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VIBRATIONAL SPECTRAL STUDIES OF 2-CHLORO-6-FLUORO BENZALDEHYDE

B.S. Yadav[1]*, S.K. Tyagi[1] and M.K. Yadav

Molecular spectroscopy and Biophysics Laboratory, D.N.(PG) College, Meerut - 250 002 (India)
[1]Department of Physics, C.S.S.S. (P.G.) College, Machhra, Meerut (India)

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ABSTRACT

The vibrational (Infrared and Raman) spectra of 2-Chloro-6-fluoro benzaldehyde have been reported. The assignments of fundamentals are proposed and discussed by assuming the molecule under C_S point group symmetry.

Keywords: Infrared & Raman Spectra, 2-chloro-6-fluoro-benzaldehyde.

INTRODUCTION

Benzaldehyde is the simplest aromatic aldehyde and the substitution of a functional group in benzaldehyde changes the spectra markedly. The vibrational spectra of benzaldehyde and its derivatives have been extensively investigated by many earlier workers[1-7] but so far no work appears to have been carried out on 2-chloro-6-fluoro benzaldehyde. The present investigation aims at giving complete vibrational assignments of frequencies of the said molecule.

EXPERIMENTAL

Spec. pure grade sample of 2-chloro-6-fluoro benzaldehyde (hereafter referred as 2,6-CFB) was purchased from Aldrich Chemical Co., U.S.A. and used as such. Its purity was confirmed by elemental analysis and melting point determination. The Infrared spectra of the compound 2,6-CFB was recorded on Perkin-Elmer spectrophotometer in the region 400-4000cm^{-1} using KBr pellets and nujolmull solvent. The laser Raman Spectrum in the region (40-4300) cm^{-1} was recorded on "Spex Rama Lab" spectrophotometer using 52mg argon-krypton laser beam of wavelength 488nm.

RESULTS AND DISCUSSION

The molecular structure of the compound 2,6-CFB is shown in Fig.-1. The laser Raman spectrum, IR spectra in KBr pellets and nujolmull are shown in Figs. - 2, 3 and 4 respectively. The observed fundamental frequencies and their proposed assignments are given in Table-1.

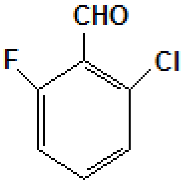


Fig.-1

Molecular Structure of
2-chloro-6-fluoro-benzaldehyde

Vibrational Spectra

The analysis of the bands and the assignments of the fundamental frequencies are made on the basis of magnitude and relative intensities of the observed bands and earlier assignments in the similar molecules.

Ring Vibrations

The molecule 2,6-CFB is a trisubstituted benzene, thus only three hydrogen atoms are left around the ring. As such three C-H valence oscillations are expected in the region 3000-3100(cm^{-1})[8]. in this study the bands observed at 3016 cm^{-1} (KBr), 3054 (nujolmull)/3050 cm^{-1} (Raman) and 3093 (nujolmull)/3090 (Raman) have

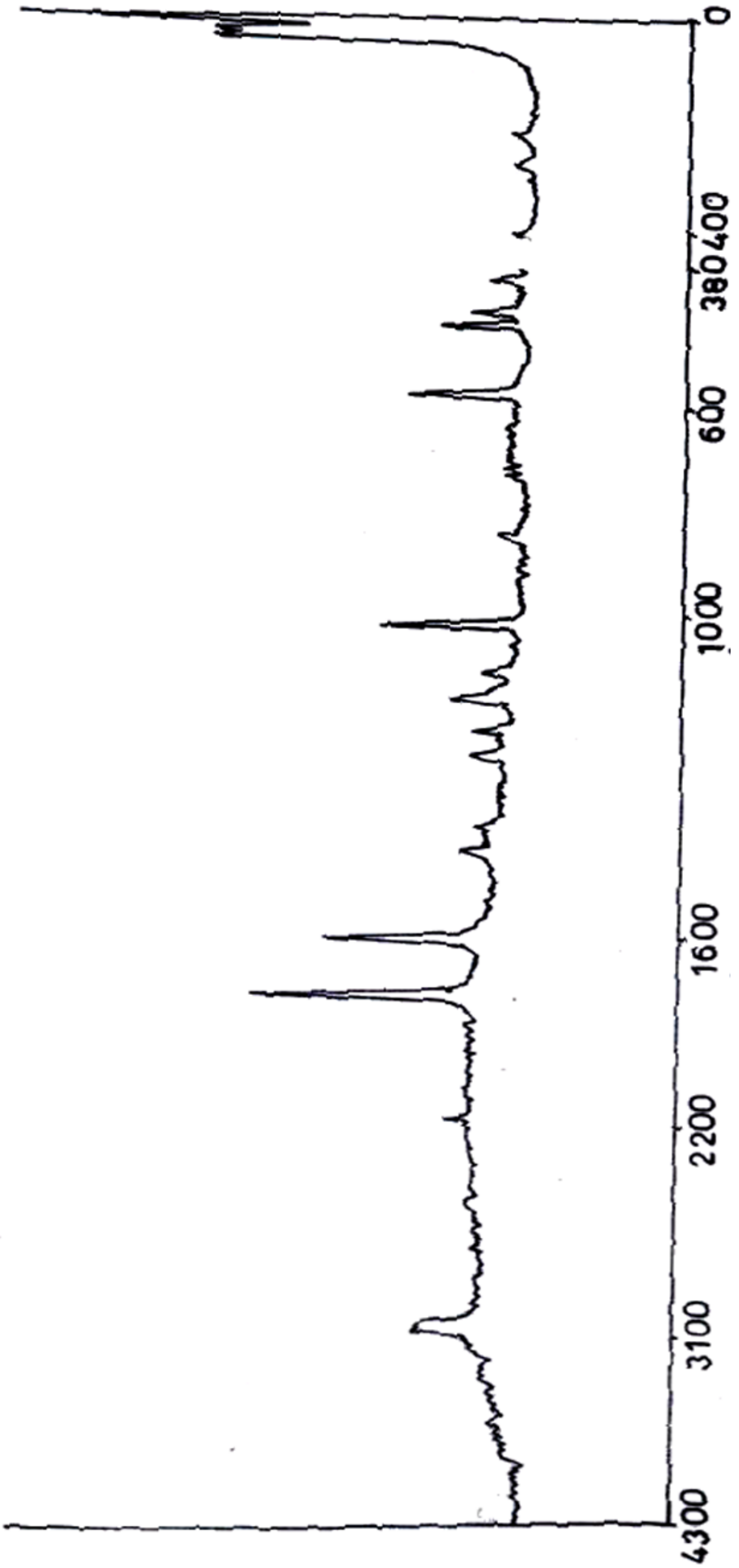
Table - 1: Vibrational frequencies (cm^{-1}) for 2,6-CFB and their assignment

IR (cm^{-1})		Raman	Assignments
KBr	Nujolmull	(cm^{-1})	
		40vs	lattice vibrations
		66S	lattice vibrations
		79S	CHO torsion
		200m	γ(C-F)
		239m	γ(C-Cl), γ(C-CHO)
		285m	β(C-Cl)
406 w		396s	β(C-CHO), γ(C-C-C) e_{2u} 404
433 w	423s	446s	γ (C-C-C)
560ms	560m	-	β(C-F), γ(C-C-C)
-	583s	578vs	β(C-C-C), e_{2g} (608)
708m	710vs	703m	γ (C-C-C), β_{2g} (703)
-	810vs	817m	ν (C-C) ring breathing
840vw	-	-	β(C=O)
	826vw	-	γ(C-H)
913vs	919vs	-	γ(C-H)
967w	989m	-	(C-C-C) Trigonal bending
1062vw	1066m	1074vs	ν(C-Cl), β(C-H)
-	1161w	1156m	β(C-H)
1194vs	1194s	1200s	ν(C-CHO)
1250s	1260s	1256s	ν(C-F)
1293ms	1282m	1298s	β(C-H)
-	1311vs	-	ν(C-C), β_{2u} (1310)
1420m	1415vs	1415w	β(C-H) in CHO
1485vs,	-	-	ν(C-C), e_{1u} (1485)
1493m	-	-	ν(C-C), e_{1u} (1485)
1560ms	-	-	ν(C-C), e_{2g} (1595)
1602s	1606s	1600vs	ν(C-C), e_{2g} (1595)
-	1683, 1708vs	1692vs	ν(C=O)
-	2824wb	-	ν(C-H) in aldehydic group
3016w	-	-	ν(C-H) aromatic
	3054vw	3050vw	ν(C-H) aromatic
	3093m	3090 vs	ν(C-H) aromatic

Where ν=stretching, β=in plane bending, γ=out of plane bending, w=weak, m=medium, s=strong, vs=very strong, vw=very weak, wb=weak broad

been taken to represent C-H stretching mode. These modes are shown in Table-1.

The group of four bands, appearing between 1400-1650cm^{-1} in the spectra of substituted benzenes represents the characteristic skeltal stretching modes. These correspond to doubly degenerate C-C stretching vibrations of benzene i.e. e_{2g} (1595) and e_{1u} (1485) modes. There are two more C-C stretching modes, b_{2u} (1310) and a_{1g} (995) of benzene, Except for the ring breathing mode, all these are known to remain practically unaffected by the substitution. In view of these, the bands assigned to the above modes (Table-1) except a_{1g} mode, are also in good agreement with the assignments given in the literature. a_{1g} (995) mode because of the closely lying b_{1u} (1010) mode, which under reduced symmetry Cs has same symmetry species as that of a_{1g} may have an appreciable interaction with it. With this Goel and Agarwal[9] & Goel and Wahid[10] assigned this mode at 825 cm^{-1} and 805 cm^{-1} in 4-methoxybenzonitrile and 5-chloro2,4-dimethoxy aniline respectively. In view of these, the ring breathing mode has been identified at 817 cm^{-1} (Raman)/810 in (nujolmull) while the band at 989 cm^{-1} (nujol) has been correlated to (C-C-C) trigonal bending mode in 2,6-CFB.



Wave number (cm^{-1})

Fig. - 2 : Laser Raman Spectrum of 2,6-CFB

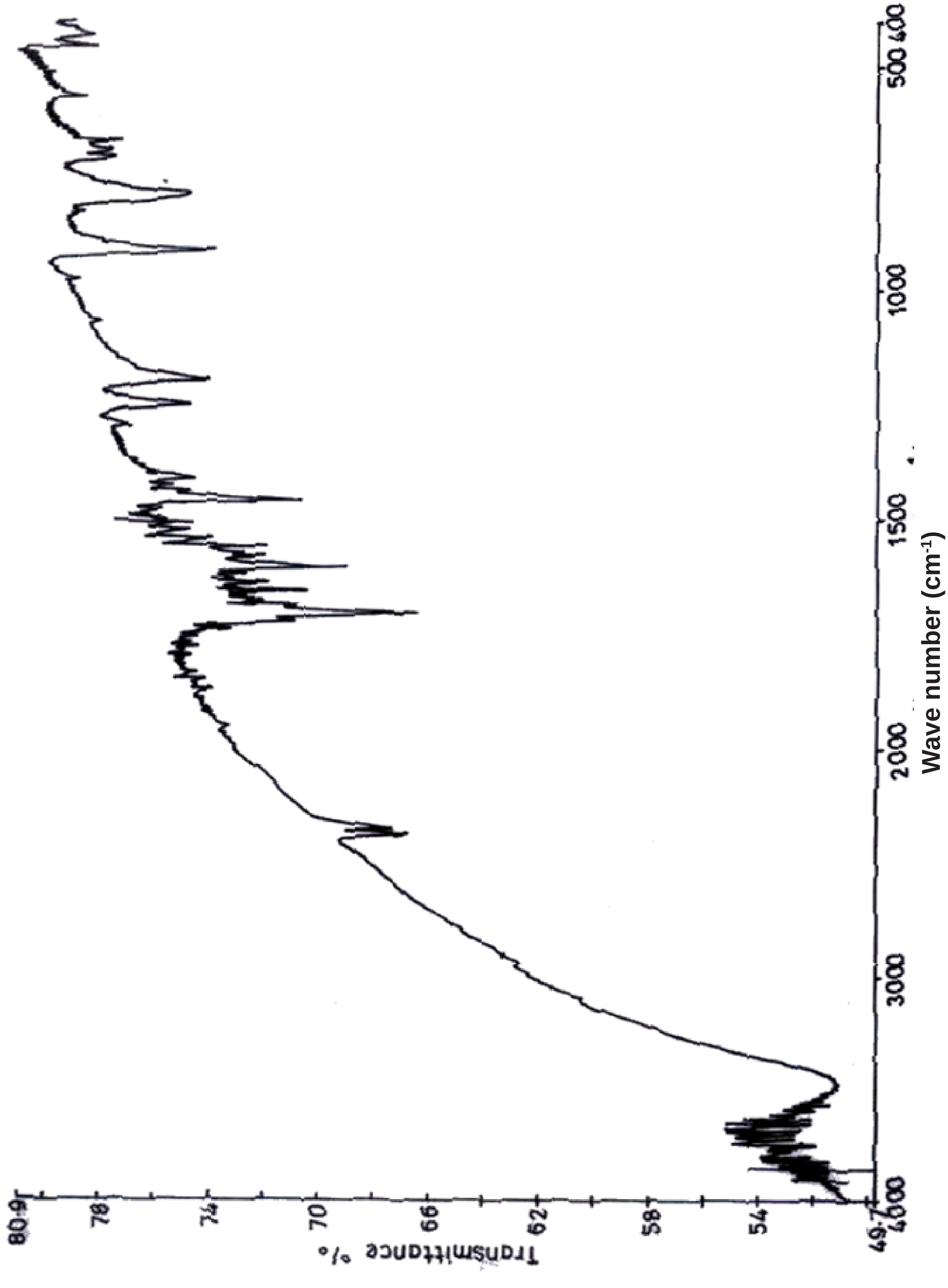
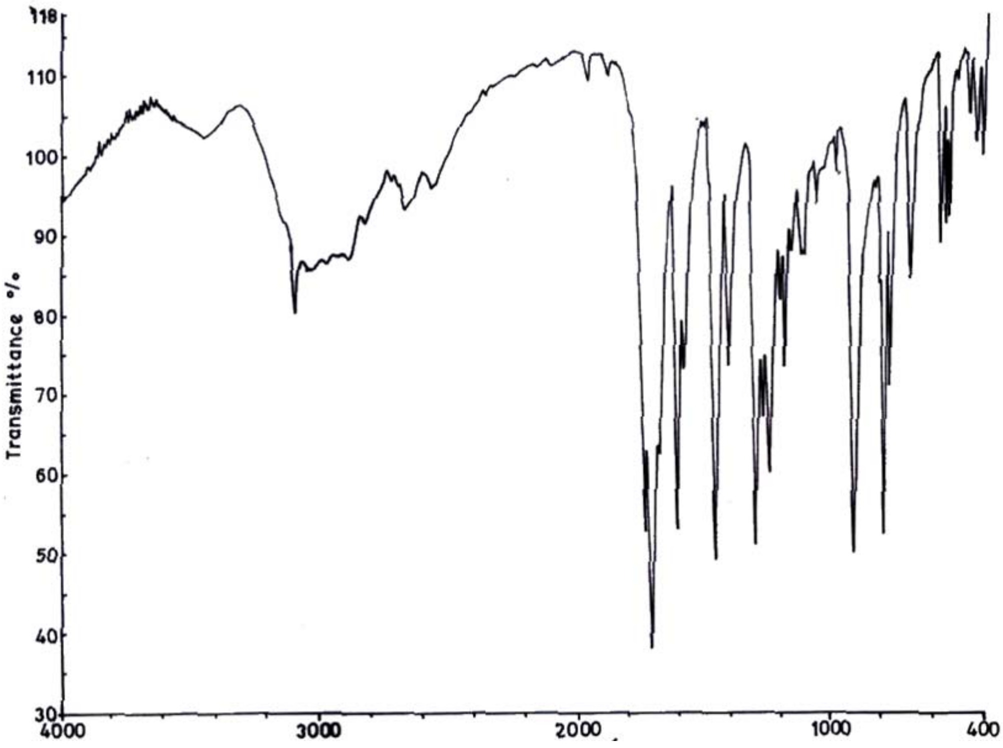


Fig. - 3: IR absorption spectrum of 2,6-CFB in KBr pellets



Wave number (cm^{-1})

Fig. - 4: IR absorption spectrum of 2,6-CFB in nujolmuff

(C-H) in plane bending and out of plane bending modes lie in the region 1000-1500 and 750-1000 cm^{-1} respectively. The bands at 1293 (KBr)/1282 cm^{-1} (nujol) with the counter part of Raman band at 1298cm^{-1}, 1161 (nujol)/1156 cm^{-1} (Raman) and 1062 (KBr) /1066 cm^{-1} (nujol) with the counter part of Raman band at 1074 cm^{-1} may be assigned to (C-H) in plane bending mode. The strong bands at 913 (KBr)/919 cm^{-1} (nujol) and weak band at 826 (nujol) may be assigned to (C-H) out of plane bending mode. These assignments find support from literature value[10,15].

The in-plane C-C-C bending vibrations of benzene lead to three such vibrations in substituted benzenes. These have been observed in the spectrum of compound and listed in (Table-1). Similarly C-C-C out of plane bending vibrations are also possible which to have been observed and mentioned in (Table-1).

C-X Vibrations

C-Cl stretching mode has been assigned at 1055 cm^{-1} in both the molecules (5-chloro-2,4-dimethoxy aniline[10] and 2,4,5,6-tetrachloro pyrimidine[11]). Hence in the present study this mode has been identified at 1062 $^{cm-}$1 (KBr)/1066 cm^{-1} (nujol) which finds support from Raman value (1074 cm^{-1}). Gupta et al[12] and Singh & Singh[13] have assigned C-Cl in plane bending at 295 cm^{-1} and 320 cm^{-1} for 2,6-di-chloro-4-nitro aniline and 2,5-dichloro nitrobenzene respectively, hence in the present study this mode has been identified at 285 cm^{-1}. In conformity with the literature assignments[14,15], the C-Cl out of plane bending mode has been identified at 239 cm^{-1} in the present study. RK Goel[16] and R.P. Singh & R.N. Singh[17] have assigned C-F stretching mode at 1240, 1228, 1195 and 1204 cm^{-1} for 2-fluoro-5-iodotoluene, 4-fluoro-2-iodotoluene, 2,4-difluoro toluene and 2,5-difluorotouene respectively. In view of these assignments, this mode has been identified at 1250 (KBr)/1260 cm^{-1} (nujol) which finds support from Raman value (1256) cm^{-1}. Tripathi et al[18] assigned the C-F in-plane bending at 620 cm^{-1} in bromopenta fluoro benzene while Sharma et al[19] assigned this mode at 411 cm^{-1} in 2-fluoro-5-bromo toluene. This mode has been identified at

560 cm^{-1} in both i.r. as well as Raman which is in good agreement with the literature value assigned by R.K. Goel[16]. The C-F out of plane mode has been assigned at 200 cm^{-1} in the said molecule. Varsanyi[20] has suggested C-CHO stretching and C-CHO in-plane bending modes of vibrations for 3,4-dihydroxy benzeldehyde at 1196 and 410 cm^{-1} respectively. In view of these, C-CHO stretching and C-CHO in-plane bending vibrations have been assigned at 1194 and 396 cm^{-1} respectively while C-CHO out-of-plane bending vibration has been assigned at 239 cm^{-1} which is in good agreement with the literature value[7].

Group Vibrations

The aldehyde group gives rise to six vibrations, namely C=O stretching, C=O in-plane bending, C=O out-of-plane bending, C-H stretching, C-H in-plane bending and C-H out-of-plane bending vibrations. The C=O stretching vibration gives rise to a prominent absorption in the region 1680-1815 cm^{-1}. In the molecule presently studied the strong band observed at 1683 cm^{-1} with the counter part of Raman band at 1692 cm^{-1} may be assigned to C=O stretching mode. The C-H stretching mode has its characteristic magnitude in the range 2700-2850 cm^{-1}. In the present case, this mode is assigned at 2824 cm^{-1}.

The C-H planar bending mode of the CHO group is observed near 1380 cm^{-1} for benzaldehyde and its derivatives[7, 21]. In the present study this mode has been identified at 1420 (KBr)/1415 cm^{-1} (nujol) which finds support from Raman value (1415) cm^{-1}. The C-H non-planar bending mode af the CHO group appears in the region 900-1010 cm^{-1}. The C=O in-plane bending vibration is observed in the region 800-860 cm^{-1} in many of substituted benzaldehydes. The band at 840 cm^{-1} can be assigned to this vibration. The CHO torsional mode is expected in the region 100-120 cm^{-1}. The strong band at 79 cm^{-1} may be assigned to this mode.

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