Materials Science Research India Volume **3**(1a), 69-72 (2006)

FTIR AND LASER RAMAN SPECTRUIM OF 1,2-DICHLORO-4-FLUORO-5- NITROBENZENE

B.S. Yadav, I.A. Siddiqui, Seema* and Sanjay Yadav

Molecular Spectroscopy and Biophysics Laboratory, D.N (P.G) College, Meerut - 250 002 (India)
*Department of Chemistry, Meerut College, Meerut - 250 002 (India)

(Received: May 12, 2006; Accepted: June 18, 2006)

ABSTRACT

The present study deals with the FTIR and Laser Raman Spectrum of 1,2-dichloro-4-fluoro-5- nitrobenzene which have been recorded in the region 4000-400 cm^{-1} and 4000-50 cm^{-1} respectively. Both the spectrum have been analyzed on the basis of Cs point group symmetry and the observed bands have been assigned to the different specific modes of vibrations. The assignment of FTIR and Laser Raman bands of the said molecule are made on the basis of magnitude and relative intensities of the observed bands. The assignment made for complex molecule under investigation are in good agreement with the earlier work on some benzene derivatives.

Key words: FTIR and Laser Raman spectra, 1,2-dichloro-4-fluoro-5- nitrobenzene, vibrational assignments.

INTRODUCTION

Some of the vibrational modes of benzene are substituent sensitive. To understand this the vibrational study of substituted benzene is desirable. The vibrational spectra of halogenated nitrobenzene are investigated by several workers[1-7] and a summary of results is given by Green and Harrison[8], Varsnayi[9]. Varsnayi[9] has summarized them along with the vibrational spectra of seven hundred benzene derivatives. Literature is available on mono, di and trisubstituted benzenes[10-11]. However on tetrasubstituted benzenes such studies are limited.The assignment was not made by any previous worker in the case of 1,2-dichloro-4-fluoro-5- nitrobenzene . The present investigation was undertaken to study the FTIR and Laser Raman spectra of said molecule.

EXPERIMENTAL

The spec-pure grade sample of 1,2-dichloro-4-fluoro-5- nitrobenzene (here after referred as 1,2,4,5-DClFNB) has been obtained from M/s Sigma Aldrich Chemical Co., U.S.A. and used as such. Its purity has been confirmed by elemental analysis and melting point determination. The FTIR spectrum of compound 1,2,4,5-DClFNB has been recorded on perkin Elmer Spectrophotometer in the region 4000-400 cm^{-1} by using KBr Pellet technique. The Laser Raman spectrum in the region 4000-50 cm^{-1} has been recorded on Spex Rama Lab spectrophotometer using 52 MW argon-krypton laser beam of wavelength 488 nm. The molecular structure of the molecule is shown in fig 1 and observed FTIR and Laser Raman spectra are shown in Figs. 2 and 3 respectively.

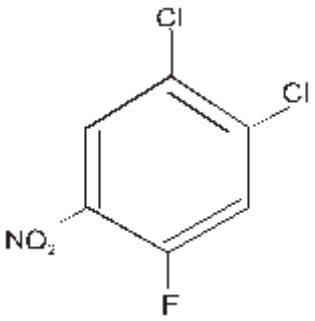

Fig. - 1: 1,2-dichloro-4-fluoro-5- nitrobenzene

RESULTS AND DISCUSION

Vibrational assignments

The vibrational analysis of 1,2,4,5-DClFNB are made on the basis of the magnitude and relative intensities of the recorded spectra and in analogy with the assignment made by the earlier workers on the similar type of molecules. The observed frequencies of 1,2,4,5-DClFNB presented in Table 1.

C-H Vibrations

Aromatic compound shows the presence of C-H stretching vibrations in the region 3100-3000 cm^{-1} [12] which is the characteristic region for ready identification of C-H stretching vibrations[13]. In this region the bands are not effected appreciably by the nature of substituents[13]. Hence the bands at 3058 and 3033 cm^{-1} in I.R and 3088 and 3011 cm^{-1} in Raman spectrum are assigned to C-H stretching modes in the present molecule. Whiffen[14] has been

Table - 1: Observed vibrational frequencies of FTIR and Laser Raman spectrum of 1,2-dichloro-4-fluoro-5-nitrobenzene

IR absorption bands of 1,2-dichloro-4-fluoro-5-nitrobenzene cm^{-1}	Intensity	Raman absorption bands cm^{-1}	Intensity	Assignments
3058	W	3088	S	ν (C-H)
3033	W	3011	W	ν (C-H)
1617	V.S	1618	S	ν (C-C)
1586	S	1592	V.S	ν (C-NO_2)
1546	V.S	1559	V.S	ν (C-C)
1536	S	1519	S	ν (C-C)
1464	V.S	1446	S	ν (C-C)
1418	W	-	-	ν (C-C)
1383	S	1360	V.S	ν (C-C)
1347	V.S	1339	V.S	Asymmetric struc.NO_2
1284	M	-	-	β (C-H)
1269	S	1268	M	β (C-H)
1230	V.S	1241	S	ν (C-F)
1138	V.S	1116	V.S	ν (C-Cl)
1101	W	1090	W	C-C-C triogonal bending
960	V.S	938	M	β (C-C)
899	V.S	885	W	γ (C-H)
867	M	866	M	γ (C-H)
846	M	826	V.S	γ (C-H)
759	M.S	740	M	ν (C-Cl)
716	S	701	M	γ (C-NO_2)
685	S	661	V.S	γ (C-C)
584	W	575	W	β (C-C)
534	M	516	W	NO_2 Rochimg
475	W	483	W	γ (C-C)
433	W	423	W	γ (C-C)
-	-	371	S	β (C-Cl)
-	-	331	M	β (C-F)
-	-	298	S	β (C-Cl)
-	-	199	S	γ (C-F)
-	-	179	M	γ (C-Cl)
-	-	107	S	γ (C-Cl)

W	:	week	M	:	Medium
S	:	Strong	M.S	:	Medium Strong
V.S	:	Very Strong	ν	:	Stretching
β	:	In plane bending	γ	:	Out of plane bending

able to show that all the bands assigned with reasonably high precision to summation bands of the C-H out of plane fundamental which occur between 1000-700 cm^{-1} [15]. The same have been observed in the spectrum of the compound.

C-C Vibrations

The ring stretching vibrations are very much prominent in the spectrum of benzene and its derivatives are highly characteristic of aromatic ring itself [16]. Benzene has two doubly degenerate vibrating e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}). The doubly degenerate vibration e_{2g} (1596 cm^{-1}) consists of lateral dilation and contraction of the ring produced mainly by stretching and compressing of C-C bands. Bands between 1680-1450 cm^{-1} in benzene derivatives are assigned to these modes. The doubly degenerated e_{1u} (1485 cm^{-1}) mode is basically a ring deformation since it involves both stretching and bending of carbon atoms[17]. Hence the bands observed at 1617,1546, 1536, 1464, 1418,1383 cm^{-1} in FTIR and 1618,1519, 1446,1360 cm^{-1} in Raman are assigned to C-C stretching vibrational modes. The in-plane carbon bending vibrations are derived from non degenerate b_{1u} (1010 cm^{-1}) and degenerate (606 cm^{-1}) modes of benzene . The non degenerate b_{1u} (1010 cm^{-1}) is observed at 960 cm^{-1} in this work. The e_{2g} (606cm^{-1}) degenerate mode has been observed at 584 cm^{-1}. The carbon out of plane bending vibrations are derived from the non degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene. In this study the carbon out of plane bending vibration under Cs symmetry are observed at 685 and 475,433 cm^{-1}. This is in good agreement with the earlier reporters. There is trigonal bending mode

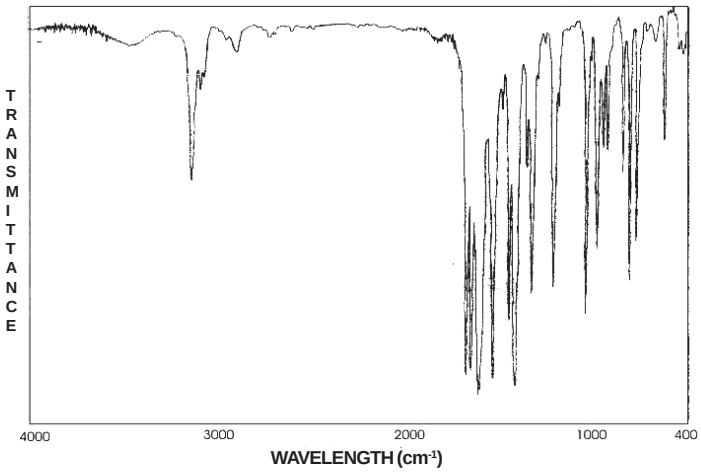

Fig. - 2: I.R. Spectra of 1,2-dichloro-4-fluoro-5-nitrobenzene in KBr pellet

near 1101 cm^{-1} in FTIR and 1090 cm^{-1} in Raman Spectrum which is also good agreement with the earlier reporters[18].

Vibration of nitro group

The nitro group substituted at the fifth position of the said molecule gives rise to C-NO_2 stretching vibration in addition to the internal vibration. The FTIR strong bands appeared at 1586 cm^{-1} is assigned to C-NO_2 stretching vibration, Medhi *et al.*[16] and Krishnakumar *et al.*[17] identified the various internal vibration of nitro group. The asymmetric deformation with a very strong FTIR band at 1347 cm^{-1} and in Raman band at 1339 cm^{-1} .The NO_2 rocking modes are observed at 534 cm^{-1} in FTIR and 516 cm^{-1} in Raman. The C-NO_2 out of plane bending modes also have been assigned 716 cm^{-1} in FTIR and 701 cm^{-1} in Raman spectrum which is shown in Table - 1. The assignments are in good agreements with those proposed in case of nitro benzene[19,20].

Vibration of chloro and fluoro group

Moonney[2,21] has assigned C-Cl vibrations of two Cl sensitive modes in the frequency interval 1129-480 cm^{-1} . The higher frequency bands have been assigned to C-Cl stretching and the lower frequency bands to C-Cl deformation modes. In the title compound the bands at 1138 cm^{-1} and 759 cm^{-1} have been assigned to C-Cl stretching while those

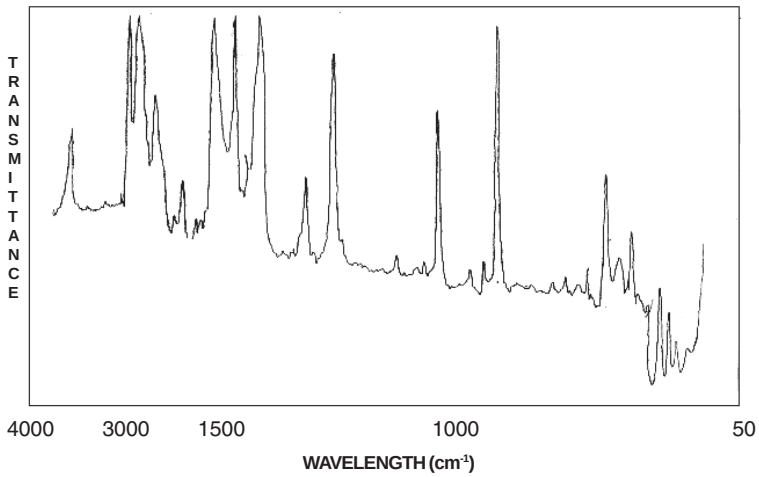

Fig. - 3: Laser Raman Spectra of 1,2-dichloro-4-fluoro-5-nitrobenzene

at 179,107 cm^{-1} in Raman spectrum assigned C-Cl out of plane bending vibrations and 371, 298 cm^{-1} assigned in plane bending vibrations. The band at 199 cm^{-1} assigned C-F out of plane bending vibration and the band at 331 cm^{-1} assigned C-F in plane bending vibration. The band at 1289 cm^{-1} in FTIR and 1274 cm^{-1} in Raman spectrum assigned C-F stretching vibration.

ACKNOWLEDGEMENTS

Authors are thankful to R.S.I.C.I..I.T, Mumbai for providing FTIR and Raman spectrum of molecule under study.

REFERENCES

1. Garrigou-Lagrange C., Lebas J.M., Josien M.L., *Spectrochim., Acta,* **12,** 305 (1958).
2. Mooney E.F., *Spectrochim. Acta*, **20,**1021 (1964).
3. Griffiths P.R., Thompson H.W., *Proc . R. Soc* London Ser A., 298,5 (1967).
4. Pommex P., Lafaix M.,Delorme P., Larezeth V., *J. Chim. Phys.,* **64,**1450 (1967).
5. Mehdi K.C., *Spetrochim. Acta,* **20,** 675 (1964).
6. Garrigou-Lagrange C., Chehata M.,Lascombe J., *J. Chim. Phys,* **63,** 552 (1966).
7. Brigodiot M., Lebas J.M., *J. Chim. Phys,* **62,** 347 (1967).
8. Green J.H.S., Harrison D.J., *Spectrochim. Acta,* **26,**1925 (1970).
9. Varsanyi G., Assignments For Vibrational Spectra of Seven Hundred Benzene Derivatives, Adam Hilger , London, (1974).
10. Yadav R.A., *Ph.D Thesis* (Banaras Hindu University, Varanasi) India (1983).
11. Shanker R., *Ph.D Thesis* (Banaras Hindu University, Varanasi) India (1991).
12. Rao C.N.R., Chemical Applications of Infrared Spectroscopy, Academic press, New York, London (1963).
13. Sundaraganeson N., Saleem H and Mohan S., *Indian J Phys,* **78**(6),489(2004).
14. Whiffen., *Spectrochim. Acta,* **7,** 253 (1955).
15. Bellamy L.J., the Infrared Spectra of Complex Molecules, Chapman and Hall London (1975).
16. Sharma M.K and Medhi K.C., *Indian J Phys,* **66** B (1), 59 (1992).
17. Arivazhagan M and Krishnakumar V., *Indian J pure and Appl Phys,* **43,** 573 (2005).
18. Yadav B.S., Kumar Nitin, Kumar Manoj and Yadav M.K., Indian J Phys,80(1). 61(2006).
19. Agarwal Y.K and Verma P.K., *Indian J Phys,* **75** B, 549 (2003).
20. Krishnakumar V and John X.R., Spectrochim. *Acta, Part* A 61,253 (2005).
21 Mooney E.F., *Spectrochim. Acta,* **19,** 877 (1968).