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Vibrational Studies Of Trifluoromethyl Benzene Derivatives III:3A4FB And 3A4CB Benzotrifluorides

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Abstract

The polarized Raman spectra of 3-amino-4-fluoro and 3-amino-4-bromo benzotrifluorides were recorded in the liquid phase using a Jovin Yvon Ramanor HG.2S spectrometer and a 1403 Spex monochromator, covering the range of 100-4000 cm^{-1}. Infrared spectra were obtained on a Perkin-Elmer 783 spectrometer and an FTIR model, Cygnus-100 spectrometer, spanning the range of 400-4000 cm^{-1}. Vibrational assignments for the observed frequencies were proposed based on the assumption of Cs point group symmetry.

Key words- Raman and IR spectra, vibrational frequencies, normal mode,3-Amino-4-fluoro and 3-Amino-4-Bromo benzotrifluorides.

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1. Introduction

This paper continues our studies on the vibrational spectra of trifluoromethyl (CF_3) benzene derivatives (Singh, 2001, Singh, 2003, Yadav, 2023). It presents the results and analysis of the polarized Raman, IR, and FTIR spectra of 3-amino-4-fluoro benzotrifluoride (3A4FB) and 3-amino-4-bromo benzotrifluoride (3A4BB). To our knowledge, the vibrational spectra of these molecules have not been previously investigated.This study was undertaken to propose consistent vibrational assignments for the phenyl ring modes, the C-X (X=CF_3, NH_2, F/Br) modes, and the internal modes of the substituent groups. Additionally, we aim to examine the effect of these substituents on the phenyl ring modes and their internal modes.Previous studies include spectroscopic analyses, NMR, and NBO calculations of 3-hydroxy benzylidyne trifluorides by Arivazhangan et al. (Arivazhagan, 2013). Vibrational spectroscopy investigations using ab initio and density functional theory on the structure of 3-amino-4-fluoro benzotrifluoride were conducted by Sundaraganesan et al. (Sundaraganesan, 2007). Furthermore, molecular structure and vibrational spectra of 3-amino-4-bromo benzotrifluorides were studied using ab initio HF and density functional methods by Sundaraganesan (Sundaraganesan, 2008).FTIR, Raman, HF, and hybrid (LSDA and B3LYP) calculations were conducted for the 1,2-dibromobenzene compound by Shakila et al. (Shakila, 2012). FTIR and Raman spectra, along with force field calculations for the vibrational analysis of certain aniline derivatives, were performed by Mukherjee (Mukherjee, 2009). Additionally, Yadav et al. (Yadav, 2006) carried out force field calculations for 2-amino-5-chloro and 2-amino-5-bromo benzotrifluoride molecules.

This work aims to propose consistent vibrational assignments for the phenyl ring modes, the C-X (X=CF_3, NH_2, F/Br) modes, and the internal modes of the substituent groups. It also examines the effects of these substituents on the phenyl ring modes and their internal modes.

2. **Experimental**

The chemicals 3A4FB and 3A4BB, of specpure grade, were purchased from Sigma Chemical Company (USA). These compounds are colorless liquids at room temperature and were distilled under vacuum prior to use. The polarized Raman spectra of these compounds were recorded in the liquid phase in the region 100-4000 cm^{-1} using a Jovin Yvon Ramanor HG.2S spectrometer and a Spex spectrometer model-1403, with the 4880 Å line of an Ar^+ laser as the source of excitation. The Raman spectrometer was calibrated using the spectra of $CHCl_3$ and CCl_4.IR spectra of these compounds were recorded in the pure liquid phase in the region 200-4000 cm^{-1} on a Perkin-Elmer 783 spectrometer, by placing the liquid between two CsI plates. The spectrometer was calibrated with the spectrum of a thin film of polystyrene. FTIR spectra in the pure liquid phase were also recorded in the region 400-4000 cm^{-1} on an FTIR spectrometer, model Cygnus-100 (Mattson Company). The accuracy of the measurements is better than ±2 cm^{-1}, and the resolution of the spectrometers was better than 2 cm^{-1} for all spectra.

3. Results and Discussion

The vibrational assignments have been proposed based on the magnitudes and relative intensities of the frequencies observed in the Raman, IR, and FTIR spectra, as well as the measurement of the depolarization ratios of the Raman lines for 3A4FB and 3A4BB. Assistance was also taken from the assignments made for molecules containing F (Lal, 1973; Cunha, 1973; Green, 1977, Yadav, 1982, Yadav,1983, Yadav,1984; Rao, 1989), Br (Varsanyi, 1969; Griffiths and Thomson, 1967,Varsanyi, 1974,Shyampati, Singh, and Shamir, 1977, Suzuki, 1977), NH_2 (Tripathi, 1979, Yadav, 1985) and CF_3 (Singh, 2001, Singh, 2003) groups. The observed fundamental frequencies and the corresponding mode assignments are presented in Tables 1 and 2. Additionally, several combination and overtone frequencies have also been observed. The discussion of the vibrational assignments for the normal modes can be divided into the following categories:

(i) Phenyl- ring modes
(ii) CF_3 group Modes
(iii) NH_2 group modes

3. (i) Phenyl - Ring Modes

The vibrational assignments for most of the 30 (21a’ + 9a”) normal modes involving the phenyl ring are straightforward. In the following discussion, only some of the interesting modes are considered. As these molecules are tri-substituted benzenes, there are 3 C-H and 3 C-X (X = CF_3, NH_2, and F or Br) stretching, planar bending, and non-planar bending modes. The C-CF_3 stretching mode is associated with one (~1320 cm^{-1}) of the four characteristic frequencies observed in CF_3-containing benzenes. For 3A4FB, this frequency is observed at 1340 cm^{-1}, and for 3A4BB, it appeared at ~1335 cm^{-1}.

The C-NH_2 stretching mode was assigned in the region 1250-1260 cm^{-1} for 5-amino-2-chloro/fluoro and 2-amino-5-chloro/bromo benzotrifluorides (Singh, 2001, Singh, 2003, Yadav, 2023). In the present case, this mode is assigned at ~1270 cm^{-1} for both molecules. The slightly higher magnitude of the C-NH_2 stretching mode for 3A4FB and 3A4BB, compared to that for the molecules reported earlier (Singh, 2001, Singh, 2003, Yadav, 2023) could be due to the presence of a halogen atom in the juxta-position of the NH_2 group. The present assignment for the C-NH_2 stretching mode is also supported by earlier work (Tripathi, 1979, Yadav, 1985).

The C-F stretching frequency appears in the region 1400-1450 cm^{-1} for fluorobenzenes (Lal,1973, Cunha, 1973; Green, 1977, Yadav, 1982, Yadav, 1983, Yadav, 1984, Rao, 1989). For 5A2FB (Singh, 2003), this mode is observed at ~1225 cm^{-1} as a very strong IR band. In the present case, a very strong IR band at 1205 cm^{-1} is observed and is assigned to the C-F stretching mode. For the C-F stretching mode, the effect of the presence of the NH_2 group in the ortho position seems to have the opposite effect to that for the C-NH_2 stretching mode.

The C-Br stretching mode is observed in the region 200-650 cm^{-1} in benzene derivatives (Varsanyi, 1969, Griffiths, 1967,Varsanyi, 1974,Shyampati, 1977, Suzuki, 1977). For 2A5BB, the frequency 633 cm^{-1} is assigned to this mode. For 3A4BB, the frequency observed at ~555 cm^{-1} is a suitable candidate for the C-Br stretching mode. Similar to the case of the C-F stretching frequency in 3A4FB, the C-Br stretching frequency in 3A4BB has a smaller magnitude than that in 2A5BB, possibly due to the reason explained above.

Vibrational modes ν_s (ring breathing) and ν_{as} (C-C-C trigonal bending) are affected by substitution (Lal, 1973, Cunha, 1973). 3A4FB and 3A4BB are 1,2,4-tri-substituted benzene derivatives (Varsanyi, 1974) categorized the substituents as heavy (mass of the atom directly attached to the ring > 25 amu) and light (mass < 25 amu). Based on the positions and the number of light and heavy substituents, he proposed frequency ranges for the 30 normal modes associated with the phenyl ring. According to Varsanyi, 3A4FB is a 1,2-di-light-4-heavy molecule, and 3A4FB is a 1,4-di-heavy-2-light molecule, as he considered the CF_3 group a heavy substituent.

However, as discussed earlier, the C-CF_3 stretching frequency appears ~1330 cm^{-1}, suggesting that the CF_3 group behaves as a light substituent. Hence, 3A4FB and 3A4BB are 1,2,4-tri-light and 1-heavy-2,4-di-light molecules. For these molecules, the ring breathing modes lie in the ranges 630-740 cm^{-1} and 1020-1060 cm^{-1}. For 3A4FB, the frequency suitable for the ring breathing mode is observed at ~745 cm^{-1}, and for 3A4BB at ~1020 cm^{-1}. In agreement with the assignment made for this mode (Varsanyi, 1969, Griffiths, 1967, Varsanyi, 1974, Shyampati, 1977, Suzuki, 1977, Tripathi, 1979,Yadav, 1985, Singh, 2001, Singh, 2003, Miller, 1988, the trigonal ring breathing (Varsanyi, 1974) is assigned at a frequency ~920 cm^{-1} for both molecules.

The Kekulé C=C stretching mode is observed in the region 1265-1295 cm^{-1} for the four molecules studied earlier (Singh, 2001, Singh, 2003). It has also been assigned in the region 1200-1300 cm^{-1} by earlier workers (Faniram, 1980, 1982, Kumpawat, 1980, Jajji,2000). In the present case, this mode is observed to have a magnitude near 1280 cm^{-1} for both molecules.

The C-H planar bending mode (Lal, 1973), which is observed as a very weak IR band at 1350 cm^{-1} for benzene, usually appears in the range 1250-1350 cm^{-1} for substituted benzenes. In the present case, the above mode is observed at 1307 cm^{-1} for the 3A4BB molecules. However, for the 3A4FB molecule, this mode could not be observed due to the presence of other strong bands in this region. From the assignments of the combination and overtone bands, it is estimated to have a magnitude of 1300 cm^{-1}.

3. (ii) CF_3 Group Modes

The CF_3 group mode gives rise to four characteristic frequencies in the regions 1300-1350 cm^{-1} (Singh , 2001) 1100-1200 cm^{-1} (Singh, 2003) and 700-800 cm^{-1} (Singh, 2001). As discussed above, the frequency in the region 1300-1350 cm^{-1} corresponds to the C-CF_3 stretching mode. The frequency in the 700-800 cm^{-1} range is due to thesymmetric stretching mode (ν_s). In the present case, the frequencies at ~770 and 745 cm^{-1} are assigned to this mode for 3A4FB and 3A4BB, respectively. The region 1100-1200 cm^{-1} contains two characteristic

The deformation modes [$\delta_s + \delta_{as}$ (a' + a")], the rocking modes ($\rho_{\parallel} + \rho_{\perp}$) and the torsion mode ($\tau$) of the CF_3 group lie below 500 cm^{-1}. The δ_s mode appears with good Raman intensity. For 3A4FB, it is observed at ~310 cm^{-1}, and for 3A4BB, it is assigned at 220 cm^{-1}. The higher electronegativity of the F atom compared to the Br atom appears to enhance the magnitude of the δ_s mode for 3A4FB compared to its value for 3A4BB. Assignments for the two δ_{as} (a' + a") and $\rho_{\parallel}$ and $\rho_{\perp}$ modes are given in Tables 1 and 2. The torsional mode (τ) of the CF_3 group lies beyond the presently investigated region. The magnitude of this mode is estimated from the assignments of the overtones and combination bands as 65 cm^{-1} for the molecule 3A4FB and 70 cm^{-1} for 3A4BB.

Assignments for the CF_3 modes are discussed in detail elsewhere (Singh,2001, Singh, 2003), and our assignments agree with the previously reported assignments.

Table 1: The vibrational Assignment of IR and Raman Bands for 3A4FB

IR bands		**FTIR Bands**	**Raman line**		**Proposed assignments with Wilson Notation**	**Species**
Pure liquid	CS_2 Solution	Pure liquid	Pure liquid			
cm^{-1}(Rel. Int)	cm^{-1} (Rel. Int)	cm^{-1} (Rel. Int)	a(cm^{-1}) (Rel. Int)	b(cm^{-1}) (Rel. Int)		
			101(w)	101(11,0.55)	γ(C-CF_3)	a”
			170(w)	173(4,0.88)	β (C-CF_3)	a’
			196(mw)	198(12,0.73)	†FR between183 and 2*101	
275(4)			275(w)		183+101	A”
285(7)			280(w)	280(5,?)	τ(NH_2)	a”
295(5)			293(m,w)	293(19,0.57)	γ(C-NH_2)	a”
315(4)	315(4)		310(m,w)	309(21,0.46)	δ_s(CF_3)	a’
340(3)	338(6)				$\rho_{\parallel}$ (CF_3)	a’
360(17)	358(13)		363(w)	363(4,0.71)	γ(C-F)	a’
375(17)	375(15)				β(C-NH_2)	a’
385(15)	380(w)				$\rho_{\perp}$(CF_3)	a’
400(21)	400(21)	402(18)	406(w)	407(6,0.82)	φ(CCC)	a”
422(23)	423(26)	411(w)			360+65	A’
450(40)		451(35)	458(v,w)		β (C-F)	a’
		470(15)	478(w)		δ_{as} (CF_3)	a’
515(56)	515(80)				δ_{as} (CF_3)	a”
		533(32)			2*280	A’
		562(15)	559(w)	560(5,0.70)	φ(CCCC)	a”
592(55)		592(35)	592(w)	594(4,0.62)	α(CCC)	a’
620(58)	618(65)	623(40)	620(w)	623(5,1.00)	α(CCC)	a’
652(38)	652(63)	657(36)			2*340	A’
668(38)	666(61)		688(w)		φ(CCCC)	a”
		721(15)	726(w)		ω (NH_2)	a”

Table 1 Contd ------

740(30)		745(15)	744(m,w)	744(33,0.35)	υ(C-C)	a’
767(45)	768(54)	771(40)	770(v,s)	770(100,0.37)	υ_{as}(CF_3)	a’
810(55)	808(56)	812(50)	805(w)		γ (C-H)	a’
			788(w)		2*400	A’
868(50)	865(50)	870(45)			γ (C-H)	a’
				908(3,1.00)	812+101	A’
920(48)	920(43)	923(40)	924(w)	923(7,0.38)	α(CCC)	a’
995(sh)					γ (C-H)	a”
1050(48)	1050*	1054(44)	1052(m,w)	1051(11,0.40)	β(C-H)	a’
1080(72)	1080(65)	1084(68)			ρ(NH_2)	a’
1120(100)	1125(98)	1115(96)	1120(w)		Y_{as}(CF_3)	a’
			1144(w)	1143(5,0.60)	β(C-H)	a’
1162(94)	1165(98)	1164(90)	1165(v,w)		υ_{as}(CF_3)	a”
			1176(w)		770+407	A”

1204(97)	1202(95)	1203(95)	1205(w)	1207(9,0.44)	υ(C-F)	a’
1270(52)	1273(40)			1269(5,0.44)	υ(C-NH$_2$)	a’
12080(55)	1285(50)		1287(w)		υ(C-C)	a’
1340(98)	1340(95)	1340(90)	1338(m,w)	1392(22,0.32)	υ (C- CF$_3$)	a’
1365(53)	1365*				1050+315,620+745	A’
130(42)	1380(61)				1280+101	A”
1390(38)					770+620	A’
					1115+275	A”
1412(36)	1410(59)				1340+65	A”
			1422(w)		1125+295	A”
			1435(v,w)		920+515	A”
					1125+310	A”
1447(89)	1446(89)	1450(85)	1447(w)	1447(7,0.50)	υ(C-C)	a’
1460(46)	1460(67)	1452(w)			1162+293	A’
1468(44)	1468(67)				2*770	A’
1483(38)			1483(w)		1120+363	A”
					1080+400	A”
1492(36)	1492(52)				1050+450	A’
1502(48)	1502(63)	1502(40)			740+767	A’
1515(73)	1516(76)	1524(50)			υ(C-C)	a’
1528(69)					1125+400	A”
1550(41)	1548(69)				101+1450	A”
1570(38)					υ(C-C)	a’
1602(67)	6102(82)	1605(60)		1608(7,0.76)	υ(C-C)	a’
1632(76) 1640(77)	1630(100) 1636(100)	1633(70) 1638(70)	1636(m,w)	1638(14,0.80)	†FRbetween β(NH$_2$) 1270+375	a’
1660(42)					1602+65	A”
1680(58)	1678(76)				1570+101	A”
					1162+515	A’
1695(38)	1695(74)				771+924 1300+400	A”
1710(35)	1712(72)				1120+592	A”
1740(32)		1738(25)			1340+400	A”
					1120+620,1447+293	A’
1755(29)	1755(56)				1460+305	A”
					1390+375	A’

765(32)	1765(54)				2*920	A’
1780(25)					1162+618 1054+726	A”
1790(20)					1340+450 1050+740	A’
1800(25)					1447+340	A’
1822(27)					1300+515 1202+620	A’
1862(30)		1864(25)			1120+744,1270+594	A’
					1300+562	A”
2310(28)	2310*				1446+868	A”
					1270+1050	A’
2350(38)	2350(25)	2343(30)			1300+1050	A’
2850(43)	2850(36)				1515+1340	A’
2920(65)	2932()49	2920(49)	2932(w)		2*1515	A’
2950(49)	2950*		2952(w)		1608+1342	A’

3020(27)	3020(28)		3020(m,w)	3032(30,0.42)	υ(C-H)	a’
		3060(v,w)	3060(m,w)	3058(41,0.55)	υ(C-H)	a’
			3078(w)		2*1602	A’
3090(31)			3091(v,s)	3093(100,0.51)	υ(C-H)	a’
3200(42)		3211(40)		3205(6,0.53)	3093+101	A”
			3236(w)	3236(8,0.50)	1636+1602	A’
3400(66)	3400(77)	3386(66)	3394(s)	3395(48,0.43)	υ(NH_2)	a’
3480(59)	3490*(12)	3486(55)	3480(w)		υ$_{as}$(NH_2)	a”
			3490	3496	3400+101	A”
			3535(w)		3480+65	A”
3640(25)					3020+620	A’

Symbol

*Frequencies observed in CCl_4 solution.

a Recorded on spex Raman spectrometer.

b Recorded on Jobin Yvon Ramanor HG.2S spectrometer.

v = very, w = weak, m = medium, s = strong.

† FR Fermi Resonance.

Table 2:Vibrational Assignment of IR and Raman Bands for 3A4BB

IR Bands		FTIR Bands	Raman Lines		Proposed Assignments with Wilson Notation	Species
Pure liquid	CS_2 Solution	Pure liquid	Pure liquid			
cm^{-1}(Rel. int)	cm^{-1}(Rel. int)	cm^{-1}(Rel. int)	a(cm^{-1})	b(cm^{-1})		
			147(w)	150(4,0.62)	β(C-CF_3)	a’
			176(m,w)	177(18,0.67)	γ(C-Br)	a’
			223(v,s)	222(81,0.35)	δ$_s$(CF_3)	a’’
			254(w)	255(4,0.55)	β(C-Br)	a’
287(8)			290(w)		(NH_2)	a’’
304(12)					223+70	A”
315(12)					γ(C-NH_2)	a’’
			330(v,w)		150+177	A”
340(18)			341(w)	346(5,0.66)	ρ$_{\parallel}$(CF_3)	a’
					254+100	A”
			366(v,w)		150+222	A’
			373(w)	377(3,0.57)	β(C-NH_2)	a’
375(19)					287+100	A’
400(20)			402(w)		ρ$_{\perp}$(CF_3)	a’’
421(26)		422(20)			φ(CCCC)	a’’
448(29)		449(25)			φ(CCCC)	a’’
		495(30)			δ$_{as}$(CF_3)	a’
515(49)	515(60)				δ$_{as}$(CF_3)	a’’
		528(20)			375+150	A”
553(39)		557(35)	557(m,w)	557(21,0.45)	υ(C-Br)	a’
590(36)				592(3,0.43)	α(CCC)	a’
650(28)	654(25)				α(CCC)	a’

695(2)					φ(CCCC)	a’’
708(24)		712(22)			$\omega(NH_2)$	a’’
744(31)	744(33)	747(30)	746(vs)	749(100,0.32)	$\upsilon_s(CF_3)$	a’
			786(w)	788(6,0.43)	340+448	A’’
					422+336	A”
802(40)	802(36)	806(35)			γ(C-H)	a’’
830(17)					654+177	A’
836(39)	864(35)	867(36)			γ(C-H)	a’’
915(31)	917(28)	920(29)			α(CCC)	a’
			981(w)		γ(C-H)	a’’
1020(42)	1020(36)	1023(40)	1019(w)	1021(44,0.32)	υ(C-C)	a’
1069(81)	1069(74)	1071(78)			β(C-H)	a’
			1080(w)	1089(4,0.33)	$\rho(NH_2)$	a’
			1103(vw)		708+400	A’
1125(97)	1125(93)	1129(92)	1120(w)		$\upsilon_{as}(CF_3)$	a’’
1142(80)	1143(33)		1145(w)	1150(3,0.58)	β(C-H)	a’
1166(87)	1167(82)	1167(83)	1169(w)		$\upsilon_{as}(CF_3)$	a’’
			1205(vw)		806+400	A’
					920+287	A’
			1235(vw)		920+315	A”
1252(67)	1253(62)	1257(65)		1268(2,0.60)	$\upsilon(C\text{-}NH_2)$	a’
1280(61)	1280(55)	1283(60)	1280(w)	1284(3,0.42)	υ(C-C)	a’
			1307(w)	1315(w)	β(C-H)	a’
1332(100)	1333(100)	1336(100)	1334(mw)	137(38,0.28)	$\upsilon(C\text{-}CF_3)$	a’
	1342(20)	1357(20)	1357(w)		1257+100 1069+287	A”
1390(34)			1385(vw)		802+590	A”
			1391(vw)		1332+70	A”
1432(73)	1432(66)	1434(70)	1431(w)	1436(10,0.36)	υ(C-C)	a’
1452(38)					1307+147	A”
1468(34)					2*749	A’
1490(50)	1490(46)	1492(48)	1490(w)	1489(4,0.36)	υ(C-C)	a’
1502(35)	1502(35)				1432+70	A’
1515(32)			1518(w)		712+802	A’
1536(37)			1536(w)		1432+100	A”
1550(34)		1543(30)			1334+222 806+744	A”
		1583(20)	1581(w)	1580(6,0.46)	υ(C-C)	a’
			1593(w)	1600(10,0.52)	υ(C-C)	a’
1620(71) 1644(37)	1620(70)	1621(70)	1612(w)	1620(13,0.48)	†FR between $\beta(NH_2)$and 1252+375	a’
1660(32)			1660(vw)		1283+375	A’
1680(31)			1672(vw)		1580+100	A”
					1334+346	A’
1695(32)					1600+100 1142+557	A’
1712(31)					1490+222	A”
					1334+375	A’
1730(31)		1734(30)			1334+400	A”
1756(22)					1334+422,1166+590	A”
1768(28)					1252+515 1020+749	A”
1780(26)					1322+448	A”
					863+917	A”

1790(26)					1280+515	A”
1825(26)					1023+802	A”
1840(26)					1252+590	A’
1865(27)	1874(25)				1490+375	A’
2325(28)					1580+650	A’
2350(28)		2343(25)			1600+749,1280+1071	A’
		2360(25)			1280+1089	A’
2850(46)	2850(49)				1253+1600	A’
2920(61)	2928(66)				1489+1431	A’
2950(48)	2950*(15)	2909(20)			2*1490	A’
				3012(2,P)	1432+1580	A’
		3047(25)		3046(6,0.37)	υ(C-H)	a’
3062(29)				3068(13,0.44)	υ(C-H)	a’
3090(29)				3084(12,0.50)	υ(C-H)	a’
				3230	3084+147	A’
				3355(4,p?)	3068+287	A”
				3366(6,p?)	3047+315	A”
3390(43)	3390(73)	3393(42)		3396(9,0.35)	$\upsilon_s(NH_2)$	a’
3490(40)	3488(73)	3491(40)			$\upsilon_{as}(NH_2)$	a’
3645(28)					3084+557	A’
3670(28)					3355+315,3390+287	A”

Symbol

*- Frequencies observed in CCl_4 solution

a- Recorded on Spex Raman Spectrometer.

b- Recorded on Jobin Yvon Ramanor HG.2S Spctrometer.

v = very, w = weak, m = medium, s = strong.

†- FR Fermi Resonance

3. (iii) NH_2 Group Modes

The stretching modes of the NH_2 group have distinct magnitudes compared to all other modes, making them easily assignable. The symmetric stretching modes (υ_s) are assigned at ~3400 cm^{-1} and ~3390 cm^{-1}, and the anti-symmetric stretching modes (υ_{as}) are assigned at 3480 cm^{-1} and 3490 cm^{-1} for the 3A4FB and 3A4BB molecules, respectively. For the molecules studied earlier (Singh, 2001, Singh,2003), the NH_2 group and the halogen atoms are in para positions, hence there is no possibility of intra-molecular hydrogen bonding. Furthermore, for these molecules, the NH_2 group at the ortho position to the CF_3 group also does not show any intra-molecular hydrogen bonding with the F atom of the CF_3 group.In the present case, the frequencies assigned to the υ_s and υ_{as} modes satisfy the empirical relation (Bellamy, 1975).

$$\upsilon_s = 0.876\, \upsilon_{as} + 345.5$$

within the experimental accuracy ±5 cm^{-1}

However, the IR spectra in CS_2 solution show broad bands in the 3300-3500 cm^{-1} region. Hence, no conclusion could be drawn regarding the presence or absence of intra-molecular hydrogen bonding from the present study.

The scissoring mode of the NH_2 group is assigned at 1636 cm^{-1} and 1640 cm^{-1} for 3A4FB and 3A4BB, respectively. It is interesting to note that, in the present case, the scissoring mode also interacts with the combinations of the $\upsilon(C\text{-}NH_2)$ and the $\beta(C\text{-}NH_2)$ modes via Fermi resonance, similar to the cases reported earlier (Singh, 2001, Singh, 2003).The assignments for the rocking, wagging, and torsional modes of the NH_2 group have been made in the regions 1080-1090 cm^{-1}, 700-725 cm^{-1}, and 280-290 cm^{-1}, respectively, in agreement with the assignments made earlier (Singh, 2001, Singh, 2003) for these modes.

4. conclusion

For the molecules 3A4FB and 3A4BB, out of the 45 normal modes of vibration, 43 (30a' + 13a") normal modes could be observed directly, and 2 normal modes have been assigned based on the assignments of the combination bands and overtone bands. The frequencies ~1335, ~1165, ~1125, and ~745 cm^{-1} appear as characteristic frequencies involving the CF_3 group, similar to the cases studied earlier report. The highest frequency (~1335 cm^{-1}) corresponds to the ring CF_3 stretching mode, whereas the remaining three frequencies are due to the three CF_3 stretching modes. A frequency that also appears to be a characteristic frequency of the CF_3 group corresponds to the symmetric deformation mode, and it shows a widely varying magnitude due to coupling with the ring modes. For 3A4FB, this frequency is identified as 220 cm^{-1}, and for 3A4BB, it is identified as ~315 cm^{-1}.Three frequencies have been identified as characteristic frequencies of the NH_2 group at ~3490, ~3400, and ~1625 cm^{-1}, corresponding to the υ_{as}, υ_s, and β modes. It is noteworthy that the β (scissoring) mode for the NH_2 group interacts with the combination bands of the C-NH_2 stretching and in-plane bending modes via Fermi resonance. The ring breathing mode is observed to have a considerably reduced magnitude for 3A4FB, whereas for 3A4BB, it has a slightly higher magnitude. The trigonal bending mode is observed to have a magnitude reduced by ~100 cm^{-1} for both molecules. The Kekulé C=C stretching mode is observed to retain its magnitudesimilar to the molecules studied earlier.

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