VIBRATIONAL INVESTIGATION, MOLECULAR STRUCTURE OF 1, 2 DICHLORO-4-FLUORO-5- NITROBENZENE

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ABSTRACT

The (DFNB) 1, 2 Dichloro-4-fluoro-5- Nitrobenzene structured to density functional theory studies using B3LYP/6-31+G (d,p) method. Characterization was done by FT-IR ,FT Raman and NMR spectroscopy techniques. Molecular electrostatic potential study was also determined.

INTRODUCTION:

Nitrobenzene very poisonous, flammable, pale yellow and liquid aromatic compound with an odor like that of bitter almonds. It is sometimes called oil of mirbane or nitrobenzol. Nitrobenzene melts at 5.85°C, boils at 210.9°C is only slightly soluble in water but is very soluble in ethanol, ether and benzene. Nitrobenzene is prepared by treating benzene with a mixture of nitric and sulfuric acid in the resulting nitration reaction one hydrogen in the benzene molecule is replaced with a nitro group.

The major use of nitrobenzene is in the production of aniline, commercially the most important amine. Nitrobenzene is heated with iron and dilute hydrochloric acid and the resulting anilinium chloride is treated with sodium carbonate to release aniline. In the pharmaceutical industry nitrobenzene is used in the production of the analgesic acetaminophen or paracetamol. Nitrobenzene is also used in shoe and floor polishes, leather dressings and paint solvents to mask unpleasant odors. As oil of mirbane, nitrobenzene was used as an inexpensive perfume for soaps and cosmetics but is now considered too toxic for such applications.

The compound 1, 2-Dichloro-4-fluoro-5-Nitrobenzene (DFNB) is used as a reagent for the detection and determination of nicotinic acid, nicotinamide and other pyridine compounds. It is also used in the manufacture of azo dyes, fungicides, rubber chemicals and explosives and as an algicide in coolant water of air conditioning systems. Contact sensitizations with DFNB have been used as a measure of cellular immunity.

Various spectroscopic studies of halogen and nitrogen substituted benzene compounds have been reported in the literature. DFNB belongs to the group of organic halogen compounds

replacing two hydrogen atoms in benzene by methyl (CH3) and a nitro group (NO2). Literature survey reveals that no detailed B3LYP with 6-31+G(d,p) basis set of FT-IR, FT-Raman and NMR (^{13}C and ^{1}H) chemical shifts calculation of DFNB have been reported so far. It is, therefore thought worth to make this theoretical and experimental vibrational spectroscopic research based on molecular structure to give the correct assignment of fundamental bands in the experimentally observed FT-IR and FT-Raman spectra. In this study, molecular geometry and vibrational frequencies are calculated using hybrid density functional method. This method predicts relatively accurate molecular structure and vibrational spectra with moderate computational effort.

2.   Experimental Details

The fine sample of 1, 2-Dichloro-4-fluoro-5-Nitrobenzene (DFNB) is purchased from Sigma-Aldrich chemicals, USA and it was used as such without any further purification. The FT-IR spectrum of the compound has been recorded in Perkin-Elmer 180 spectrometer in the range of 4000–400 cm^{-1}. The spectral resolution is ±2 cm^{-1}. The FT-Raman spectrum of the compound was also recorded in same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating in the region 3500–100 cm^{-1} at 1064 nm line width with 200 Mw powers. ^{13}C and ^{1}H NMR spectra were taken in CDCl3 solutions and all signals were referenced to TMS on a BRUKER TPX-400 FT-NMR spectrometer.

3.   Computational Details

The molecular structure of the DFNB molecule in the ground state is computed by B3LYP/6-31+G (d,p) method. The optimized structural parameters are used in the vibrational frequency calculations at B3LYP level. The DFT calculations were carried out for DFNB with GAUSSIAN 09W program package. Initial geometry generated from the standard geometrical parameters was minimized without any constraint, which invokes Becke's three parameter hybrid method with Lee-Yang-Parr correlation functional (LYP), implemented with the same basis set for better description of the bonding properties. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry.

The multiple scaling of the force constants were performed according to scaled quantum mechanical (SQM) procedure using linear scaling in the natural internal coordinate representation. Transformation of force field, the subsequent normal coordinate analysis (NCA) including the least square refinement of the scale factors and calculation of the total energy distribution (TED) were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius .The calculated frequencies are scaled by 0.9689 scale factor. As a result, the unscaled frequencies, reduced masses, force constants, infrared intensities and Raman activities were obtained. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers.

## 4.   Results and Discussion

4.1. Vibrational assignments

The labeling of atoms of DFNB is shown in Fig. 1. The molecule contains two Cl and a NO2 group connected with benzene ring. Experimental and simulated spectra of FT-IR and FT-Raman are presented in Figs. 2 and 3, respectively.

The DFNB molecule consists of 14 atoms, which undergoes 36 normal modes of vibrations. On the assumption of C1 group of symmetry, the numbers of vibration modes of the 36 fundamental vibrations of the molecule are distributed as 25 in-plane and 11 out-of-plane vibrations of same symmetry species.

The vibrational frequencies calculated at B3LYP level are scaled by 0.905 and the range of wave numbers above 1700 cm^{-1} are scaled as 0.958 and below 1700 cm^{-1} scaled as 0.983 for title compound. After scaled with the scaling factor, the deviation from the experiments is less than 10 cm^{-1} with a few exceptions. The force fields determined were used to calculate the vibrational total energy distribution (TED) among the normal coordinates.
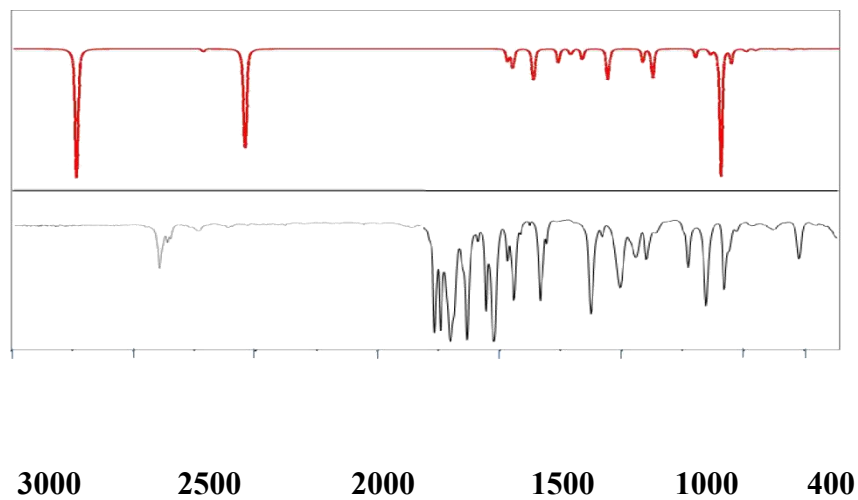
Wavenumber (cm⁻¹)

Fig.2. Comparison of experimental and calculated spectra of DFNB.
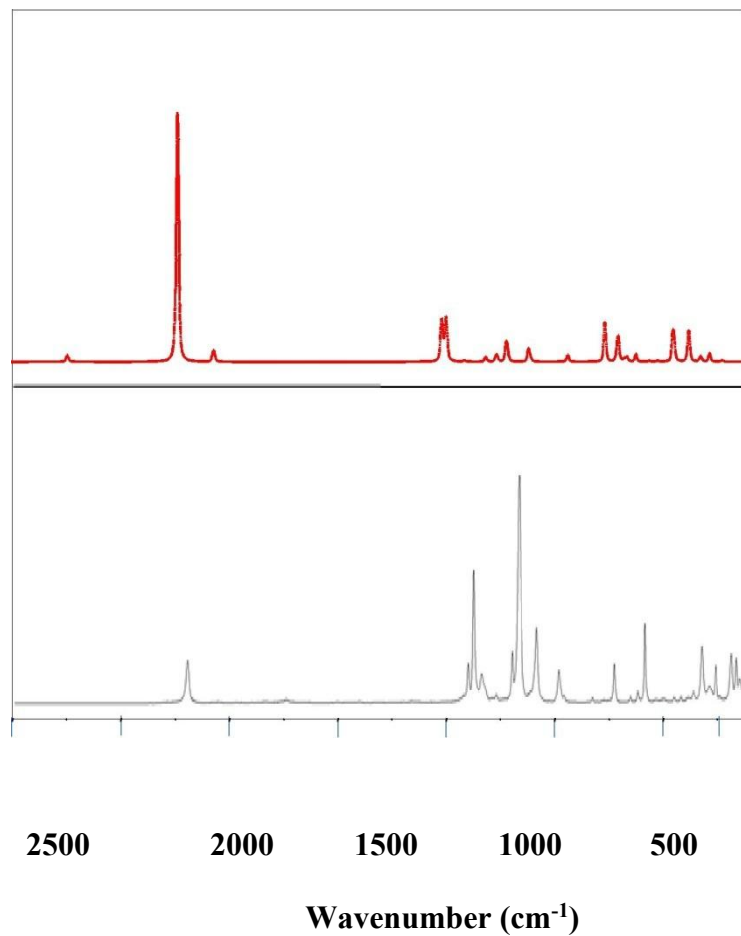
Wavenumber (cm⁻¹)

Fig.3. Comparison of experimental and calculated spectra of DFNB.

The observed FT-IR, FT-Raman and theoretically calculated frequencies by B3LYP/6-31+G(d,p) method along with **Table** their assignments, IR intensities (Km mol^{-1}) and Raman intensities (Å^4 amu^{-1}) of DFNB.

No.	Observed wavenumbers (cm^{-1})		Calculated wavenumbers (cm^{-1})		IR Intensities	Raman intensities	Vibrational Assignments
	FT-IR	FT-Raman	Unscaled	Scaled			
1	1800(s)		1709	1693	246.38	11.80	NO2asym(98)
2		1600(vw)	1658	1584	78.21	64.62	NO2sym(95)
3	1625(s)		1625	1544	33.83	60.61	CC(92)
4	1500(m)		1518	1485	186.57	1.01	CC(89)
5	1425(w)	1425(vw)	1425	1401	111.02	61.16	CC(88)
6	1360(w)	1400(s)	1413	1396	213.22	143.64	CC(84)
7		1311(w)	1349	1318	26.14	3.46	CC(82)
8			1309	1285	72.77	47.12	CC(81)
9	1250(m)	1260(vw)	1241	1202	2.99	0.92	CH(71)
10		1170(vw)	1168	1121	92.84	39.45	CH(75)
11	1100(s)	1150(vs)	1125	1104	4.25	2.76	CF(65)
12	1060(m)	970(m)	975	956	80.32	1.92	CN(61)
13			930	905	23.21	1.01	CH(56)
14			864	845	17.01	3.04	CCl(60)
15		800(vw)	863	831	18.35	7.78	CCl(52)
16			764	712	12.59	1.84	NO2rock(54)
17		740(m)	734	711	38.22	1.74	CH(51)
18			694	654	29.59	9.91	NO2sciss(59)
19		630(vw)	664	633	0.01	0.23	CCl(52)
20			619	592	1.08	0.37	CN(51)
21		610(vw)	611	574	2.42	1.96	CCl(51)
22		500(vw)	537	512	9.59	0.76	NO2wagg(43)

1.1. C-H vibrations

In benzene like molecule C–H in-plane bending vibrations interact with C–C stretching vibrations and are observed as a number of bands in the region 1000–1300 cm^{-1}. The FT-IR band

identified at 1250(m) cm^{-1} and FT-Raman band at 1260(vw), 1170(vw) cm^{-1} were assigned to C–H in-plane bending vibration of DFNB.

The C–H out-of-plane bending vibrations occur in the region 900–667 cm^{-1}. The bands observed at 740(m) cm^{-1} in FT-Raman spectrum of DFNB. The theoretically calculated values for C–H vibrational modes by B3LYP/6-31+G(d,p) method gives good agreement with experimental data.

4.1.2. Ring Vibrations

Most of the ring vibrational modes are affected by the substitutions of functional groups. The characteristic ring stretching vibrations are assigned in the region 1650–1300 cm^{-1} [25]. Therefore, the C–C stretching vibrations of DFNB are found at 1625(s), 1500(m), 1425(w), 1360(w) in FT-IR spectrum and 1425(vw), 1400(s), 1311(w) in FT-Raman spectrum for DFNB. The theoretically computed values for C–C vibrational modes by B3LYP/6-31+G(d,p) method gives excellent agreement with experimental data. Small changes in wavenumber observed for these modes are due to the changes in force constant/reduced mass, resulting mainly due to addition of fluorine group to nitro.

4.1.3. C–Cl vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations is possible due to the presence of heavy atoms on the periphery of the title molecule. In DFNB, the C−Cl stretching vibrations appeared at 800(vw) cm^{-1} in FT-Raman spectrum. The C−Cl in-plane bending vibrations were found at 630(vw) and 610(vw) cm^{-1} in FT-Raman spectrum.

4.1.4. Nitro group vibrations

Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric stretching vibrations of the nitro group at 1570–1485 and 1370–1320 cm^{-1}, respectively, Hydrogen bonding has a little effect on the nitro group asymmetric stretching vibrations. The strong and very weak bands at 1800 cm^{-1} and 1600 cm^{-1} have been assigned to asymmetric and symmetric stretching modes of nitro group. Aromatic nitro compounds have a band of weak to medium intensity in the region 590–500 cm^{-1} due to the out-of-plane bending deformations mode of nitro group. This is observed at 500 cm^{-1} in FT-Raman spectrum. The in-plane nitro group deformations vibrations have a week to medium absorption in the region 775– 660 cm^{-1}. In DFNB, the nitro group deformation is found within the characteristics region.

4.1.5. C–N vibrations

The C–N stretching and C–N bending vibrations of a nitro group occur near 870 and 610 cm^{-1}, respectively. The bands are assigned to C–N stretching vibration of a nitro group for DFNB have been found at 1060(m) and 970(m) cm^{-1}. The C–N out-of-plane bending vibrations are occurred within the characteristics region. From these observations it is found that the stretching bond; C–N is influenced by other modes. After scaling down, the computed value for C–N stretching vibration by B3LYP/6-31+G(d,p) methods nearly coincide with observed values of FT-IR and FT-Raman and these assignments are in good agreement with literature data.

Conclusion

The vibrational frequencies of the fundamental modes of the DFNB have been precisely assigned and analyzed and the theoretical results were compared with the experimental vibrations The observed and calculated fundamental frequencies B3LYP method using6-31+G(d,p) basis set shows similar profiles in both position and intensities making normal mode assignments with confidence. The assignments made were compared with the experimental values.

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