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Electronic and Vibrational Spectral Studies of Pentafluoro-Benzoic Acid and Pentafluoro-Benzonitrile

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The infrared and Raman spectra of pentafluorobenzonitrile and pentafluorobenzoic acid and the near ultraviolet spectra of the vapours of pentafluorobenzonitrile corresponding to $^1A_{1g} \rightarrow {}^1B_{2u}$ and $^1A_{1g} \rightarrow {}^1B_{1u}$ transitions of benzene are reported. Assignments of fundamentals are proposed. Spectra in various polar and non-polar solvents are also reported in the ultraviolet region and the effect of solvents and pH discussed.

INTRODUCTION

The infrared and Raman Spectra of benzonitrile, its mono- and di-derivatives have been studied in detail by various workers[1-7]. The electronic spectra of mono-halogenated benzonitrile also appear in the literature[3,8-11]. The vibrational spectra of carboxylic acids have also been studied by various workers[12-17]. Such compounds are of high interest because of their high symmetry and thermal stability. The present paper reports the vibrational and electronic spectra of vapours of pentafluorobenzonitrile and the vibrational spectra of pentafluorobenzoic acid. The electronic spectra in various solvents have also been recorded and the effect of pH and solvents is also discussed.

EXPERIMENTAL

The pure chemicals pentafluorobenzonitrile and pentafluorobenzoic acid (hereafter referred as PFB and PFBA respectively) were obtained from EGA-CHEMIE, WEST GERMANY. Their purity was confirmed by elemental analysis and m.pt. determination (b.pt. of PFB is 164°C and m.pt. of PFBA is 100–102°C). The far-infrared and infrared spectra for both the molecules have been recorded on NICOLET FT-IR Spectrophotometer. The Laser Raman spectra of both the molecules have been recorded on Spex-Model 1401 Spectrophotometer using 6471 Å Krypton-Argon ion line of spectra Model-164 laser with power 200 mw and slit width of 2 cm^{-1}. The time constant was kept 0.25 sec. and 1 sec. and scanning speed was 100 cm^{-1}/min. and 25 cm^{-1}/min. for PFB and PFBA respectively. Near ultraviolet absorption spectra of the vapours of pentafluorobenzonitrile has been recorded on Beckman DK–2A ratio recording spectrophotometer using 10 cm^{-1} pathlength cell and temperatures upto 30–50°C. Inspite of our best efforts we could not record the ultraviolet absorption spectra of the vapours of pentafluorobenzoic acid. However, the electronic spectra in various solvents (water, methanol, ethanol, CCl_4, $CHCl_3$ and benzene) were recorded on Backman M–35 spectrophotometer. The pH of the solutions, in above solvents and with HCl and NaOH were measured using Systronics Digital pH meter Model–335. On account of the poor solubility of these molecules in non-polar solvents the concentration could not be observed.

RESULTS AND DISCUSSION

The infrared and Raman spectra of PFB and PFBA along with the frequencies of similar molecules are shown in Tables 1, 2. The analyses and assignments of the electronic spectra of vapours of PFB are given in Tables 3 & 4. Table 5 represents the position of 0,0 bands and red shift for PFB compared to benzonitrile. The electronic transitions in various solvents are shown in Table 6. Both the molecules may be assumed to belong to the point group C_{2v} as such the 30 fundamental vibrations divide among the symmetry species of the point group ($12a_1 + 10b_2$) in plane (a′) and ($3a_2 + 6b_1$) out-of-plane (a″) vibrations.[18]

Electronic Spectra

Under reduced symmetry, the forbidden transitions of benzene $^1A_{1g} \rightarrow {}^1B_{2u}$ (2600 Å System) and $^1A_{1g} \rightarrow {}^1B_{1u}$ (2100 Å System) become allowed. The system corresponding to $^1A_{1g} \rightarrow {}^1B_{2u}$ extends from 2769 to 2723 Å and the second system corresponding to $^1A_{1g} \rightarrow {}^1B_{2u}$ transition extends from 2235 to 2077 Å in PFB. The spectra in various solvents and the studies on similar molecules[6] have enabled to chose the 0,0 band in $^1A_{1g} \rightarrow {}^1B_{2u}$ (2600 Å System) at 36377 cm^{-1} and at 45269 cm^{-1} in $^1A_{1g} \rightarrow {}^1B_{1u}$ (2100 Å System) in PFB. The observed G. S. and E. S. fundamentals are well correlated with their corresponding i.r. and Raman values (Table 4) and are discussed alongwith the vibrational spectra.

Vibrational Spectra

In all substituted benzenes, four bands are usually observed in the region 1400–1650 cm^{-1}. These bands are the components of e_{2g} (1595 cm^{-1}) and the e_{1u} (1485 cm^{-1}) C–C stretching vibration of benzene. The Raman bands observed at 1655 and 1446 cm^{-1} in PFB and at 1657, 1517 and 1412 cm^{-1} in PFBA have been assigned to the above mode. The 1600 cm^{-1} band usually lie within the range 1625–1575 cm^{-1} for most aromatic materials[19]. With para substitution and due to the presence of highly electronegative snbstituents there is a small shift towards higher

TABLE 1

VIBRATIONAL FREQUENCIES FOR PENTAFLUOROBENZONITRILE AND THEIR ASSIGNMENTS

C_6F_6[24]	C_6F_5Cl[22]	C_6H_5CN[9]	C_6F_5CN IR	C_6F_5CN Raman	Assignments*
125	116	—	—	105 w	γ(C—F)
—	—	—	—	133 sb	γ(C≡N)
215	178	—	173 s	—	γ(C—F)
208	202	208	200 vw	—	—
264	217	—	213 vvs	—	γ(C—F)
			264 276 mwb	270 vvw	γ(C—CN)
			306 vs	310 w	γ(C—F)
315	310	—	316 vs	322 w	β(C—F)
379	370	380	388 mb	385 s	β(C—CN), γ(C—F)
			414 s	412 s	β(C—C) o.p.b.
			427 vs	425 s	β(C—F)
443	441	—	—	450 w	—
		460	471 vvs	470 s	β(C≡N), (C—C) o.p.b.
559	516	547	535 s	535 vvs	β(C—F), (C—C) i.p.b.
640	589	—	607 ms	590 s	(C—C) i.p.b.
			652 vvs	—	β(C—F)
691	716	—	733 vvs	—	(C—C) o.p.b.
			796 vvs	—	310 + 270 + 213
			850 s	845 mw	Trigonal bending
			903 vs	—	590 + 310
1019 994	1013 986	1002	991 vvs	965 955 mw	ring breathing
			1044 vvs	1035 vvw	733 + 310
—	1102		1132 vvs	—	ν(C—F)
1157	1153	—	1161 w, sh	1163 w	ν(C—F)
			1203 vvs	—	ν(C—CN)
1253	1274	—	1265 vs	—	ν(C—F)
			1282 vs	—	ν(C—F)
		1332	1326 vvs	1330 mw	ν(CC),ν(C—F)
			1378 vvs	1375 vvw	991 + 385
			1406 ms	—	991 + 412

TABLE 1 (Contd.)

C_6F_6[24]	C_6F_5Cl[22]	C_6H_5CN[9]	C_6F_5CN		Assignments*
			IR	Raman	
1440	1448	1450	1450 vvs	1450 vs	ν(CC)
1530	1518	1493	1521 vsb	—	ν(CC)
			1582 s	—	ν(CC)
1655	1643	1600	1627 vvs	1655 s	ν(CC)
			1724 s	—	1132 + 607
			1750 vs	—	1330 + 425
			1840 vs	—	1265 + 590
			1921 s	—	1330 + 607
			2056 vvs	—	1446 + 607
			2110 s	—	1521 + 590
			2164 ms	—	1521 + 652
			2200 ms	—	—
		2217	2253 vvs	2250 s	ν(C≡N)
			2271 vvs	—	1330 + 955
			2447 vs	—	1130 + 1132
			2483 vs	—	1130 + 1161
			2544 s	—	1521 + 1035
			2571 s	—	1446 + 1132
			2605 ms	—	1446 + 1132
			2605 s	—	2×1326
			2677 vs	—	1627 + 1035
			2694 m	—	1521 + 1163
			2765 s	—	1446 + 1130
			2791 s	—	165 + 1132
			2844 m	—	—
			2906 mw	—	1655 + 1265
			2930 vs	—	1521 + 1446
			3029 s	—	—
			3145 s	—	1627 + 1521
			3190 s	—	1655 + 1521
			3298 ms	—	2 × 1655
			3370 m	—	2250 + 1132
			3667 s	—	2250 + 1446
			3791 vs	—	3 × 1265

*Visual intensities are shown against each wave number, vvs- very very strong, vs- very strong, s- strong, m- medium, mw- medium weak, w- weak, vvw- very very weak, ν-stretching, β- and i.p.b.—in-plane-bending, γ and o.p.b.—out-of-plane bending.

TABLE 2

VIBRATIONAL FREQUENCIES FOR PENTAFLUOROBENZOIC ACID AND THEIR ASSIGNMENTS

C_6F_6[24]	C_6F_5Cl[22]	C_6H_5COOH[17]	C_6H_5COOH		Assignments*
			IR	Raman	
			62 mbw	—	Lattice vib.
			71 vs	—	γ twist
			75 vs	—	Lattice vib.
			83 s	—	Lattice vib.
			95 s	—	γ(OH - - - O)
			103 s	—	ν(OH - - - O)
			108 vvs	—	γ(C—F)
125	116	—	116 vs	—	γ(C—F)
			121 vvs	—	γ(C—F)
			141 msb	—	—
			152 m	155 vw	γ(C—F)
215	178	190	—	190 ms	ν(OH - - - O)
315	310	—	—	310 vw	γ(C—COOH)
		—	—	330 ms	γ(C—F)
	357	—	—	342 s	β(C—F)
379	370	388	—	380 s	β(C—F)
		428	—	408 vvs	(C—C) o.p.b.
445	441	—	—	454 vvs	(C—C) o.p.b.
			472 vs	—	β(C—F)
		—	—	515 vvs	β(C—F)
		551	551 vs		(CCO) rock
	622	616	—	590 vvs	(C—C) i.p.b.
		668	—	661 m	(C—C) i.p.b.
			—	703 s	γ(C=O)
691	716	709	724 vvs	—	(C—C) o.p.b.

TABLE 2 Contd.)

C_6F_6[24]	C_6F_5Cl[22]	C_6H_5COOH[17]	C_6H_5COOH		Assignments
			IR	Raman	
		799	778 s	—	δ(OCO), trigonal bending
		930	920 vs	920 wb	γ(OH)
1019 994	1013 986	1000	1008 vvs	—	ring breathing
		1129	1115 vs	1122 vw	ν(CF)
1157	1153	1186	1150 s	1150 vw	ν(CF)
1253	1274	1289	1256 vvs	1252 mb	δ(OH)+ν(CO), ν(CF)
		1321	1318 vs	1320 s	ν(C—COOH), ν(CC)
		1420	1424 vs	1412 s	ν(CO)+δ(OH), ν(CC)
1490	1448	1499	1494 s	—	ν(CC)
1530	1518	1585	1529 vs	1517 ms	ν(CC)
1655	1643	1600	1645 vs	1657 vs	ν(CC)
		1695	1715 vvs	—	ν(C=O)
			—	2238 s	1320+920
			2341 mw	—	—
			2357 m	—	—
			2500 m	2480 m	
			2562 ms	2550 ms	1320+1252
			2641 s	2625 s	ν(OH) main satellit.
			2721 m	2710 w	1412+1320
			2888 w	2850 mb	
			2941 w	—	—
		3072	3012 mwb	3000 wb	ν(OH) bonded
			3424 mb		

*Symbol as given in Table 1.

TABLE 3

ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF PENTAFLUOROBENZONITRILE

Intensity	Position of the bands (cm^{-1})	Separation from 0,0 band (cm^{-1})	Assignments
	$^1A_{1g} \rightarrow {}^1B_{2u}$ (2600 Å system)		
vw	36114	0−263	0−263
w	36153	0−224	0−224
m	36232	0−145	0−145
ms	36271	0−106	0−106
m	36297	0−80	0−80
s	36324	0−53	0−53
vvs	36377	0,0	0,0
vs	36456	0+79	0+79
s	36514	0+137	0+137
s	36630	0+253	0+253
ms	36724	0+347	0+253+79
	$^1A_{1g} \rightarrow {}^1B_{1u}$ (2100 Å system)		
ms	44743	0−526	0−526
m	44883	0−386	0−386
s	44984	0−285	0−285
vvs	45269	0,0	0,0
vw	45475	0+206	0+206
vw	45579	0+310	0+310
vvs	45851	0+582	0+582
vw	46147	0+878	0+582+310
vs	46232	0+963	0+963
ms	46339	0+1070	0+1070
s	46533	0+1264	0+1264
ms	46707	0+1438	0+1438
ms	47125	0+1856	0+1264+582
m	47192	0+1924	0+963×2
vs	47416	0+2147	0+2147
vvw	47801	0+2532	0+1264×2
vw	48031	0+2762	0+1264×2+208
vsb	48146	0+2877	0+963×3

TABLE 4

CORRELATION OF THE FUNDAMENTAL VIBRATIONAL FREQUENCIES OF PENTAFLUOROBENZONITRILE IN IR, RAMAN AND UV SPECTRA AND THEIR ASSIGNMENTS

IR	Raman	UV 2600 Å system GS	UV 2600 Å system ES	UV 2100 Å system GS	UV 2100 Å system ES	Assignments
—	105	106	—	—	—	γ(C—F)
—	133	146	137	—	—	γ(C≡N)
213	—	224	—	—	—	γ(C—F)
264 276	270	263	253	285	206	γ(C—CN)
388	385	—	—	386	310	β(C—CN), γ(C—F)
535	535	—	—	526	—	(C—C) i.p.b.
607	590	—	—	—	582	β(C—F)
903	—	—	—	—	878	590+310
991	965 955	—	—	—	963	Ring breathing
1203	—	—	—	—	1070	ν(C—CN)
1326	1330	—	—	—	1264	ν(CC), ν(C—F)
1450	1446	—	—	—	1438	ν(CC)
2253	2250	—	—	—	2147	ν(C≡N)

*Symbols as given in Table 1.

TABLE 5

POSITION OF 0,0 BANDS AND RED SHIFT FOR BENZONITRILE AND PENTAFLUOROBENZONITRILE

Molecule	Position of 0,0 band (cm^{-1})	Shift with respect to benzene (cm^{-1})	References^{+}
Benzonitrile	36516	—	Ref. No. 6
3-Methoxybenzonitrile	35143	1373	Ref. No. 6
4-Methoxybenzonitrile	35330	1186	Ref. No. 6
Pentafluorobenzonitrile	36377	139	Present work

TABLE 6

ELECTRONIC TRANSITIONS (in cm^{-1}) OF PENTAFLUOROBENZONITRILE AND PENTAFLUOROBENZOIC ACID IN VARIOUS SOLVENTS

Solvent	Refractive index of the solvent	Pentafluoro-benzonitrile 2600 Å band	Pentafluoro-benzoic acid 2600 Å band
Water	1.3380	2800	2620
Methanol	1.3362	2785	2665
Ethanol	1.3773	2798	2675
$CHCl_3$	1.4580	2800	2760
C_6H_6	1.5236	2800	2796
CCl_4	1.4729	2800	2780

wave-number (1650–1585 cm^{-1}). In both the present molecules the presence of highly electronegative substituents (F and CN) this band is shifted upto 1650 cm^{-1}. One E. S. fundamental observed at 1438 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1u}$ System) has been assigned to e_{1u} mode in PFB. In absence of its G. S. fundamental the Raman band observed at 1446 cm^{-1} has been taken to represent this mode in the ground state. The ring breathing mode 1 (a_{1g}, 995 cm^{-1}) of benzene, usually appears as a very strong and polarized band in the Raman spectra and may lie in the region 690–1000 cm^{-1}. No strong Raman band could be observed in any of the molecule under study. Pandey and Singh[9] has assigned this band at 1002 cm^{-1} in benzonitrile and in benzoic acid this band has been assigned at 1000 cm^{-1} by Green[17]. In view of this the very strong i.r. band at 991 cm^{-1} with its corresponding weak and broad Raman band at 965 cm^{-1} has been assigned to the above mode in PFB. Similarly the intense i.r. band at 1008 cm^{-1} in PFBA has been assigned to the ring breathing mode. One very strong band at 46232 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1u}$ System) having a separation of 963 cm^{-1} has been traced upto three quantas and to lower frequencies by the formation of hydrogen bond. In benzoic acid it is observed at 1701 cm^{-1} by Dyer[26] and at 1695 cm^{-1} (having a corresponding Raman value at 1632 cm^{-1}) by Green[17]. The substitution of α-halogens results in the carbonyl absorption shifting towards higher frequencies. Acids with α-fluorine substitution are, however, likely to absorb at even higher frequencies compared to chloro- and bromo-acids. In the present study this mode has been assigned at 1715 cm^{-1} in PFBA.

The C≡N stretching mode is characteristically observed around 2253

cm^{-1}. A very strong Raman band at 2250 cm^{-1} with corresponding strong i.r. band at 2253 cm^{-1} in PFB has thus been assigned to the above mode. In the electronic spectrum of PFB a very strong band at 47416 cm^{-1} having a separation of 2147 cm^{-1} in $^1A_{1g} \rightarrow {}^1B_{1u}$ system has been taken to represent the CN stretching mode in the excited state. In view of the assignments made by Goel *et al.*[6] for out-of-plane C–N mode, the band at 133 cm^{-1} in PFB has been taken to represent the above mode. One E.S. fundamental 137 cm^{-1} in $^1A_{1g} \rightarrow {}^1B_{2u}$ system has also been correlated to the above mode (Table 4). The hot band observed at 145 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{2u}$ System) represents its ground state value which is supported from the corresponding Raman value (Table 4).

The OH stretching frequencies of acids have been extensively studied[21,27,28]. Intermolecular hydrogen bonds show a frequency shift, and the bands are broadened. The OH absorptions occur as broad bands with a series of minor peaks over the range 3000–2500 cm^{-1} in benzoic acid existing in dimeric form. In most of the cases the main peak is near 3000 cm^{-1}. with a main satellite band near 2650 cm^{-1}. Here we have assigned the main peak due to hydrogen bonded OH stretching as a broad weak i.r. band at 3012 cm^{-1} with its Raman band at 3000 cm^{-1} and main satellite band at 2625 cm^{-1} in PFBA. The other bands in this region have been analysed as the combination bands as given in literature[21].

The first two regions near 1400 cm^{-1} and 1250 cm^{-1} in carboxylic acid arise from coupled vibrations involving the in-plane OH deformation and the C–O stretching mode while the third around 920 cm^{-1} is due to the out-of-plane OH deformation of the dimeric form[21]. Green[17] has assigned the above modes in benzoic acid as $\nu(CO) + \delta(OH)$ and $\delta(OH) + \nu(CO)$ at 1420 and 1287 cm^{-1} respectively. These modes have been assigned at 1412 and 1252 cm^{-1} in PFBA. The out-of-plane OH deformation mode is reasonably intense and broad. This breadth suggests an origin in a hydrogen bonded system, and is in fact characteristic of dimeric form and is not found in the spectra of monomers[21]. This mode has been assigned at 920 cm^{-1} in PFBA which is well correlated by the assignment made by Green[17] at 930 cm^{-1} in benzoic acid. Green[17] has assigned two planar bending modes corresponding to symmetric $\delta(OCO)$ and rocking $\rho(CCO)$ and out-of-plane wagging mode of the carboxylic group (which is principally $\gamma(C=O)$ but likely involving motions of both oxygen atoms) at 799, 551 and 709 cm^{-1} respectively in benzoic acid. Accordingly, these modes have been well assigned in the case of PFBA (Table 2).

Novett and Perry[29] have suggested the range for C–F in-plane-bending modes between 250 to 650 cm^{-1} in case of C_6F_5X compounds. Taking into consideration the factors of atomic mass and force constants, the five out-of-plane (C–F) deformation modes should lie in the region 300–400

cm^{-1} [23,29,30] in pentafluorobenzene derivatives. Accordingly, we have assigned these modes in PFB and PFBA (Tables 1, 2).

The spectrum below 300 cm^{-1} is rather complex, containing very low out-of-plane deformation, torsional modes besides lattice and hydrogen-bond vibrations. For a planar cyclic (R–COOH) molecule there should be six low frequency fundamentals associated with stretching and bending of the hydrogen bonds. Carlson *et. al.*[31] obtained the first complete far infrared vapour spectra of dimeric formic and acetic acids, observing three bands for each compound. Jakobsen *et al.*[32] established the complete set of six frequencies for formic and acetic acid cyclic dimer within the range 250–60 cm^{-1}. Jakobsen[32] termed these six hydrogen bond frequencies as, two stretchings, one in-plane bending, two out-of-plane bending and one twisting of the one monomer unit against the other along the hydrogen atom. The hydrogen-bonded frequencies of a single crystal of benzoic acid was first described by Klausberger[16]. Hydrogen bond vibrations of the carboxylic ring can be described by the relative motion of two monomers in terms of crystal structure. In the present case of PFBA two vibrations have been observed in the far i. r. spectra at 95 and 103 cm^{-1} and assigned as out-of-plane bending and stretching of hydrogen bond. One Raman active fundamental observed at 190 cm^{-1} has been taken to represent another stretching mode of hydrogen bond. The twisting mode may be assigned at 71 cm^{-1} by a very strong i. r. band. Because of the strong mixing between external modes and hydrogen bond vibrations it is believed that the later might also exhibit an increase in frequency. In the electronic spectra the two additional bands on the higher wavelength side of the 0, 0 band at 36324 and 36297 cm^{-1} having separation 53 and 80 cm^{-1} respectively and one band on the lower wavelength side of the 0, 0 band 36456 cm^{-1} having separation 79 cm^{-1} have been observed with intensities comparable to that of 0, 0 band. These bands can be correlated as the difference bands as reported in literature[9,33].

Shift of 0, 0 Band

When benzene is substituted with a single functional group, the fine structure band generally appear to be diminished in complexity.[26] As reported by Goel *et. al.*[6] in 3- and 4-methoxybenzonitriles a red shift is observed in $^1A_{1g} \rightarrow {}^1B_{2u}$ transition of PFB compared to that in benzonitrile (0, 0 band at 36516 cm^{-1}). Becker[34] has suggested that the amount of red shift is lesser in case of fluorobenzene compared to chlorobenzene. Fluorine atom has large inductive effect compared to migration effect due to its large electron affinity and ionization potential, while for chlorine the migration effect predominates resulting in more red shift with chlorine compared to fluorine. The amount of red shift is very less in case of PFB (Table 5) compared to other molecules which may be explained as suggested above. Such red shift has also been reported in literature[9].

Solvent Effect

Polar solvents and those which can form hydrogen bonds tend to interact electrostatically with various chromophores which changes the charge distribution in the molecule and results in increased delocalization.[35] Becker *et al.*[34] have suggested a blue shift of the band relative to the band position in a non-hydrogen bonding solvent, since the hydrogen bonding which stabilizes the ground state will be weakened by the shift of electron density away from the nonbonding centre upon excitation. Water being most polar and highest protic is strongly hydrogen bonding solvent, hence the hydrogen bonding will be more in water than in methanol or ethanol. As suggested above, in the present study while going from non-polar solvent to polar solvent for 2600 Å system a blue shift is observed. In case of PFB the trend is not regular in case of water which may be because of the poor solubility. When both solute and solvents are polar then it is seen that the $\pi - \pi^*$ band shift to lower frequency with increasing dielectric constant of the solvent[36]. As the polarity of the solute increases tendency of blue shift will be enhanced. Since the polarity of the benzoic acid is less compared to benzonitrile, thus the comparative effect of fluorine substitution will be more in benzonitrile than benzoic acid. It is evident that greater is the possibility of hydrogen bonding by the solvent greater will be the blue shift. Hence, benzoic acid (PFBA) also shows a large amount of blue shift while going from non-polar to polar solvent. Both the present molecules show a red shift with increasing refractive index of the solvents (Table-5), which also finds support by the work of Mataga and Kubota[37].

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REFERENCES

1. J. H. S. Green and D. J. Harrison, *Spectrochim. Acta*, **32A**, 1279 (1979).
2. S. P. Sinha and C. L. Chatterjee, *Spectrosc. Lett.*, **9**, 461 (1976).
3. P. D. Singh, *Indian J. Pure Appl. Phys.*, **7**, 430 (1969).
4. H. F. Shruwell, A. S. Blair and R. J. Jakobsen, *Spectrochim. Acta*, **24A**, 1257 (1968).
5. R. K. Goel, S. D. Sharma and S. N. Sharma, *Indian J. Pure Appl. Phys.*, **17**, 55 (1979).
6. R. K. Goel and M. L. Agarwal, *Spectrochim. Acta*, **38A**, 583 (1982).
7. H. Shruwell and A. S. Blair, *Spectrochim. Acta*, **21A**, 1267 (1968).
8. M. Bass, *J. Chem. Phys.*, **18**, 1403 (1958).

9. S. M. Pandey and S. J. Singh, *Indian J. Pure Appl. Phys.*, **14**, 587 (1976).
10. T. S. Vardarajan and S. Parthsarthy, *Indian J. Pure Appl. Phys.*, **11**, 341 (1973).
11. J. L. Carison, R. E. Witkowski and W. G. Fateley, *Spectrochim. Acta*, **22A**, 1117 (1966).
12. R. J. Jakobsen, T. Mikawa and J. W. Brasch, *Spectrochim. Acta*, **23A**, 2199 (1967).
13. M. Suzuki and T. Shimanouchi, *J. Molec. Spectrosc.*, **28**, 394 (1968).
14. S. Tariq, P. K. Verma and Aquell Rashid, *Indian J. Pure Appl. Phys.*, **20**, 759 (1982).
15. M. Mishra, R. N. Gupta and R. C. Pandey, *Indian J. Pure Appl. Phys.*, **10**, 536 (1972).
16. G. Klausberger, K. Furic and L. Coulomb, *J. Raman Spectrosc.*, **6**, 277 (1977).
17. J. H. S. Green, *Spectrochim. Acta*, 33A, 575 (1977).
18. R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).
19. N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).
20. R. J. Jakobsen, *Spectrochim. Acta*, **21**, 127 (1965).
21. L. J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hall, London, pp. 79, 367 (1975).
22. J. J. Hyams, E. R. Lippincott and R. T. Bailey, *Spectrochim. Acta*, **22**, 695 (1966).
23. J. H. S. Green, D. J. Harrison and C. P. Stockley, *Spectrochim. Acta*, **33A**, 423 (1977).
24. D. Steels and D. H. Whiffen, *Trans Faraday Soc.*, **55**, 369 (1959).
25. C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, p. 208 (1963).
26. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Princeton Hall International Inc., Englewood Cliffs, N.J., p. 46 (1969).
27. J. H. S. Green, *Spectrochim. Acta*, **17**, 607 (1969).
28. G. Varsanyi, Vibrational Spectra of Benzene derivatives, Academic Press, New York (1969).
29. B. A. Novett and A. Perry, *Spectrochim. Acta*, **31A**, 101 (1975).
30. D. A. Long and D. Steels, *Spectrochim. Acta*, **19**, 1955 (1963).
31. G. L. Carlson, R. E. Witkowski and W. G. Fateley, *Spectrochim. Acta*, **22A**, 1117 (1966).
32. R. J. Jakobsen, Y. Mikawa and J. W. Brasch, *Spectrochim. Acta*, **23A**, 2199 (1967).
33. R. K. Goel and M. L. Agarwal. *J. De Chimie Physique*, **79** no. 10 (1982).
34. R. S. Becker, A. B. F. Duncan, F. A. Matsen, D. A. Scott and W. West, Chemical Applications of Spectroscopy, John Wiley & Sons, New York, p. 268 (1968).
35. I. L. Finar, Organic Chemistry, Vol. 2, E.L.B.S., Longman House, Essex, p. 19 (1975).
36. H. Suzuki, Electronic Absorption Spectra and Geometry of Organic Molecules, Academic Press, New York, p. 97 (1967).
37. Noboru Mataga and Tanekzu Kubota, Molecular Interactions and Electronic Spectra, Marcel Dekker Inc., New York (1970).

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