

Vibrational spectra and normal coordinate analysis for substituted trifluoromethyl benzenes

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Abstract. The polarised Raman spectra of the three isomeric trifluoromethyl benzonitriles have been recorded in the region $50\text{--}4000\text{ cm}^{-1}$. The near and far IR spectra of these compounds have been recorded in the region $200\text{--}4000\text{ cm}^{-1}$ and $33\text{--}700\text{ cm}^{-1}$ respectively. To check the vibrational assignments normal coordinate analysis was performed using general valence force field. Very good agreement has been achieved between the observed and the calculated fundamental frequencies. It has been possible to resolve the controversies about the assignments of the C-CF₃ stretching and CF₃ symmetric stretching modes in substituted trifluoromethyl benzenes. Vibrational assignments together with the force fields for three isomers are reported for the first time.

Keywords. Raman spectra; infrared spectra; vibrational spectra; normal coordinate analysis; force fields.

1. Introduction

In recent times, fluorinated compounds have become very important on account of their wide range applications. Fluorinated compounds are widely used as heat transfer fluids, chemical intermediates, polymers and so on. The present paper is in continuation of our studies of the vibrational spectra of substituted trifluoromethyl (TFM) benzenes Yadav and Singh (1984, 1985). In this paper, the results and analysis of the polarised Raman and infrared spectra of *o*-, *m*- and *p*-TFM benzonitriles are reported in the light of normal coordinate analysis. As far as we know, the vibrational spectra of the three isomeric TFM benzonitriles have not been reported so far. The aim of the present investigation is (i) to propose consistent vibrational assignments for the internal modes of the CF₃ group, (ii) to propose consistent vibrational assignments for the ring modes including the breathing and trigonal C-C-C in-plane bending modes, (iii) to see whether the CF₃ group behaves as a heavy substituent, (iv) to study the effect of CF₃ and CN groups in the *o*-, *m*- and *p*-positions of the substituted benzenes on their internal modes of vibrations and (v) to evaluate consistent force fields for the three isomeric TFM benzonitriles.

2. Experimental

All the three substances, *o*-, *m*- and *p*-TFM benzonitriles, were purchased from Alfa Ventron Corporation (USA) and were of specpure grade; *o*- and *m*-isomers are

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colourless liquids at room temperature whereas the *p*-isomer is solid at room temperature and melts at $\approx 50^\circ\text{C}$ to form a colourless liquid. All the three substances were used as such for recording spectra.

The polarised Raman and near and far IR spectra of *o*- and *m*-TFM benzonitriles were recorded in the liquid phase at room temperature in the region $50\text{--}4000\text{ cm}^{-1}$ as described earlier (Yadav and Singh 1984, 1985). For recording the Raman spectra of *p*-TFM benzonitrile, the quartz sample cell was placed on a hot metal plate and the temperature was gradually increased till the sample had completely melted and its polarised Raman spectra were recorded in the molten state after a steady state had been achieved. The near IR spectrum of *p*-TFM benzonitrile was recorded in nujol mull.

Under the experimental conditions employed, measurements in all the three cases (Raman and near and far IR spectra) are accurate to $\pm 3\text{ cm}^{-1}$ and the resolution of the spectrometers was better than 2 cm^{-1} .

3. Normal coordinate analysis

Similar to the cases of isomeric trifluoromethyl benzaldehydes (Yadav and Singh 1984) and *p*-trifluoromethyl aniline (Yadav and Singh 1985) for the normal coordinate calculations, the *o*-, *m*- and *p*-TFM benzonitrile molecules have been assumed to belong to C_s point group. However, a local C_{3v} point group symmetry for the CF_3 group was assumed. The 42 normal modes of vibrations for each of the three isomeric TFM benzonitriles (total number of atoms = 16) are distributed as: $28a' + 14a''$ and in detail the distribution is as follows:

(i) Phenyl ring- $21a' + 9a''$ (ii) CF_3 group- $5a' + 4a''$ and (iii) CN group- $2a' + 1a''$. The distribution of normal modes for the phenyl ring is obvious and for the CF_3 group it has already been discussed in detail (Yadav and Singh 1984, 1985) and for the CN group, the distribution is given below:

C_s point group	a' species	a'' species
CN group	$\text{C}\equiv\text{N}$ stretch $\text{C}\equiv\text{N}$ in-plane bend	$\text{C}\equiv\text{N}$ out-of-plane bend

The symmetry coordinates for the phenyl ring part were constructed as per Whiffen (1955) and those for the CF_3 group as per Hollenstein and Günthard (1971). Because of some practical difficulties the CN group was taken to be a single mass point of equivalent atomic mass = 26 a.m.u. In the absence of any structural information for the three isomeric TFM benzonitriles, the geometrical parameters were taken from the work of Bürger *et al* (1982) for $\text{CF}_3\text{--CH=CH--CF}_3$ and Lide (1954) for $\text{C}_6\text{H}_5\cdot\text{CN}$ with hexagonal phenyl ring geometry. The calculations of G and F matrices and fundamental frequencies were made using the computer programme of Schachtschneider and Snyder (1963). General valence force field was used to calculate the fundamental frequencies. The force constants were transferred from the work of Yadav and Singh (1984, 1985) for substituted TFM benzenes and Kuwae and Machida (1979) for benzonitrile. The diagonal and off-diagonal force constants were initially adjusted by trial and error to give the best possible fit between the observed and calculated fundamental frequencies and finally an iterative procedure was used to further refine

the force constants. The final sets of constants for *o*-, *m*- and *p*-TFM benzonitriles are given in table 1.

4. Results and discussion

The vibrational assignments for the observed frequencies have been proposed on the basis of magnitudes and relative intensities of the frequencies observed in the Raman

Table 1. Valence force constants for *o*-, *m*- and *p*-TFM benzonitriles.

Force constant number	Description and notation ^a	Value ^b		
		<i>o</i>	<i>m</i>	<i>p</i>
1	C-C stretch (R)	6.527	7.325	7.201
2	C-CF ₃ stretch (R_1)	4.840	4.343	4.946
3	C-CN stretch (R_2)	4.650	4.154	4.342
4	C-H stretch (R_3)	5.106	5.160	5.155
5	C-F stretch (R_4)	4.851	4.953	5.050
6	C-C-C angle bend (α)	0.943	0.934	1.014
7	F-C-F angle bend (α_1)	1.800	1.800	1.831
8	C-C-F angle bend (α_2)	1.212	1.215	1.210
9	C-CF ₃ out-of-plane bend (γ_1)	0.532	0.532	0.522
10	C-CN out-of-plane bend (γ_2)	0.265	0.300	0.286
11	C-H out-of-plane bend (γ_3)	0.300	0.265	0.254
12	C-C-C torsion (ϕ)	0.085	0.085	0.085
13	CF ₃ torsion (τ)	0.005	0.005	0.005
14	C-CF ₃ in-plane bend (β_1)	1.754	1.756	1.742
15	C-CN in-plane bend (β_2)	1.249	1.355	1.324
16	C-H in-plane bend (β_3)	0.950	0.953	0.946
17	$(RR)^o$	1.155	0.758	0.651
18	$(RR)^m = (RR_1)^m = (RR_2)^m = (RR_4)^m$	-0.625	-0.350	-0.350
19	$(RR)^p = (RR_1)^p = (RR_2)^p = (RR_4)^p$	-0.134	0.350	0.350
20	$R_1 R_2 = (R_3 R_3)^o$	0.065	0.125	0.106
21	$R_4 R_4$	1.558	1.300	1.399
22	$(\alpha\alpha)^o$	-0.190	-0.134	-0.032
23	$\alpha_1 \alpha_1$	-0.113	0.247	0.235
24	$\alpha_2 \alpha_2$	0.649	0.664	0.420
25	$\gamma_1 \gamma_2 = (\gamma_3 \gamma_3)^o$	-0.008	-0.010	0.004
26	$(\phi\phi)^o$	0.007	-0.005	0.052
27	$\beta_1 \beta_2 = (\beta_3 \beta_3)^o$	-0.054	-0.009	0.013
28	$(\beta_3 \beta_3)^m$	-0.020	0.023	-0.021
29	$(\beta_3 \beta_3)^p$	0.062	0.043	-0.078
30	$R_i \alpha_i = R_i \alpha_{i+1}$	0.305	0.707	0.782
31	$R_i \beta_i = -R_i \beta_{i+1}$	-0.024	-0.062	-0.006
32	$-\alpha_{i+1} \beta_i = \alpha_{i+1} \beta_{i+2}$	-0.094	-0.158	-0.180
33	$-\phi_{i+1} \gamma_{i+1} = \phi_{i+1} \gamma_i$	0.020	0.018	0.011
34	$(RR_1)^o$	-0.396	-0.682	0.276
35	$(RR_2)^o$	-0.178	-0.224	0.395
36	$R_1 R_4$	1.184	1.192	1.365

^a *o*, *m* and *p* stand for *ortho*, *meta* and *para* interactions respectively; subscript *i* represents the position of *R*, α , β and γ in the ring.

^b The units for the force constants are as follows: stretch = m dyne/A; stretch/stretch = m dyne/A; stretch/bend = m dyne; bend = m dyne A; bend/bend = m dyne A.

and infrared spectra, depolarisation ratio of the Raman lines and potential energy distributions of the fundamental frequencies calculated from normal coordinate analysis. In addition, assistance has also been taken from the vibrational assignments proposed for benzene derivatives containing CF_3 (Yadav *et al* 1982; Yadav and Singh 1982, 1984, 1985) and CN (Green 1961; Jakobsen 1965; Green and Harrison 1976; Kuwae and Machida 1979; Ram *et al* 1980–81) groups.

The discussion of the normal modes of vibrations of *o*-, *m*- and *p*-TFM benzonitriles can be divided into the following three groups: (i) phenyl ring modes, (ii) CF_3 group modes and (iii) CN group modes.

The phenyl ring modes for the *o*-, *m*- and *p*-TFM benzonitrile molecules are discussed separately whereas the CF_3 and CN group modes are discussed together for the three isomeric molecules.

4.1. Phenyl ring modes

4.1a *o*-TFM benzonitrile: The frequencies observed in the Raman and IR spectra of *o*-TFM benzonitrile together with their relative intensities, Raman depolarisation ratio, calculated fundamental frequencies and corresponding potential energy distributions and proposed vibrational assignments are presented in table 2. For assignments of most of the fundamental frequencies table 2 is self-explanatory. However, some of the phenyl ring modes deserve some discussion.

The Kekule mode gives rise to its characteristic frequency in the region $1200\text{--}1400\text{ cm}^{-1}$ for substituted benzenes and is easily assigned on account of its nearly pure C–C stretching nature. In the present case, the frequency 1278 cm^{-1} is assigned to this mode.

For all *o*-disubstituted benzenes a strongly polarized Raman line at $\approx 1040\text{ cm}^{-1}$ is observed with good intensity and the corresponding IR band is observed with strong intensity. In the Raman spectrum of *o*-trifluoromethyl benzonitrile the frequency 1036 cm^{-1} is observed with strong intensity and low depolarisation ratio and the potential energy for this frequency contains appreciable contribution from C–C stretching force constant. Similar to the case of *o*-trifluoromethyl benzaldehyde (Yadav and Singh 1984) this frequency (1036 cm^{-1}) is assigned to the ring breathing mode.

In *o*-disubstituted benzenes the trigonal C–C–C in-plane bending mode 12 of the benzene is sensitive to the position and nature of the substituents and is drastically reduced in magnitude due to its interaction with other planar modes. The frequency 805 cm^{-1} is assigned to this mode. This frequency arises from strong interaction of the C–C–C in-plane bending mode with the C–F and C–C stretching modes.

For all benzene derivatives containing CF_3 groups, a broad band near 1330 cm^{-1} appears with very strong intensity in the IR spectrum whereas in the Raman spectrum it is polarised and appears with intensity ranging from weak to strong. Yadav and Singh (1984, 1985) have suggested that this frequency arises due to the C– CF_3 stretching mode for substituted TFM benzenes. In the present case, the frequency, 1320 cm^{-1} which arises from strong mixing of the C– CF_3 stretching mode with the C–C and C–F stretching, C–H in-plane bending and CF_3 deformation and rocking modes, is assigned to the C– CF_3 stretching mode.

The C–CN stretching frequency appears in the region $1100\text{--}1300\text{ cm}^{-1}$ for benzene derivatives containing a CN group. Kuwae and Machida (1979) have assigned the frequencies 1192 and 1122 cm^{-1} to this mode for $\text{C}_6\text{H}_5 \cdot \text{CN}$ and $\text{C}_6\text{D}_5 \cdot \text{CN}$ molecules.

Table 2. Observed and calculated fundamental frequencies for *o*-trifluoromethyl benzonitrile^a.

Observed		Infrared		Calculated		Species	Proposed assignments
Raman	Pure liquid	Pure liquid	CCl ₄ solution	cm ⁻¹	Potential energy distribution ^b		
cm ⁻¹	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	cm ⁻¹		
		3210	12			A''	0 + 2241 + 964
		3134	21			A'	0 + 2 × 1584
3090	20 (0.32)	3104	28		3099 4 (97)	a'	C-H stretch
3080	sh	3070	26		3079 4 (98)	a'	C-H stretch
3043	sh				3052 4 (100)	a'	C-H stretch
		3030	sh		3036 4 (101)	a'	C-H stretch
		2980	41			A'	0 + 2241 + 743
		2930	40			A'	0 + 1497 + 1454
		2400	5			A'	0 + 1605 + 805
2258	sh	2254	sh			A'	0 + 1605 + 654
2238	100 (0.4)	2244	69			a'	C≡N stretch
2188	2 (0.67)					A'	0 + 1036 + 1153; 0 + 1454 + 743
		1960	13			A'	0 + 1584 + 380
						A''	0 + 1201 + 771
		1850	15			A'	0 + 1114 + 743; 0 + 1201 + 654
		1734	78			A'	0 + 1175 + 557
						A''	0 + 964 + 771
		1638	24			A'	0 + 1320 + 318; 0 + 1150 + 493
1607	39 (0.69)	1602	58		1642 1 (62), 2 (25), 16 (12), 6 (8)	a'	C=C stretch
1586	8 (0.54)	1581	76		1596 1 (69), 16 (15), 3 (8), 6 (8)	a'	C=C stretch
		1540	13			A'	0 + 1320 + 220
1503	5 (0.57)	1491	76		1533 1 (65), 16 (33)	a'	C=C stretch

Table 2. (Continued)

Raman		Observed		Infrared		Calculated		Species	Proposed assignments
Pure liquid		Pure liquid		CCl ₄ solution		Potential energy distribution ^b			
cm ⁻¹	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	Rel. int.	cm ⁻¹			
1458	1 (p†)	1450	86	1455	42	1475	1 (46), 16 (33)	a'	C=C stretch
		1429	52					A'	0+1114+318
								A"	0+771+654
1323	12 (0-32)	1316	100B	1322	98	1335	16 (35), 1 (29), 2 (20), 7 (10), 5 (9), 8 (7)	a'	C-CF ₃ stretch
1280	12 (0-33)	1275	91	1275	44	1296	1 (75)	a'	C=C stretch (Kekule mode)
1238	1 (p†)	1233	85	1235	13	1224	16 (60), 1 (15), 5 (14), 7 (6)	a'	C-H i.p. bend
1201	31 (0-38)		36	1201	36	1212	1 (33), 16 (25), 5 (15), 3 (11), 6 (8), 7 (6)	a'	C-CN stretch
1176	12 (0-61)	1174	100B	1184	94	1200	5 (44), 7 (16), 3 (13), 16 (11), 6 (10), 8 (7), 1 (6)	a'	CF ₃ asym. stretch
						1197	5 (81), 7 (29), 8 (15)	a"	CF ₃ asym. stretch
						1125	6 (21), 1 (20), 16 (13), 5 (13)	a'	C-H i.p. bend
		1134	100B	1153	100			a'	C-H i.p. bend
		1114	98B	1118	47	1089	16 (50), 1 (3)	a'	C-H i.p. bend
1064	12 (0-22)	1058	98	1061	62	1060	1 (101), 16 (32)	a'	C-H i.p. bend
1039	52 (0-28)	1032	94	1039	44	1000	1 (66), 16 (40)	a'	C-C stretch (ring breathing mode)
1008	1 (dp†?)	1008	57			1002	11 (92), 12 (24)	a"	C-H o.p. bend
		964	90			939	11 (86), 12 (36)	a"	C-H o.p. bend
938	1 (≈1)	932	sh					A"	0+654+284
870	1 (≈1)	864	sh			868	11 (70), 12 (25)	a"	C-H o.p. bend
		836	26					A"	0+557+284
807	2 (0-4)	802	39			814	6 (25), 5 (21), 1 (8)	a'	C-C-C i.p. bend
771	sh (dp†)	771	95			768	12 (39), 11 (22)	a"	C-C-C torsion
		749	66			729	11 (83), 12 (19)	a"	C-H o.p. bend

745	39 (0.26)	740	66	Beckman IR-11 ^c (Pure liquid)	725	<i>a'</i>	CF ₃ sym. stretch
657	9 (0.48)	689	52	<i>ms</i>	622	<i>A''</i>	0 + 555 + 127
610	2 (≈1)	651	86	<i>m</i>	6 (49), 1 (8), 2 (8), 5 (8), 7 (7), 8 (5)	<i>a'</i>	C-C-C i.p. bend
558	6 (0.53)	596	32	<i>ms</i>		<i>A''</i>	0 + 318 + 284
		555	84	<i>sh</i>		<i>a'</i>	C≡N i.p. bend
		500	<i>sh</i>		519	<i>a'</i>	C-C-C torsion
496	19 (0.38)	490	44		509	<i>a''</i>	CF ₃ sym. deformation
					509	<i>a'</i>	CF ₃ asym. deformation
382	6 (0.38)	406	8	<i>mw</i>	444	<i>a''</i>	C-C-C torsion
		378	36	<i>w</i>	438	<i>a'</i>	C-C-C i.p. bend
		362	<i>sh</i>		402	<i>a'</i>	C-CN i.p. bend
318	17 (0.51)	318	55	<i>w</i>	280	<i>a''</i>	C≡N o.p. bend
		284	8	<i>mw</i>	290	<i>a'</i>	CF ₃ sym. deformation
220	7 (0.72)	220	9	<i>vw</i>	226	<i>a''</i>	CF ₃ perpendicular rock
163	<i>sh</i> (dpt)			<i>vw</i>	184	<i>a''</i>	CF ₃ parallel rock
143	<i>sh</i> (pt?)			<i>vw</i>	131	<i>a'</i>	C-CN o.p. bend
127	49 (0.89)			<i>vw</i>	121	<i>a''</i>	C-CF ₃ i.p. bend
				<i>vw</i>	66	<i>a''</i>	C-CF ₃ o.p. bend
				<i>vw</i>		<i>a''</i>	CF ₃ torsion

^a Abbreviations used: Rel. int. = Relative intensity; Dep. = Depolarisation ratio; *sh* = shoulder; *B* = broad; *pt* = polarised; *dpt* = depolarised; *i.p.* = in-plane; *o.p.* = out-of-plane; *sym.* = symmetric; *asym.* = anti-symmetric; *deform.* = deformation; *ms* = medium strong; *m* = medium; *w* = weak; *mw* = medium weak; *vw* = very weak; *vw* = very very weak.

^b Numbers outside the brackets are the force constant numbers defined in table 1 and those within the brackets are the corresponding contributions.

^c The frequencies observed in the spectrum of pure liquid, recorded on Beckman IR-11 spectrometer.

[†] *p* and *dp* are used for those Raman lines for which depolarisation ratio could not be determined precisely.

For *o*- and *p*-amino benzonitriles, Ram *et al* (1980–81) have assigned the 1187 and 1177 cm^{-1} frequencies to this mode. In the present case, although the region 1100–1300 cm^{-1} contains a number of frequencies, the potential energy distribution for only the 1201 cm^{-1} frequency has a contribution from the C–CN stretching force constant and therefore, the frequency 1201 cm^{-1} is assigned to the C–CN stretching mode.

4.1.b *m*-TFM benzonitrile: Table 3 presents the frequencies observed in the Raman and IR spectra of *m*-TFM benzonitrile together with their relative intensities, Raman depolarisation ratio, calculated fundamental frequencies and corresponding potential energy distribution and proposed assignments.

The Kekule mode, in the present case also, is assigned on account of the major contribution from the C–C stretching force constant to the frequency 1386 cm^{-1} .

In the region 640–1135 cm^{-1} , there are two strong Raman lines, namely, 736 and 1003 cm^{-1} either of which can be assigned to the ring breathing mode on the basis of only intensity considerations but as discussed later, the frequency 736 cm^{-1} is assigned to the CF_3 symmetric stretching mode and we assign the frequency 1003 cm^{-1} to the ring breathing mode, which is supported by normal coordinate analysis and also by the work of Singh and co-workers (Yadav and Singh 1982, 1984; Yadav *et al* 1982, Szostak 1979 and Katon *et al* 1980) for *m*-substituted benzenes.

As in the case of *o*-TFM benzonitrile, in this case also the trigonal C–C–C in-plane bending mode is considerably reduced and the frequency 809 cm^{-1} is assigned to this mode. This frequency arises from a mixing of the C–C–C in-plane bending mode with the C–F, C–C, C–CN and C– CF_3 stretching and C–H in-plane bending modes.

The frequency 1332 cm^{-1} , observed with weak and very strong intensities in the Raman and IR spectra respectively, is a characteristic frequency of the CF_3 group and is assigned to the C– CF_3 stretching mode. As in the case of the *o*-isomer, in this case also this frequency arises from a mixing of the C– CF_3 stretching mode with other planar modes. On the basis of potential energy distributions and vibrational assignments made for benzene derivatives containing a CN group (Green 1961; Jakobsen 1965; Green and Harrison 1976; Kuwae and Machida 1979; Ram *et al* 1980–81) the frequency 1242 cm^{-1} is assigned to the C–CN stretching mode.

4.1.c *p*-TFM benzonitrile: The frequencies observed in the Raman and the IR spectra of *p*-TFM benzonitrile along with their relative intensities, depolarisation ratio of Raman lines, calculated fundamental frequencies and corresponding potential energy distributions and proposed assignments are presented in table 4.

In the present case the frequency 1391 cm^{-1} is assigned to the Kekule vibrations. This frequency arises from a mixing of a number of modes with the C–C stretching mode. However, the C–C stretching mode is dominantly involved in this frequency. The ring breathing mode for *p*-disubstituted benzenes has been assigned near 825 cm^{-1} by Yadav and Singh (1984, 1985) and Tripathi and Katon (1979). On the basis of Raman intensity, potential energy distribution and Raman depolarisation ratio, the frequency 806 cm^{-1} is assigned to the ring breathing mode for *p*-TFM benzonitrile. Although this mode is allowed in both the Raman and infrared spectra in the present case (point group- C_s), it has been observed in the infrared spectrum as a shoulder only. It appears that this mode retains its principal characteristics of the 992 cm^{-1} frequency of benzene (D_{6h} point group) where this mode is allowed in the Raman spectrum but forbidden in the IR spectrum.

Table 3. Observed and calculated fundamental frequencies for *m*-trifluoromethyl benzonitrile^a.

Raman		Observed		Infrared		Calculated		Species	Proposed assignments
Pure liquid	Rel. int. and dep. cm ⁻¹	Pure liquid	Rel. int. cm ⁻¹	CCl ₄ solution	Rel. int. cm ⁻¹	cm ⁻¹	Potential energy distribution ^b		
		3440	21					A'	0+2241+1192
		3200	sh					A'	0+2×1614
		3130	sh			3135	4 (96)	a'	C-H stretch
		3096	58			3082	4 (99)	a'	C-H stretch
3082	11 (0.43)					3079	4 (99)	a'	C-H stretch
3023	1 (pt)	3020	sh			3028	4 (103)	a'	C-H stretch
		2930	24					A''	0+2241+694
		2785	15					A'	0+2241+550; 0+1614+1176
		2710	15					A'	0+2241+471
		2670	17					A'	0+1391+1287
		2626	20					A'	0+2241+387
		2516	18					A''	0+1614+903
								A'	0+1440+1071
		2470	14					A''	0+1614+860
								A'	0+1332+1145
		2370	17					A''	0+2241+135
		2282	sh					A''	0+1287+991
2238	80 (0.45)	2244	97					a'	C≡N stretch
2183	0 (dpt?)	2185	sh					A''	0+1180+1003
		2066	17					A'	0+1332+735
		2030	17					A'	0+1483+550
								A''	0+1332+694
								A'	0+1332+650
		1980	24					A''	0+1287+694

Table 3. (Continued)

Raman		Observed		Infrared		Calculated		Species	Proposed assignments
cm ⁻¹	Rel. int. and dep.	Pure liquid	Rel. int.	Pure liquid	Rel. int.	cm ⁻¹	Potential energy distribution ^b		
1923	29	1806	29	1806	29	1624	1 (70), 2 (16), 16 (14), 6 (7)	A''	0+1332+592
1862	24	1735	30	1735	30	1602	1 (93), 16 (14), 6 (7)	A''	0+1003+860
1806	29	1658	30	1658	30	1490	1 (73), 16 (16)	A'	0+1483+387
1616	9 (0.48)	1591	sh	1591	sh	1454	1 (106), 16 (15), 2 (6)	A'	0+1071+736
1597	7 (0.51)	1483	77	1483	77	1408	1 (54), 16 (30), 3 (13), 14 (6), 6 (5)	A'	0+1003+736
1461	sh	1461	sh	1461	sh	1325	16 (26), 7 (21), 2 (16), 5 (9), 7 (6), 8 (5)	A'	0+1332+328
1436	97	1436	97	1436	97	1286	16 (59), 1 (29), 15 (5)	a'	C=C stretch
1391	46	1391	46	1391	46	1235	1 (19), 16 (18), 3 (13), 5 (12), 6 (8), 8 (6), 7 (8)	a'	C=C stretch
1443	2 (0.46)	1442	47	1442	47	1191	5 (72), 7 (23), 16 (13), 1 (9), 8 (6)	A'	0+809+650
1337	10 (0.29)	1336	100	1336	100	1200	5 (85), 7 (27), 8 (15), 9 (6)	a'	C=C stretch
1288	1 (p)	1285	84	1285	84	1155	16 (66), 1 (14)	a'	C=C stretch (Kekule vibration mode)
1247	45	1247	45	1247	45	1092	16 (56), 1 (23), 3 (6), 5 (5)	a'	C=C stretch
1228	sh	1228	sh	1228	sh	1047	1 (56), 16 (35)	A''	0+903+328
1193	11 (0.33)	1200	sh	1200	sh	1000	1 (29), 6 (49)	a'	CF ₃ stretch
1180	sh	1180	99B	1180	99B			a'	C-H i.p. bend
1140	1 (0.60)	1150	99B	1147	86			a'	C-CN stretch
1113	2 (0.46)	1100	sh	1102	41			a'	0+647+471
1085	1 (p†)	1090	sh	1085	56			a'	CF ₃ asym. stretch
1071	1 (0.45)	1071	99	1071	40			a'	CF ₃ asym. stretch
1018	sh (p†)							a'	C-H i.p. bend
1005	100 (0.29)	1000	62	1000	62			a'	C-H i.p. bend
								a'	0+550+471
								a'	C-C stretch (ring breathing mode)

Table 4. Observed and calculated fundamental frequencies for *p*-trifluoromethyl benzonitrile^a.

Raman		Observed				Calculated				Species	Proposed assignments
Pure liquid		Infrared		CCl ₄ solution		Potential energy distribution ^b					
cm ⁻¹	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	Rel. int.	cm ⁻¹	Rel. int.	cm ⁻¹			
3088	10 (0.44)	3130	sh			3121	4 (97)			a'	C-H stretch
3018	1 (p†)	3070	33			3108	4 (97)			a'	C-H stretch
2240	100 (0.45)					3057	4 (101)			a'	C-H stretch
		2240	79			3032	4 (101)			a'	C-H stretch
		1970	24							A''	C≡N stretch
		1945	19							A'	0+1124+836
		1920	25							A'	0+1409+547
		1838	19							A''	0+1183+739
		1790	14							A''	0+1183+644
		1720	11							A''	0+1051+739
		1670	10							A'	0+1183+547
1620	20 (0.61)	1612	27							A'	0+1124+547
		1572	19			1607	1 (94), 16 (19), 6 (8)			a'	C=C stretch
1513	2 (0.5)					1592	1 (97), 16 (7), 6 (7), 14 (5)			a'	C=C stretch
		1409	69		26	1514	1 (113), 16 (22)			a'	C=C stretch
		1395	sh		18	1419	16 (46), 1 (37), 2 (19)			a'	C=C stretch
						1391	1 (56), 16 (27), 5 (10), 14 (10), 8 (6), 15 (5)			a'	C=C stretch (Kekule vibration mode)
1358	1 (p†)					1364	16 (64), 1 (11), 5 (9)			a'	C-H i.p. bend
1324	8 (0.4)	1320	97B		100	1311	2 (39), 16 (20), 7 (13), 5 (9), 8 (9), 1 (7)			a'	C-CF ₃ stretch
1213	3 (p†)					1227	16 (44), 1 (14)			a'	C-H i.p. bend
1198	sh					1211	5 (87), 7 (27), 8 (15)			a''	CF ₃ asym. stretch
1186	34 (0.39)	1180	100B		65	1184	1 (35), 3 (33), 6 (11), 15 (11)			a'	C-CN stretch

1138	1 (0-6)	1140	100B	1136	94	1145	5 (47), 8 (14), 23 (11), 16 (7), 9 (6)	a'	$\left\{ \begin{array}{l} \text{CF}_3 \text{ asym. stretch} \\ \text{Fermi resonance between} \\ \text{1124 and 644 + 488} \end{array} \right.$
1113	1 (0-50)	1104	110B	1100	65				
1074	8 (0-40)	1066	sh	1066	85	1090	16 (71), 1 (25)	a'	C-H i.p. bend
1043	1 (p)	1056	97	1050	sh	1054	1 (59), 16 (41)	a'	C-H i.p. bend
1023	3 (p)	1022	88	1019	86	1000	1 (49), 6 (40), 16 (10)	a'	C-C-C i.p. bend
968	1 (\approx 1)	961	sh			964	12 (73), 11 (67)	a''	C-H o.p. bend
912	1	920	sh				0 + 784 + 141; 0 + 547 + 371	A''	
880	1	861	89			870	11 (52), 12 (39)	a''	C-H o.p. bend
		836	91			817	11 (85), 12 (44)	a''	C-H o.p. bend
811	48 (0-31)	800	sh			829	1 (30), 5 (18), 6 (16), 3 (9), 16 (8)	a'	C-C stretch (ring breathing mode)
786	11 (0-36)	781	sh			768	5 (30), 6 (23), 3 (15), 1 (7), 7 (7), 8 (5), 16 (5)	a'	CF ₃ sym. stretch
738	3 (0-77)	739	78			746	11 (76), 12 (32), 9 (5)	a''	C-H o.p. bend
645	10 (0-85)	643	28			658	12 (83), 9 (30), 8 (14), 10 (9), 5 (5)	a''	C-C-C torsion
		602	28			587	6 (105), 16 (5)	a'	C-C-C i.p. bend
543	4(0-63)	551	19					a'	C \equiv N i.p. bend
		488	11			485	7 (78), 5 (42)	a''	CF ₃ asym. deform.
						483	7 (85), 5 (35)	a'	CF ₃ asym. deform.
465	2 (\approx 1)					481	10 (43), 12 (41), 9 (16), 8 (14)	a''	C-C-C torsion
		441	6			435	6 (31), 3 (26), 2 (21), 1 (7), 7 (6), 5 (5)	a'	C-C-C i.p. bend
						417	12 (79), 11 (35)	a''	C-C-C torsion
						395	14 (35), 15 (31), 8 (31), 7 (8), 1 (6), 5 (5)	a''	C-CN i.p. bend
368	1 (\approx 1)	373	4					a''	C \equiv N o.p. bend
						319	12 (136), 8 (50), 10 (14)	a''	CF ₃ perpendicular rock
294	33 (0-38)					298	6 (37), 2 (28), 7 (14), 8 (9), 3 (6), 1 (5)	a'	CF ₃ sym. deform.
220	2 (p [†] ?)					245	15 (55), 8 (44), 1 (11)	a'	CF ₃ parallel rock
188	7 (dpt [†])					211	12 (111), 8 (45), 9 (12), 10 (8)	a''	C-CN o.p. bend
173	2 (p [†] ?)					156	8 (60), 14 (46), 15 (6), 1 (5)	a'	C-CF ₃ i.p. bend
141	10 (dpt [†])					100	12 (80), 9 (19), 11 (17), 8 (13), 10 (5)	a'	C-CF ₃ o.p. bend
						20	13 (94), 12 (8)	a''	CF ₃ torsion

a,b See table 2, also for abbreviations.

The trigonal C–C–C in-plane bending mode of benzene is observed to have nearly the same magnitude in the present case. The frequency 1023 cm^{-1} is assigned to this mode. The potential energy for this frequency has contributions from C–C in-plane bending, C–C stretching and C–H in-plane bending force constants. As in the case of the *o*- and *m*-isomers, the frequency 1322 cm^{-1} is a characteristic frequency of the CF_3 group and is assigned to the C– CF_3 stretching mode. This frequency arises from a mixing of the C– CF_3 stretching mode with other planar modes.

A polarised Raman line of medium-strong intensity is observed at 1183 cm^{-1} . The corresponding IR band of very strong intensity is also observed. The potential energy distribution for this frequency contains appreciable contribution from the C–CN stretching force constant and this frequency is assigned to the C–CN stretching mode.

4.2 CF_3 group modes

Under the point group C_{3v} , the CF_3 group gives rise to three non-degenerate modes (symmetric stretching, symmetric deformation and torsion) and three degenerate modes (anti-symmetric stretching, anti-symmetric deformation and rocking). On reduction of the symmetry from C_{3v} to C_s , each of the three degenerate modes splits up into two components. One component of each belongs to the symmetric species a' and the other one to the anti-symmetric species a'' . Hereafter, components under the species a' and a'' will be called symmetric and anti-symmetric components respectively.

For benzene derivatives containing CF_3 group(s), the CF_3 anti-symmetric stretching modes appear in the region $1100\text{--}1200\text{ cm}^{-1}$ with strong IR intensities but with varying Raman intensities. On the basis of potential energy distributions, relative intensities in the Raman and IR spectra and Raman depolarisation ratios, the frequencies 1175 , 1191 and 1124 cm^{-1} are assigned to the symmetric component of the degenerate CF_3 stretching mode for the three isomeric TFM benzonitriles respectively. The corresponding anti-symmetric components are assigned at 1197 , 1180 and 1198 cm^{-1} for the three isomers respectively.

The CF_3 symmetric stretching mode is expected to appear in the Raman spectrum with greater intensity as compared to the anti-symmetric CF_3 stretching modes. Yadav and Singh (1984, 1985) have assigned a frequency $\approx 750\text{ cm}^{-1}$ to the mode $\nu_s(\text{CF}_3)$ for isomeric TFM benzaldehydes. In the present case, the frequencies 743 , 736 and 785 cm^{-1} are observed with high intensities in the Raman spectra of the three isomeric TFM benzonitriles. Moreover, these frequencies have higher Raman intensities compared to the corresponding frequencies 1175 , 1191 and 1124 cm^{-1} , which have been assigned to the anti-symmetric CF_3 stretching mode. Therefore, the frequencies 743 , 736 and 785 cm^{-1} are assigned to the CF_3 symmetric stretching mode for the three isomers. Normal coordinate analysis also supports the assignments of these frequencies to the CF_3 symmetric stretching mode.

The assignment of CF_3 anti-symmetric deformation mode (species a') is made easier due to the large contributions from the CF_3 deformation mode to the potential energy distributions for the frequencies 493 , 471 and 483 cm^{-1} for the three isomeric TFM benzonitriles respectively. These frequencies arise from strong mixing of CF_3 stretching and deformation modes. Similarly, the frequencies 509 , 481 and 488 cm^{-1} are assigned to the anti-symmetric components of the degenerate CF_3 deformation mode of the three isomers.

For all TFM benzenes a characteristic frequency is observed in the region

290–340 cm^{-1} . This frequency has good intensity in the Raman spectrum and usually medium intensity in the IR spectrum. In the Raman and IR spectra of nine related compounds* that we have studied, the magnitudes and relative intensities of absorption at this frequency match closely and compel us to believe that this frequency is essentially associated with the CF_3 group. In the Raman spectra of all the three isomeric TFM benzonitriles this frequency appears with medium intensity and is polarised. In the IR spectra for the *o*- and *m*-isomers this frequency has been observed with medium-strong intensity whereas for the *p*-isomer it has not been observed. In the light of potential energy distribution, relative intensities in the Raman spectra and Raman depolarisation ratios, the frequencies 318, 328 and 294 cm^{-1} are assigned to the CF_3 symmetric deformation modes for the three isomers respectively. Our assignment for this mode in the present case is in agreement with that of the isomeric TFM benzaldehydes (Yadav and Singh 1984) and *p*-TFM aniline (Yadav and Singh 1985).

The CF_3 rocking modes appear in the region 200–400 cm^{-1} . Moreover, the parallel rocking mode- $\rho_{\parallel}(\text{CF}_3)$ is observed to have lower magnitude compared to the perpendicular rocking mode— $\rho_{\perp}(\text{CF}_3)$ (Yadav *et al* 1982; Yadav and Singh 1982). In the present case, the frequencies 220, 232 and 220 cm^{-1} are assigned to the $\rho_{\parallel}(\text{CF}_3)$ mode for the three isomers respectively and the frequencies 282, 286 and 319 cm^{-1} are assigned to the $\rho_{\perp}(\text{CF}_3)$ mode.

Berney (1964a, b, 1969, 1971, 1973) has assigned the CF_3 torsional mode below 100 cm^{-1} for a number of compounds containing CF_3 group(s). In the present case, the frequencies 57, 72 and 20 cm^{-1} are assigned to this mode for the three isomeric TFM benzonitriles respectively.

4.3 CN group modes

For aromatic nitriles the $\text{C}\equiv\text{N}$ stretching frequency is very characteristic in magnitude and appears near 2240 cm^{-1} usually with strong intensities in both the Raman and IR spectra. The frequencies 2241, 2241 and 2240 cm^{-1} have been observed with very strong intensities in the Raman as well as the IR spectra of *o*-, *m*- and *p*-TFM benzonitriles respectively. These frequencies are assigned to the $\text{C}\equiv\text{N}$ stretching mode.

The $\text{C}\equiv\text{N}$ in-plane bending mode gives rise to its characteristic frequency in the neighbourhood of 550 cm^{-1} . In the case of benzonitriles-*h*₅ and *d*₅ Kuwae and Machida (1979) have assigned the frequencies 546 and 531 cm^{-1} to this mode. The frequencies 554, 536 and 550 cm^{-1} have been assigned to this mode by Ram *et al* (1980–81) for *o*-, *m*- and *p*-amino benzonitriles respectively. In the present case, the frequencies 557, 550 and 547 cm^{-1} are assigned to the $\text{C}\equiv\text{N}$ in-plane bending mode for the three isomers respectively.

Force field calculations on benzonitriles-*h*₅ and *d*₅ by Kuwae and Machida (1979) have shown that the frequencies 376 and 351 cm^{-1} in these arise from the $\text{C}\equiv\text{N}$ out-of-plane bending mode. The frequencies 362, 346 and 371 cm^{-1} are assigned to this mode for *o*-, *m*- and *p*-TFM benzonitriles respectively.

* *o*-, *m*-, and *p*-TFM benzonitriles; *o*-, *m*- and *p*-TFM benzaldehydes (Yadav and Singh 1984); *p*-TFM aniline (Yadav and Singh 1985); *m*- $\text{C}_6\text{H}_4\cdot(\text{CF}_3)_2$ (Yadav *et al* 1982) and *m*- $\text{F}\cdot\text{C}_6\text{H}_4\cdot\text{CF}_3$ (Yadav and Singh 1982).

5. Summary and conclusions

Fairly consistent assignments for the internal modes of the CF_3 group for the three isomeric TFM benzonitriles are proposed. In all the three cases, the $\nu_s(\text{CF}_3)$ mode is observed to have greater intensity in the Raman spectra, compared to the $\nu_{as}(\text{CF}_3)$ modes. Similarly for the *m*- and *p*-isomers the $\delta_s(\text{CF}_3)$ mode is observed to have greater intensity in the Raman spectra than the $\delta_{as}(\text{CF}_3)$. However, for the *o*- isomer the $\delta_s(\text{CF}_3)$ mode has somewhat lower intensity in the Raman spectra than the $\delta_{as}(\text{CF}_3)$ modes.

For the *o*- and *m*-isomers, the ring breathing mode is observed to have nearly the same magnitude ($\approx 1000 \text{ cm}^{-1}$) as for benzene (992 cm^{-1}) whereas for the *p*-isomer, its magnitude is considerably reduced ($\approx 800 \text{ cm}^{-1}$). The C–C–C in-plane bending mode is assigned to considerably lower magnitude ($\approx 800 \text{ cm}^{-1}$) for the *o*- and *m*-isomers compared to benzene (1010 cm^{-1}) whereas for the *p*-isomer, this mode is observed to have nearly the same magnitude ($\approx 1020 \text{ cm}^{-1}$). Thus it appears that in the *o*- and *m*-positions of the substituents, the trigonal C–C–C in-plane bending mode strongly interacts with other planar modes whereas in the *p*-positions of the substituents, the ring breathing mode strongly interacts with other planar modes.

For all the three isomeric TFM benzonitriles, the C– CF_3 stretching frequency has been assigned at $\approx 1320 \text{ cm}^{-1}$. The assignment of this frequency with such a high magnitude to the C– CF_3 stretching mode suggests that the CF_3 group may not be assumed to be a heavy substituent as was suggested by Varsanyi (1969). The magnitude of the C–X stretching mode, where X is a heavy substituent, is expected to be less than 800 cm^{-1} (Varsanyi 1969). The present assignment is in agreement with the suggestion of D'Cunha and Kartha (1975). Consistent force fields for the three isomeric TFM benzonitriles have been evaluated for the first time.

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