034	0.2333
55	R _i β _i = -R _{i+2} β _i		-0.0218	0.1117
56	R _{i+2} β _i = - R _{i+3} β _i		0.0679	0.1451
57	R _i β _i = - R _{i-1} β _i		-0.0940	0.0
58	α _i β _{i+1} = - α _i β _{i-1}	β=β	-0.0554	0.1920
59	α _i β _{i+1} = - α _i β _{i-1}	β=β ₂	-0.0479	0.4089
60	α _i β _{i+1} = - α _i β _{i-1}	β=β ₃	-0.2085	0.5817
61	γ _i Φ _i = -γ _i Φ _{i-1}	(γ≡γ)	-0.0049	0.0000
62	γ ₁ Φ ₁ = -γ ₁ Φ ₁₋₁	(γ≡γ ₂)	0.0000	0.0000
63	γ ₁ Φ ₁ = -γ ₁ Φ ₁₋₁	(γ≡γ ₃)	0.0000	0.0000
64	(Rt ₁) ^o		0.0303	0.8413
65	(Rt ₂) ^o		0.9959	0.9113
66	(Rt ₃) ^o		0.6903	0.4114
67	t ₁ u		0.3489	0.3258
68	α ₁ α ₂		-0.3599	0.1388
69	α _i β _{i+1} = - α _i β _{i-1}	β=β ₁	0.0650	1.0573
70	γ ₁ Φ ₁ = -γ ₁ Φ ₁₋₁	(γ≡γ ₁)	0.0000	0.0000

@ abbreviations used : o.p.b. – out-of- plane bending; i.p.b – in-plane bending; o, m, p stand for ortho, meta and para interactions, respectively. R_i and α_i stand for R and α, respectively and subscript i represents the position R and α in the ring . The subscript i in β_i represents the position of β in the ring. Similar conditions are applicable to γ_i also.

#The units for force constants are as follows: stretch = m dyn/A^o; stretch/ stretch = m dyn /A^o; stretch / bend = m dyn; bend = m dyn/A^o; bend/bend = mdyn /A^o

*The force constants with zero dispersion were kept constants during the final calculation.

III. Result and Discussion

The molecules 5A2CB and 5A2FB belong to the categories 1,2-di-heavy-4-light and 1,4-di-light-2-heavy substituted benzenes, respectively, because the Cl and CF₃ groups are treated as heavy substituents and the NH₂ and F groups are treated as light substituents. The frequency ranges for the phenyl ring modes for these two categories are proposed by Varsanyi [59]. The calculated frequencies, along with their PEDs and the corresponding IR and Raman frequencies (taken from the ref. [47]) and the normal mode assignments are given in Tables-3 and 4 for 5A2FB and 5A2CB, respectively. The discussion of the normal mode assignments can be divided into the following three categories: (i) Phenyl ring and the C(Ph)-X (X / H / CF₃ / NH₂ / Cl / F group modes, (ii) NH₂ group modes and (iii) CF₃ group modes.

Table 3: Observed and calculated fundamental frequencies (cm⁻¹) for 5A2FB

Observed frequencies ^a					Calculated frequencies			
Raman lines		FT-IR bands	Infra red bands		cm ⁻¹	PEDs	Proposed assignments	Species
liquid	liquid	liquid	liquid	CS ₂ solution				
-	3488(s,p)	3478(42)	3480(66)	3480(47)	3513	7(100)	v _{as} (NH ₂)	a'
-	3393(7,p)	3390(47)	-	3390(51)	3367	7(99)	v _s (NH ₂)	a'
-	3078(2,0.29)	-	3070(44)	3070(16)	3053	3(99)	ν(C-H)(2)	a'
-	3047(11,0.3)	3055(15)	-	3050(17)	3049	3(99)	ν(C-H)(20a)	a'
-	3026(8,0.36)	-	3020(41)	3021(11)	3045	3(99)	ν(C-H)(20a)	a'
-	1630(13,0.33)	1633(65)	1632(67)	1630(32)	1662	11(92),12(17),4(11)	β(NH ₂)	a'
-	-	-	1642(61)	1640(24)	1622	a'
-	1610(9,0.33)	1621(67)	1620(66)	1620(w)	1620	1(64),21(10),8(8),5(6)	ν(C=C)8b	a'
-	-	-	1572(45)	1570(21)	1567	1(77),8(9),22(7)	ν(C=C)8a	a'
-	-	1503(85)	1505(90)	1502(63)	1501	1(47),22(37),4(7),5(5)	ν(C=C)19b	a'
-	1455(6,0.37)	1454(65)	1452(77)	1450(57)	1453	1(41),22(27),99(12),24(6),8(5)	ν(C=C)19a	a'
1344(s)	1341(55,0.16)	1337(80)	1340(80)	1340(66)	1356	1(50),6(14),22(10),2(8),9(7),10(6),12(5)	ν(C-CF ₃)7a	a'
-	-	1312(50)	1310(66)	1308(41)	1300	1(59),22(43),2(18),6(9),4(6),8(6)	ν(C-C)14Kekule	a'
-	-	1269(45) (45)	-	1269(52)	1266	22(43),4(6),1(15),5(4)	β(C-H)(3)	a'
1271(mw)	1270(21,0.17)	1261(87)	1258(91)	1258(81)	1247	1(25),6(22),5(17),22(15)	ν(C-F)(13)	a'
1228(w)	1226(7,0.33)	1229(85)	1225(91)	1225(81)	1213	22(37),4(21),6(12),8(7)	ν(C-NH ₂)1	a'
1139(w)	1143(4,0.51)	1140(100)	-	-	1155	22(27),6(26),1(25),8(9)	v _{as} (CF ₃)	a'
1120(w)	1125(4,0.51)	1126(98)	1125(100)	1125(100)	1114	1(42),22(36),6(6)	β(C-H)(18a)	a'
1050(w)	1047(16,0.13)	1050(65)	1047(70)	1046(48)	1050	12(52),1(20)	ρ(NH ₂)	a'
910(s)	906(69,0.1)	908	905(25)	905(39)	893	1(38),22(14),2(9),8(8)	ν(C-C)ring breathing(1)	a'
667	666(14,0.21)	667(20)	664(23)	665(34)	646	8(52),4(12),5(8),2(5)	α(C-C-C)(12)	a'
587(w)	584(7,0.30)	585(30)	585(37)	580(31)	555	9(21),8(14),1(11),10(11),6(67),9(43)	α(C-C-C)6a	a'
493(w)	492(9,0.41)	493(40)	505(50)	495(36)	499	6(67),9(43)	δ _{as} (CF ₃)	a'
470(mw)	469(67,0.20)	469(32)	470(30)	470(29)	480	8(45),1(10),9(9),23(9),10(7),22(6)	β(C-F)9b	a'
379(mw)	377(26,0.31)	-	376(10)	375(15)	392	8(46),23(30),1(8),10(7),22(6)	α(C-C-C)6b	a'
-	-	-	333(11)	331(20)	329	8(41),5(21),1(13),22(8),10(6)	β(C-NH ₂) 9a	a'
278(mw)	276(26,0.23)	-	-	270(8)	278	24(3),10(27),23(14),1(12)	ρ _l (CF ₃)	a'
-	-	-	-	-	188	10(34),8(16),9(13),2(13),21(13),23(9),24(5)	δ _s (CF ₃)	a'
-	130(100,0.26)	-	-	-	131	21(61),10(34),24(27)	β(C-CF ₃)(15)	a'
1170(w)	1170(7,0.22)	1159(80)	1160(87)	1158(76)	1170	6(88),9(28),10(6)	v _{as} (CF ₃)	a''
-	-	940(18)	940(17)	940(5)	950	14(73),18(41)	γ(C-H)(17b)	a''
-	-	872(27)	870(28)	870(40)	879	14(75),18(47)	γ(C-H)(5)	a''
-	-	824(32)	821(34)	822(37)	834	14(68),18(28)	γ(C-H)(11)	a''
723(w)	722(4,0.66)	712(20)	-	720(25)	719	17(92)	ω(NH ₂)	a''
-	-	-	690(19)	690(27)	703	16(32),18(30),13(15),10(7)	Φ(C-C-C-C)(4)	a''
-	-	534(50)	530(54)	532(47)	515	9(31),10(25),13(8),6(7),14(7)	Φ(C-C-C-C)(16a)	a''
-	-	-	-	-	489	6(22),10(23),13(8),10(7),14(5)	δ _{as} (CF ₃)	a''
-	-	-	428(8)	422(13)	434	16(40),18(34),15(15),11(5)	γ(C-NH ₂)10a	a''
-	-	-	353(13)	355(17)	377	20(69),18(10),10(8),14(5)	τ(NH ₂)	a''
-	-	-	-	-	332	18(29),20(26),14(17),15(14),10(5)	γ(C-F)10b	a''
-	-	-	-	-	278	10(32),15(24),18(23),14(5),13(5),	ρ _l (CF ₃)	a''
-	167(11,0.46)	-	-	-	162	18(68),14(10)	Φ(C-C-C-C)(16b)	a''
-	-	-	-	-	124	13(42),18(18),10(17),15(9),14(6),19(91)	γ(C-CF ₃) 17a	a''
-	-	-	-	-	68	19(91),	τ(CF ₃)	a''

Table 4 : Observed and calculated fundamental frequencies (cm⁻¹) for 5A2CB

Observed frequencies ^a					Calculated Frequencies			
Raman line		FTIR bands	IR bands		cm ⁻¹	PEDs ^b	Proposed assignments ^c	Species
Liquid	liquid	liquid	liquid	CS ₂ Solution				
-	-	-	3490(33)	3490(34)	3484	7(100)	v _{as} (NH ₂)	a'
3395(w)	3496(19,p)	-	3400(44)	3400(29)	3396	7(99)	v _s (NH ₂)	a'
-	3070(24,039)	-	-	-	3052	3(99)	ν(C-H) (2)	a'

Force Field Calculations for 5-Amino-2- Fluoro- and 5-Amino-2- Chloro Benzotrifluorides

3041(w)	3064(19,0.67)	-	3052(30)	-	3045	3(99)	v(C-H) (20a)	a'
-	3030(11,0.16)	-	-	-	3041	3(99)	v(C-H) (20b) (20b)	a'
1655(w)	-	-	1658(21)	-	1652	11(88),12(26),4(11)	β (NH ₂)	a'
1623 (m,w)	1628(25,0.66)	1626(55)	1625(67)	1622(52)	1652	'' ''	''	a'
1607 (m,w)	1610(27,0.72)	1608(40)	1608(48)	-	1611	1(67),22(20), 8(8)	v(C=C)(8b)	a'
1658 (m,w)	1668(7,p)	1688(35)	1685(39)	-	1678	1(75),8(9),22(8)	v(C=C)(8a)	a'
1486(w)	1488(10,0.70)	1486(70)	1482(85)	1483(76)	1492	22(42),1(35),2(9)	v(C=C)(19b)	a'
1441(w)	1443(7,0.36)	1446(80)	1442(96)	1445(60)	1430	1(33),22(20),2(12),8(9), 4(8),6(5)	v(C=C)(19a)	a'
1334 (m,w)	1338(19,044)	1336 (70)	1332(91)	1335(70)	1341	22(28),1(21),2(12),8(12), 4(8),6(6)	v(C-CF ₃)(7b)	a'
1282 (v,w)	-	-	1285 (v,w)	-	1269	1(76),22(27),12(22),6(10)	v(C=C)(14) Kekule mode	a'
1255 (m,w)	1259(20,0.38)	1256(75)	1252(92)	1552(70)	1238	4(24),24(15),6(13),2(12), 9(5)	β (C-H)(3)	a'
1146 (v,w)	1140(7,p)	1147(85)	1145 (100)	1145(80)	1171	1(48),6(33),22(26),9(8)	ν_{as} (CF ₃)	a'
1113 (m,w)	1115(33,034)	1116(60)	1113(89)	1115(49)	1136	6(30),5(29), 9(18),4(12), 22(5)	v(C-NH ₂)(13)	a'
1086(w)	-	-	1090(71)	-	1096	6(40),1(32),22(24),9(9)	β (C-H)(18a)	a'
1057(w)	1057(7,0.83)	-	-	-	1064	1(66),22(37)	β (C-H)(18b)	a'
1026 (m,s)	1027(47,0.36)	1029(50)	1025(65)	1030(31)	1026	1(29),22(25),56(13),8(18), 4(7)	α (C-C-C) (12)	a'
1011 (v,w)	1005(3)	-	-	-	1011	12(46),1(28),22(12)	ρ (NH ₂)	a'
900 (m,w)	904(26,0.36)	902(36)	898(49)	900(13)	911	1(49),22(20), 8(6)	v(C-C) ring breathing(1)	a'
748(s)	748(89,0.33)	750(40)	745(40)	-	729	8(24),1(18),2(12), 6(11)	ν_s (CF ₃)	a'
667(m,w)	668(24,0.46)	669(55)	665(71)	665(26)	658	5(26),8(26),4(18)	v(C-Cl)(7a)	a'
564(w)	563(8,0.71)	569(46)	570(46)	-	580	8(35),2(23),10(44),6(7), 1(5)	α (C-C-C) (6a)	a'
-	530(13,0.57)	534(50)	529(57)	-	560	23(20),1(19),21(11),24(10), 6(6)	β (C-NH ₂)(9b)	a'
-	468(5,0.87)	465(38)	465(43)	-	469	9(64),6(25)	δ_{as} (CF ₃)	a'
-	350(10,0.68)	-	352(21)	355(22)	358	8(30),5(28)1(6),9(6),10(6)	α (C-C-C) (6b)	a'
-	-	-	328(13)	320(9)	339	23(32),10(21),6(12),1(9), 8(7)	ρ_{II} (CF ₃)	a'
-	-	-	275(2)	270(3)	265	24(21),18(18),2(17),9(16), 10(15),23(5)	δ_s (CF ₃)	a'
-	22(7,0.81)	-	-	-	193	23(24),24(20),19(13),2(10), 8(6),9(9)	β (C-Cl)(9a)	a'
-	-	-	-	-	118	21(50),24(39),1(7),10(5)	β (C-CF ₃)(15)	a'
1174(w)	1174(5,0.6)	1174(750)	1172(90)	1172(74)	1166	6(89),10(18),11(11)	ν_{as} (CF ₃)	a''
-	-	-	-	-	1039	14(60),10(20)	γ (C-H)(17b)	a''
870(v,w)	-	871(45)	870(61)	868(28)	898	14(61),18(20)	γ (C-H)(5)	a''
-	339(11,0.50)	741(44)	720(46)	-	712	17(96)	ω (NH ₂)	a''
-	-	-	690(39)	-	667	13(33),10(13),18(17),6(7), 10(5)	Φ (C-C-C-C) (4)	a''
-	530(13,0.57)	534(50)	523(57)	-	502	18(34),15(21),14(14),9(12), 10(5)	Φ (C-C-C-C) (16a)	a''
-	-	-	-	-	452	9(56),6(32),13(6),15(6)	δ_s (CF ₃)	a''
366(w)	368(6,0.100)	-	-	-	372	16(39),15(22),18(17),20(8)	γ (C-NH ₂)(10a)	a''
352(v,w)	-	-	-	-	350	20(82),16(6)	τ (NH ₂)	a''
-	-	-	285(2)	-	287	14(43),18(26),13(20),10	ρ_{II} (C-CF ₃)	a''

						(8)		
234(w)	239(7,0.81)	-	-	-	257	18(45),15(22),16(14),14(6)	γ (C-Cl)(20b)	a ⁺
122(v,s)	123(76,0.94)	-	-	-	123	18(35),14(25),13(24),15(6),16(5)	γ (C-CF ₃)(17a)	a ⁺
-	-	-	-	-	107	18(81),14(8),16(5)	Φ (C-C-C)(16b)	a ⁺
-	-	-	-	-	54	19(89),18(6)	τ (CF ₃)	a ⁺

3.1 Phenyl Ring and C(Ph)-X (X = H / CF₃ / NH₂ / Cl / F) Group Modes

Due to replacement of the H atom by X (X = CF₃, NH₂ and C-X) group the symmetry of benzene is lowered from the D_{6h} point group to the C_s. Hence, each one of all the 10 doubly degenerate modes (modes 6-10 and 16-20) of benzene splits in two components, giving rise to 20 normal modes. Therefore, in tri-substituted benzene one has 30 normal mode due to the phenyl ring as: 6 ring stretching, 3 ring planar bending, 3 ring torsion, 3 C-H stretching, 3 C-H in-plane bending and 3 C-H out-of-plane bending, 3 C-X stretching, 3 C-X in-plane and 3 C-X out-of-plane bending modes.

3.1.1 Ring stretching modes

Out of the 6 C-C stretching modes the modes 8a, 8b, 19a, 19b, 14 and 1, the modes 8a & 8b and 19a & 19b appear in very narrow spectral ranges and are easily assigned in the region 1400-1625 cm⁻¹ due to their characteristics magnitudes. For 5A2FB the frequencies 1620, 1572, 1505 and 1455 cm⁻¹ are assigned to the C-C stretching modes 8b, 8a, 19b and 19a, respectively with the corresponding calculated frequencies 1620, 1567, 1501 and 1453 cm⁻¹, respectively. Similarly, for 5A2CB the observed frequencies 1608, 1585, 1482 and 1442 corresponding to the calculated frequencies 1611, 1578, 1492 and 1430 cm⁻¹ are assigned to the modes 8a, 8b, 19b and 19a, respectively. The choice of the components a and b of the modes 8 and 19 is based on the ranges for the magnitudes of these modes suggested by Varsanyi [59]. From the Tables 3 and 4 it could be seen that there is a very good agreement between the observed and calculated frequencies for these modes. It may be noted from the Tables 3 and 4 that the modes 8a, 8b and 19a have major contributions from the ring stretching and small contributions planar force constants. However, the mode 19b has comparable contributions from the ring stretching and the C-H planar deformation force constants and small contributions from several planar force constants. It may be noted that irrespective of the light/heavy nature of the substituted CF₃, the component b appears with higher magnitude compared to the component a for both the modes 8 and 19. The PEDs for these modes suggest that the modes 8a, 8b have major contribution from the C-C stretching force constant and some contribution from the C-C-C angle bending and the C-H planar bending force constants. The modes 19a and 19b have comparable contributions from the C-C stretching and C-H planar bending force constants. In addition, the mode 19a has some contribution due to the C-CF₃ stretching force constant where as the modes 19b has some contribution from the C-C-C angle bending force constant.

The ring C-C stretching mode 14, known as the Kekule C-C stretching mode, corresponding to the benzene frequency 1309 cm⁻¹, which is spectroscopically forbidden both in the IR and Raman spectra of benzene. However, it appears as an extremely weak IR frequency for benzene. It is one of the substituent sensitive modes. In the present case for the 5A2FB molecule an IR band at 1310 cm⁻¹ with the medium strong intensity and for the 5A2CB molecule an IR band at 1285 cm⁻¹ observed with medium intensity corresponding to the weak Raman line 1282 cm⁻¹ are assigned to this mode. The PEDs for this mode suggest that this mode arises mainly due to the C-C stretching force constant with some mixing of the C-H planar bending and C-CF₃ stretching modes for 5A2FB where as for 5A2CB there is mixing with the NH₂ rocking mode also. The ring C-C stretching mode 1 corresponding to the phenyl ring breathing vibration appears as the strongest Raman line at 991 cm⁻¹ and is strongly polarized. It is also one of the substituent sensitive modes. As this mode for 1, 2, 4- tri-substituted benzenes is derived from the most symmetry mode of benzene, it must retain its characteristic feature of the intensity and polarization in the Raman spectra to some extent. For 5A2FB the frequency 905 cm⁻¹ appears with very strong intensity and low depolarization ratio in the Raman spectrum and with medium IR intensity. This frequency is the most suitable candidate for the ring breathing mode. From the PEDs for this frequency it is seen to arise due to strong mixing of the C-C stretching with the C-H planar bending, the C-CF₃ and the C-C-C angle bending modes. Similarly, for 5A2CB also the ring breathing mode 1 is assigned at ~900 cm⁻¹. Here also this frequency appears with good intensity and low depolarization ratio in the Raman spectrum. However, this frequency arises due to mixing of C-C stretching and C-H planar bending modes.

3.1.2 Ring Planar Bending Modes

Benzene has two planar ring deformation mode as 6 and 12. As mentioned earlier the mode 6 splits into 6a and 6b for 1,2,4-tri-substituted benzenes. For benzene the 6 and 12 have magnitudes 606 and 1010 cm^{-1} . Due to Varsanyi [59] all the three modes 6a, 6b and 12 are substituent and position dependent. For both the molecules 5A2FB and 5A2CB the modes 6a and 6b have similar trend for their magnitudes. The angle bending mode 12 is one of the substituent sensitive modes and it finds place in discussion in almost all the articles related to the vibrational studies of benzene derivatives. For 5A2FB it could be assigned at 664 cm^{-1} where as for 5A2CB the frequency 1025 cm^{-1} is assigned to this mode.

3.1.3 Ring Torsion Modes

Phenyl ring torsions correspond to the modes 4, 16a and 16b of benzene for which these modes have magnitude 707, 404, and 404 cm^{-1} . For 5A2FB the mode 4 is assigned at 690 cm^{-1} , where as for 5A2CB it is associated with the frequency 690 cm^{-1} . For both the molecules this frequency is observed in the IR spectrum only. The remaining two torsional modes of the phenyl ring could be assigned at 530 and 167 cm^{-1} for 5A2FB where as for 5A2CB these modes are assigned at 523 and 106 (calc.) cm^{-1} .

3.2 C-X (X = H / CF₃/ NH₂ / Cl / F) Group Modes

For these molecules, the assignments for the C-H stretching modes are straight forward. In 1, 2, 4-tri-substituted benzenes the modes 3, 18a and 18b correspond to the C-H planar bending modes [59]. The mode 3 is assigned at 1269 cm^{-1} and 1255 cm^{-1} for 5A2FB and 5A2CB, respectively. For both the molecules this mode appears to be a strongly mixed mode. The other two C-H planar bending modes are assigned at 1125, 1015 cm^{-1} for 5A2FB and 1090, 1057 cm^{-1} for 5A2CB. It appears from PEDs that for 5A2CB one of the C-H planar bending frequency (1090 cm^{-1}) arises due to mixing of the C-C and CF₃ stretching and C-H planar bending modes, where as the other frequency (1057 cm^{-1}) arises due to the C-C stretching and C-H planar bending modes. For 5A2FB the higher frequency arises due to strong mixing of the C-C, C-NH₂ and CF₃ stretching and C-H planar bending modes.

Out of the 3 non- planar C-H bending modes 5, 11 and 17b, the mode 17b appears to have the highest magnitude [59]. In the present case the frequencies 821, 870 and 940 cm^{-1} are assigned to the 3 C-H non- planar bending modes for 5AFB and similarly for the 5A2CB molecule the frequencies 828, 870 and 1036 cm^{-1} (calc.) are assigned to the 3 C-H non planar bending modes. In both the cases these three frequencies appear to arise due to mixing of the C-H non planar bending modes with the C-C-C ring torsional modes. From the intensity pattern of these frequencies the lowest frequency (~820 cm^{-1}) is assigned to the mode 11 known as the umbrella wagging mode. Similarly, the middle frequencies (~870 cm^{-1}) are assigned to the mode 5 and the highest frequencies (940 and 1036 cm^{-1}) are assigned to the mode 17b for both these molecules. It may be noted that for 5A2CB, the frequency corresponding to the mode 17b could not be observed experimentally.

As mentioned earlier there are three stretching modes due to the ring substituents, namely, the C-CF₃, C-NH₂ and C-F/C-Cl stretching modes, similar to the case of 2A5CB and 2A5BB here also the C-CF₃ stretching mode is assigned at 1340 cm^{-1} . The PED for this mode contains contribution from the C-CF₃ stretching force constants and other several planar stretching and bending force constants for both the molecules. For the 5A2FB molecule the most suitable candidate for the C-NH₂ mode is the frequency 1225 cm^{-1} based on the PED, intensities in Raman and IR and the depolarization ratio. In the light of the PED the C-NH₂ stretching frequency is associated to a frequency at 1115 cm^{-1} for 5A2CB. This frequency appears with stronger IR intensity and medium Raman intensity and low depolarization ratio. The C-F stretching appears strongly in the IR spectra in the region 1400 -1450 cm^{-1} for substituted benzenes. In the present case a frequency ~1260 cm^{-1} is observed with very strong IR intensity. The Raman line corresponding to this frequency has good intensity and low depolarization ratio. The force field calculation suggests the calculated frequency 1247 cm^{-1} could be associated to the C-F stretching frequency corresponding to the observed frequency ~1260 cm^{-1} . The PED for this frequency suggests that this results due to strong mixing of the C-F stretching mode with several planar modes. The C-Cl stretching frequency, as mentioned earlier is expected to appear in the region 600-800 cm^{-1} . A frequency at ~665 cm^{-1} appears with good IR and Raman intensities and low depolarization ratio. The calculated frequency corresponding to this frequency appears to have appreciable contribution from the C-Cl stretching force constant and hence, this frequency is assigned to C-Cl stretching mode for 5A2CB. In this case also this is not a pure mode as it arises due to strong mixing amongst the C-Cl and C-NH₂ stretching and C-C-C angle bending modes. Out of the three C-X (X=C-CF₃ / NH₂ / F/Cl) planar bending modes the C-CF₃ planar bending is expected to have the smallest magnitude. For 5A2FB and 5A2BB the force field calculations also favours the above idea. For 5A2FB and 5A2CB strong Raman lines observed at 130 cm^{-1} and 122 cm^{-1} are assigned to the C-CF₃ planar bending modes. For 5A2FB it arises due to mixing of the C-CF₃ and C-Cl planar bending and the CF₃ rocking modes, where as for 5A2CB it is a result of mixing of the C-CF₃ and C-Cl planar bending modes. The C-NH₂ and C-X (X = F, Cl) planar bending modes are expected to appear at higher magnitudes than that of C-CF₃ planar mode. The normal co-ordinate calculation suggests that the C-NH₂ planar bending mode can be

associated to a frequency at 534 cm⁻¹ for 5A2CB where as for 5A2FB a frequency at 331 cm⁻¹ can be assigned to this mode. The planar C-Cl bending mode is calculated to be 192 cm⁻¹. No observed frequency could be correlated to this mode, where as the C-F planar bending mode is calculated to be 480 cm⁻¹ and is correlated to the observed frequency 470 cm⁻¹ with good Raman and medium IR intensities, both of these β(C-Cl) and β(C-F) are strongly mixed modes.

Out of the 3 C-X (X = CF₃ / NH₂ / F/Cl) modes the C-CF₃ out of plane bending mode is expected to have the lowest magnitude. For 5A2CB the frequency 122 cm⁻¹ and for 5A2FB the frequency 124 cm⁻¹ (calc.) cm⁻¹ is assigned to this mode. The C-NH₂ non-planar bending mode is associated to the IR frequency 424 cm⁻¹ for 5A2FB; while for 5A2CB the Raman frequency 366 cm⁻¹ is assigned to 332 cm⁻¹ and non-planar C-Cl bending mode is correlated to the Raman frequency at 234 cm⁻¹.

3.3 Internal Mode of the NH₂ Group

Out of the 6 NH₂ modes the modes ν_s(NH₂) and ν_{as}(NH₂) could be easily assigned owing to their characteristic magnitudes. For 5A2FB these modes are assigned at 3390 cm⁻¹ and 3480 cm⁻¹ and for 5A2CB the frequencies 3400 cm⁻¹ and 3490 cm⁻¹ are assigned to these modes. The magnitudes of these two modes ν_s and ν_{as} satisfy the empirical relation given by Bellamy [29],

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

for both the molecules, suggesting that the two NH bonds of the NH₂ group are identical in these molecules. The PEDs suggest that these are pure NH₂ stretching modes. There are two frequencies in the region of β(NH₂) mode. For 5A2CB the frequencies are 1625 and 1655 cm⁻¹ and for 5A2FB these are 1632 and 1642 cm⁻¹. The average of the two frequencies in both the cases is assigned to the β(NH₂) mode, i.e. for 5A2FB the frequency 1637 cm⁻¹ and for 5A2CB the frequency 1640 cm⁻¹ is assigned to the β(NH₂) mode. For 5A2FB the doublet is explained as arising due to the Fermi resonance between the β(NH₂) fundamental at 1637 cm⁻¹ and combination band at 1260+375 cm⁻¹; whereas for 5A2CB the two frequencies 1625 and 1655 cm⁻¹ are explained in terms of Fermi resonance between the β(NH₂) fundamental at 1640 cm⁻¹ and the combination band at 905 +745 =1650 cm⁻¹.

The rocking mode of the NH₂ group appears in the region 1000-1100 cm⁻¹. The frequencies 1005 and 1047 cm⁻¹ are assigned to this mode for 5A2CB and 5A2FB, respectively. The PEDs for this mode suggest that it arises due to mixing of the rocking mode with the ring stretching mode for 5A2FB where as for 5A2CB it mixes with the C-H planar bending and C-C ring stretching modes. The wagging and the torsional modes of the NH₂ group are pure wagging and torsional mode for 5A2CB and these are assigned at 720 and 352 cm⁻¹. For the 5A2FB molecule the wagging is a pure wagging mode; while, the torsional mode mixes slightly with the ring torsional mode and the CF₃ deformation and rocking modes. For this molecule the frequencies 720 and 355 cm⁻¹ are assigned to the wagging and torsional modes of the NH₂ group.

3.4 Internal Mode of the CF₃ Group

The CF₃ group has 9 internal modes of vibration. In all the substituted benzene molecules containing CF₃ group (s) there are four frequencies, one in the region 1300-1350 cm⁻¹, two in the region 1100-1200 cm⁻¹ and one in the region 700-800 cm⁻¹ which appear to be associated with the normal modes involving the CF₃ group. In the present case also for 5A2FB one observes the frequencies involving the CF₃ groups. As discussed earlier the frequency 1340 cm⁻¹ could be assigned to the C-CF₃ stretching mode. The frequencies 1160 cm⁻¹ and 1140 cm⁻¹ are assigned respectively to the anti-symmetric (a'') and symmetric (a') components of the anti-symmetric CF₃ stretching mode. The PEDs for these frequencies suggest that the C-CF₃ stretching mode and ν_{as}(CF₃) (a'') mode localized within the CF₃ group. Corresponding to the fourth characteristic vibration of the CF₃ group in the region 700-800 cm⁻¹ two frequencies are observed at 745 and 785 cm⁻¹. The force field calculation places only one planar frequency in this spectral region. Appearance of the doublet could be explained in terms of the Fermi resonance between the CF₃ symmetric stretching at {(785+745)/2} = 765cm⁻¹ (a') and the combination band 505 (a'') +270 (a'') = 775 cm⁻¹ (a').

For 5A2CB the four characteristic CF₃ group frequencies are 1334 cm⁻¹, 1175, 1145 and 745 cm⁻¹. The frequency 1335cm⁻¹ is assigned to the mode ν(C-CF₃) and the rest three frequencies 1175, 1145 and 745 cm⁻¹ are assigned to the modes ν_{as}(CF₃) (a'+a'') and ν_s(CF₃) modes, respectively. The patterns of the PEDs for the frequencies, 1145 and 745 cm⁻¹ for 5A2CB are similar to those of 5A2FB.

The CF₃ group has three deformation modes, namely, δ_s(a') and δ_{as}(a'+a''), which appear in the region 400-500 cm⁻¹. In the case of 5A2FB these mode are assigned at 505 (a'') and 493 (a') cm⁻¹. The symmetric CF₃ deformation mode δ_s(CF₃) is assigned at 188 cm⁻¹ (calc.). The PEDs show that the δ_{as}(a'+a'') modes are mixed and localized modes; while, the δ_s(CF₃) mode is mixed mode, the mixing being with the modes associated with the CF₃ group as well as the phenyl ring modes.

For the 5A2CB molecule the mode δ_s is assigned at 275 cm⁻¹ where as the frequencies 465 and 452 (calc.) cm⁻¹ are assigned to the modes δ_{as}(CF₃) (a') and δ_{as}(CF₃) (a''), respectively. The rocking of the CF₃ group is assigned at 328 cm⁻¹ (a') and 285 cm⁻¹ (a'') where as for 5A2CB it is assigned at 278 cm⁻¹ (a') and 270

cm⁻¹ (a'') for 5A2CB. The torsional mode of the CF₃ group has the lowest magnitude of all the normal modes and it is calculated to be 68 and 54 cm⁻¹ for 5A2FB and 5A2CB, respectively.

IV. Conclusions

Out of the 6 ring stretching modes 8a, 8b, 19a, 19b 14 and 1, the first four modes, namely, 8a, 8b, 19a and 19b do not show variation in the magnitudes for both the molecules. The Kekule ring stretching modes 14 appears at 1310 cm⁻¹ for 5A2FB and 1283 cm⁻¹ for 5A2CB suggesting that there is an effect of the nature of the substituent at the position 2. The ring breathing mode 1 has nearly the same magnitudes for 5A2FB and 5A2CB (~900cm⁻¹). The trigonal bending mode 12 appears at 666 cm⁻¹ for 5A2CB and 1026 cm⁻¹ for 5A2FB. Out of the three torsional modes of the ring, the mode 4 seems to retain its magnitude in the range 660-700 cm⁻¹. The remaining two ring torsion modes appear to depend on the nature and position of the substituent. Out of the 9 C-H modes the three C-H stretching modes appear quite sensitive to the position and the nature of the substituents. Out of the 3 planar C-H bending modes, the mode 18b also appears to be insensitive where as the modes 3 and 18a appear to be position and nature sensitive. All of the 3 C-H non-planar bending modes, the modes 17b and 11 are sensitive to the nature and position.

The C-CF₃ stretching mode is observed in the range 1325 -1340 cm⁻¹ for both the molecules suggesting that the CF₃ group behaves as a light substituent contrary to the suggestion of Varsanyi [59]. The C-NH₂ stretching mode appears to have its magnitude in the region 110-1300 cm⁻¹ for both the molecules. The symmetric stretching frequency of the CF₃ group is observed in a very narrow frequency range 740-770 cm⁻¹ for the two molecules and it appear as a very strong and polarized Raman line. The two anti-symmetric stretching modes are observed in the range 1100-1200 cm⁻¹; a'' components is assigned at a higher magnitude than the a' component. One can see that the modes δ_s, δ_{as} (a' and a''), ρ_{||} and ρ_⊥ of the CF₃ group are sensitive to the nature and position of the substituent. The PEDs for all the modes excepting the τ mode suggest that all of these are strongly coupled mode, the coupling being with different ring substituent (s) modes allowed by the symmetry. The internal modes of the NH₂ group ν_{as}, ν_s and β are insensitive to the position and nature of the substituent. The remaining three modes ρ, ω and τ appear to be substituent and position sensitive. From the PEDs of these mode it appears that the modes ν_a, ν_{as}, β and ω are highly localized group modes for both the molecules. The mode τ is a mixed (non-localized) mode for 5A2FB and 5A2CB. The vibrational spectra of 5A2FB and 5A2CB could be explained by treating these molecules isotopomers of each other.

Acknowledgements

The authors are grateful to the staff members of the Computer Centre, Banaras Hindu University for their co-operation during the computational work.

References

- [1]. H W Thompson, R B Temple, J.Chem. Soc. 1432 (1948)
- [2]. H Sponer, J D S Lowe J. Opt. Soc. **39** (1949)
- [3]. W T Cave, H W Thompson, Disuss. Fraday Soc. **9** 35 (1950)
- [4]. H Sponer, M L N Sastri, J. Chemical Phy. **20** 1428 (1952)
- [5]. D C Smith, E E Ferguson, R L Hudson, J R Nielsen, Chem, j. Chem. Phy. **21** 1457 (1953)
- [6]. E E Furguson, L Mikkelson, J R Nilsen, D C Smith, Chem. Phy. **21** 1731 (1953)
- [7]. R R Randle, D H Whiffen, J. Chem.Soc. 1311 (1955)
- [8]. N A Narasihman, J R Nilsen, R J Theimer, J. Chem. Phy. **27** 740 (1957)
- [9]. D W Scott, D R Douslin, J F Messerly, S S Todd, I A Hosenlopp, T C Kincheloe, J P McCallough, J. Am. Chem. Soc. **81** 1015 (1959)
- [10]. I A Rao, V R Rao J. Mol. Spectrosc. **6** 447 (1961)
- [11]. R T Bailly, S G Hasson, Spectrochim. Acta **24A** 1891 (1968)
- [12]. D A Condit, S M Crave, J E, Katon Appl. Spectrosc. **28** 402 (1974)
- [13]. R D Cunha, V B Kartha, Can. J. Sectrosc. **28** 18 (1975)
- [14]. B B, Lal, I S Singh, Indian J. Phy. **50** 478 (1976)
- [15]. M R Padhye, S A Agnihotri, V Raghvendra, Indian J. Chem. **14A** 792 (1976)
- [16]. J H S Green, D J Harrison, Spectrochim. Acta **33A** 583 (1977)
- [17]. H Bürger, H Niepel, G Powelke, Spectrochim Acta **36A** 7 (1980)
- [18]. R Eujen, H Burger, H Oberhammer, J. Mol.. Struct. **71** 109 (1981)
- [19]. R A Yadav, Shyampati singh, and N P Singh, Indian J. Pure Appl. Phys **20** 674 (1982)
- [20]. R A Yadav, I S Singh, Indian J. Pure Appl. Phys. **20** 677 (1982)
- [21]. R A Yadav, I S Singh, Indian J. Pure Appl. Phys **583** 556 (1984)
- [22]. R A Yadav, I S Singh, Proc. Indian Acad. Sci. (Chem. Sci.) **95** 471 (1985)
- [23]. R A Yadav, I S Singh, Spectrochim. Acta **41A** 191 (1985)
- [24]. L J Beliamy, R L Williams, Spectrochim. Acta **9** 341 (1957)
- [25]. D Hadzi, M Skrblijak, J. Chem. Soc. 843 (1957)
- [26]. K B Whestel, W E Rberson, M W Krell, Anal. Chem. **30** 1598 (1958)
- [27]. K B Whestel, W E Rberson, M W Krell, Anal. Chem. **32** 1281 (1958)
- [28]. A R Katrizky, R A Jones, J. Chem. Soc. 3674 (1959)
- [29]. J E Stewart, J. Chem. Phys.**10** 1259 (1959)
- [30]. J C Evan Spectrochim. Acta **16** 428 (1960)

- [31]. R Allerhand, P Schlyer, Von, J. Am. Chem. Soc. **85** 37 (1963)
- [32]. J D C Brand, D R Williams, T J Cook, J. Mol. Spectrosc. **20** 359 (1966)
- [33]. M A Shashidhar, K S Rao, E S Jaya, Jayadevappa, Spectrochim. Acta **26A** 2373 (1970)
- [34]. M M Szostak, J. Raman. Spectrosc. **8** 43 (1979)
- [35]. G N R Tripathi, J E Katon, J. Chem. Phys. **70** 1383 (1979)
- [36]. M P Kumpawat, A Ojha , N D Patel, Can. J. Spectrosc. **25** 1 (1980)
- [37]. R B Singh, N P Singh, D K Rao Indian J. Pure Appl. Phys. **19** 740 (1981)
- [38]. R Shankar, R A Yadav, I S Singh, O N Singh, Indian J. Pure Appl. Phys. **23** 339 (1985)
- [39]. N Shyam Sundar, Spectrochim. Acta, **41A** 905 (1985)
- [40]. R M P Jaisawal Ind. J. Phys **60B** 118 (1986)
- [41]. N Shyam Sundar, C Santhamma, Spectrochim. Acta **44A** 69 (1988)
- [42]. V R Sarma Indian J. Pure Appl. Phys. **4** 226 (1966)
- [43]. R A Yadav, R Shankar, J. Raman Spectrosc. **18** 555 (1987)
- [44]. P Murlidhar Rao, G Ramana Rao J. Raman Spetrosc. **20** 529 (1989)
- [45]. R A Yadav PhD Thesis, Banaras Hindu University Varanasi India 1983
- [46]. R Shankar PhD Thesis Banaras Hindu University Varanasi India 1991
- [47]. N P Singh PhD Thesis, Purvanchal University Jaunpur India 1994
- [48]. R K Yadav PhD Thesis Purvanchal University Jaunpur India 2005
- [49]. N P Singh, R A Yadav Indian J. Phys. **75B** 347 (2001)
- [50]. R K Yadav, N P Singh and R A Yadav Indian J. Phys. **77B** 421 (2003)
- [51]. R A Yadav, R K Yadav and N P Singh Spectrochim Acta Part A **64** 454 (2006)
- [52]. D H Whiffen, Phil. Trans. R. Soc. **248A** 131 (1955)
- [53]. H Hollestein, and H Günthard, Spectrochim. Acta **27A** 2027 (1977)
- [54]. A Yamanguchi, T Miyazawa, T Shimanouchi, S Miszushima, Spectrochim. Acta **10** 170 (1957)
- [55]. J H Schachtschneider, Vibrational Analysis of Polyatomic Molecules Parts V and VI Technical Report Nos. 231 and 57 Shell Development Co. Emeryville, CA 1964 and 1965
- [56]. RA Kydd, PhD Thesis, University of British Columbia, Canada 1969
- [57]. H Bürger, G Powelke, H. Oberhammer J. Mol. Struct. **84** 49 (1982)
- [58]. V K Rastogi, V Jain, M A Palafox, D N Singh, R A Yadav, Spectrochim. Acta **57A** 209 (2001)
- [59]. G Varsanyi Vibrational Spectra of seven Hundred Benzene Derivatives Academic Press, New York 1974