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Vibrational Analysis and Non Linear Optical Activity of 3-fluoro-4-methylbenzonitrile

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ABSTRACT

The optimized molecular geometry, mulliken atomic charges, highest occupied molecular orbitals (HOMO) energy, lowest unoccupied molecular orbitals (LUMO) energy, polarizability and the first order hyperpolarizability of 3-fluoro-4-methylbenzonitrile has predicted with the help of quantum chemistry calculations by density functional theory (DFT) with B3LYP using 6-311++G(d,p) basis set. FTIR and FT-Raman spectra are investigated and compared with the observed data. Observed HOMO-LUMO energy gap offers the evidence for the presence of intermolecular interactions in the compound. First order hyperpolarizability calculated by quantum calculations infers that the title compound was an efficient tool for future applications in the field of non-linear optics. Natural bond orbitals and the thermodynamical properties were also studied by DFT.

Keywords: 3-fluoro-4-methylbenzonitrile, density functional theory (DFT), FTIR, FT-Raman, HOMO, LUMO.

INTRODUCTION

Benzonitrile is an aromatic organic compound. Derivatives of benzonitrile find application in industries and medical field (M. Alcolea Palafox, 2003). Benzonitrile compounds are used as preservatives for food products. They are used for making aniline blue a dye. In medical field many benzonitrile derivatives in solid form are used as urinary antiseptic and vapour form are used for disinfecting bronchial tubes (Hermann Imgartinger, 2000). Since the derivatives of benzonitrile have wide applications,many studies are reported on such compounds. First order hyperpolarizability and HOMO-LUMO energy are the most important tools to predict the NLO activity of a compound. Quantum chemistry calculations provides the entire information about the structural, vibrational, electronic, optical, thermodynamic and other related properties of a molecule (David Pegu, 2013). Hence the present analysis was carried out to study the molecular properties of 3-fluoro-4-methylbenzonitrile and to elucidate useful information about the molecule.

EXPERIMENTAL

The compound 3-Fluoro-4-methyl benzonitrile (3F4MBN) was purchased from sigma-Aldrich Chemical Company, USA with a purity of not less than 99% and used as such for experimental studies. FT-Raman spectra of 3F4MBN was inscribed using 1064 nm line of Nd:YAG laser as the exciting wavelength in range 50-3500 cm^{-1} on a EZRaman, Enwaveoptronics, USA IFS 66 V spectrometer. Fourier transform infrared (FTIR) spectra was inscribed using 8400S Bruker, AlphaT,Germany infrared spectrophotometer using KBr pellet technique in the range 4000–400 cm^{-1}. The spectra has been inscribed at normal temperature with a scanning speed 30 cm^{-1} min-1.

Computational

All calculations has been met with Gaussian 09 program package [M.J. Frisch, 2009] with the aid of DFT with B3LYP using 6-311++G(d,p) basis set and results were viewed using GAUSS VIEW program. HOMO and LUMO energy was obtained from time dependent density functional theory. NBO analysis has been executed using same basis set to study molecular interaction between filled and vacant orbitals. Polarizability and hyperpolarizability were also calculated.

Table 1: Geometrical Parameters of 3--fluoro- 4-methylbenzonitrile

Parameter	B3LYP	Parameter	B3LYP	Parameter	B3LYP
BondLength(Å)	6-311G++(d,p)	Bond Angle(°)	6-311G++(d,p)	Dihedral angle	6-311G++(d,p)
C1-C2	1.554	C2-C1-H11	109.5741	H11-C1-C2-C3	-150.8946
C1-H11	1.0675	C2-C1-H12	108.9205	H11-C1-C2-C7	29.386
C1-H12	1.072	C2-C1-H13	109.8545	H12-C1-C2-C3	89.2887
C1-H13	1.0814	H11-C1-H12	109.5449	H12-C1-C2-C7	-90.4308
C2-C3	1.3571	H11-C1-H13	109.3711	H13-C1-C2-C3	-30.7176
C2-C7	1.5456	H12-C1-H13	109.562	H13-C1-C2-C7	149.563
C3-C4	1.5425	C1-C2-C3	120.0591	C1-C2-C3-C4	-178.7972
C3-H14	1.0713	C1-C2-C7	119.9809	C1-C2-C3-H14	1.1997
C4-C5	1.3563	C3-C2-C7	119.9594	C7-C2-C3-C4	0.9223
C4-H15	1.0712	C2-C3-C4	119.8227	C7-C2-C3-H14	-179.0808
C5-C6	1.5359	C2-C3-H14	120.3491	C1-C2-C7-C6	177.7006
C5-C9	1.5345	C4-C3-H14	119.8282	C1-C2-C7-C8	-2.5711
C6-C7	1.362	C3-C4-C5	120.2109	C3-C2-C7-C6	-2.0191
C6-H16	1.0687	C3-C4-H15	119.6262	C3-C2-C7-C8	177.7092
C7-F8	1.3528	C5-C4-H15	120.1614	C2-C3-C4-C5	1.422
C9-N10	1.1563	C4-C5-C6	120.064	C2-C3-C4-H15	-179.0196
		C4-C5-C9	119.8784	H14-C3-C4-C5	-178.5748
		C6-C5-C9	120.0563	H14-C3-C4-H15	0.9835
		C5-C6-C7	119.9799	C3-C4-C5-C6	-2.6347
		C5-C6-H16	119.9932	C3-C4-C5-C9	176.9544
		C7-C6-H16	120.0269	H15-C4-C5-C6	177.8093
		C2-C7-C6	119.9001	H15-C4-C5-C9	-2.6016
		C2-C7-F8	120.2341	C4-C5-C6-C7	1.5281
		C6-C7-C8	119.8652	C4-C5-C6-H16	-178.4505
				C9-C5-C6-C7	-178.0602
				C9-C5-C6-H16	1.9612
				C5-C6-C7-C2	0.8132
				C5-C6-C7-C8	-178.9161
				H16-C6-C7-C2	-179.2082

RESULTS AND DISCUSSION

Geometric Structure

The optimized geometrical structure of 3-fluoro- 4-methylbenzonitrile is shown in Fig. 1. The optimized bond length, bond angle and dihedral angle are calculated using B3LYP 6-311++G(d,p) basis set. The geometrical parameters calculated are shown in Table 1. These parameters can be utilized to elucidate other parameters of the compound under investigation.

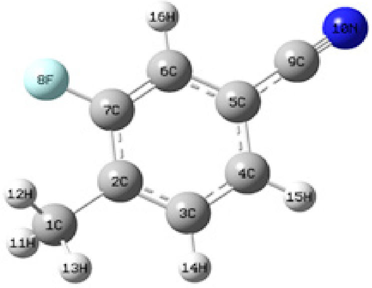

Fig.1.Optimized geometry of 3-fluoro-4-methyl benzonitrile

Vibrational Analysis

The investigated compound has 16 atoms and so it possess 42 normal modes of vibrations. Vibrational frequencies calculated and observed are shown in Table 2.

C-H vibrations

C-H stretching vibrations in aromatic compounds appear in the range 3100-3000 cm^{-1} (M. Silverstein, 1989). In this study the peak at 3078 cm^{-1} and 3068 cm-1 in the FTIR spectrum and FT-Raman Spectra respectively are ascribed to C-H stretching vibrations. The corresponding calculated values are 3086 cm^{-1} and 3060 cm^{-1} which are in accordance with the observed values. For substituted benzenes, the three in-plane C-H vibrations appear in a range 1300-1000 cm^{-1} and three out-of-plane bending vibrations appear in a range 1000-750 cm^{-1} (J. Sharmi Kumar, 2015). The peaks at 1142, 1194, 1214, 1252 cm^{-1} and at 1132, 1200 cm^{-1} in the FTIR spectrum and FT-Raman Spectrum are ascribed to in-plane C-H bending vibrations which are in accordance with the calculated values 1130, 1171, 1216 and 1276 cm^{-1} . The peaks at 831, 886 and 951 cm^{-1} and at 867, 936 cm^{-1} in the FTIR spectrum in the FT-Raman Spectrum are ascribed to out- of -plane C-H bending vibrations which are in accordance with the calculated values 836, 896 and 950 cm^{-1} .

C-C vibrations

Ring C-C stretchingvibration appears in a range 1650-1400 cm^{-1} (N. Sundaraganasan, 2009). Peaks at 1492 cm^{-1}, 1562 cm^{-1} and at 1494 cm^{-1}, 1591 cm^{-1} in the FTIR spectrum and FT-Raman Spectrum are ascribed to C-C vibrations. The corresponding worked out values are 1494 cm^{-1}, 1564 cm^{-1} and 1492 cm^{-1}, 1531 cm^{-1} which are in accordance with the observed data.

C-F vibrations: C-F vibration appears in the range 1360-1000 cm^{-1} (K. Sambathkumar, 2015). The sharp peak at 1270 cm^{-1} and at 1285 cm^{-1} in the FTIR spectrum and FT-Raman Spectra are ascribed to C-F vibrations and are in accordance with calculated values 1270 cm^{-1}and 1276 cm^{-1}.

C≡NVibrations: C≡N vibration appears around 2200 cm^{-1}(S.Gunasekaran, 2006).The peak at 2244 cm^{-1} and at 2221 cm^{-1} in the FTIR spectrum and FT-Raman Spectra are ascribed to C≡N vibrations which are in accordance with calculated values 2242 cm^{-1} and 2238 cm^{-1}.

CH_3 group vibrations: The title compound has only one substituted methyl (CH_3) group in the fourth position of the benzene ring. A methyl group is associated with nine fundamental mode of vibrations namely, the symmetric stretching mode (CH_3 sym. stretch), asymmetric stretching mode (CH_3 asym. stretch), in-plane hydrogen stretching mode, the symmetric deformation mode(CH_3 sym. deform), asymmetric deformation mode(CH_3 asy. deform), the in-plane rocking mode (CH_3 ipr), out-of-plane rocking mode (CH_3 opr) and twisting (tCH_3) mode. Substituted methyl groups in the aromatic ring systems are typically specified as electron donating groups (D. Lin-Vein, 1991).

Generally CH_3 vibration appear in a range (2900-3000 cm^{-1}) (M. Murugan, 2012). Peak at 3000 cm^{-1} and at 2986 cm^{-1} in the FTIR spectrum and FT-Raman Spectra are ascribed to CH_3 symmetrical stretching mode vibration which are in accordance with the calculated value 3035 cm^{-1}. The peak at 1499 cm^{-1} in the FTIR spectrum corresponds to CH3 in plane bending modes which is in accordance with the calculated value 1492 cm^{-1}. The peak at 1069 cm^{-1} in the FTIR spectra harmonize to CH_3 in rocking mode vibration which is in accordance with the calculated value 1060 cm^{-1}.

Table 2: Observed and calculated (FT-IR, FT-Raman) vibrational frequencies of the title compound

Mode	Label	Experimental (cm^{-1})FT-IR	FT-Raman	B3LYP/6-311++G(d,p)	IR Intensity (Km/mol)	Raman Activity	Vibrational assignments
1	A			95.7103	0.0009	0.3696	τCH$_3$
2	A			104.1663	1.438	0.4454	τC≡N
3	A		154	148.0831	5.0946	3.2263	βC≡N
4	A		194	197.8587	3.2846	1.3948	γC-CH$_3$+γC≡N
5	A		273.7	276.2751	2.2767	0.3873	βC-CH$_3$+βC-F
6	A		280	282.9399	2.3928	0.6734	ωC-F
7	A		414	409.8928	1.4935	4.0477	γC-CH$_3$
8	A		423	432.2994	1.4908	3.9706	16aγC-C-C
9	A		434	436.6913	1.945	1.5209	βC-C-C
10	A	513.3	462.6	491.5191	2.5994	1.6762	16bγC-C-C
11	A	560.4	544	545.9524	3.7765	7.3407	16bβC-C-C
12	A	611.8	615.8	603.8151	2.6259	0.9818	16aβC-C-C
13	A	632.4	620	643.1389	10.0649	1.2955	6aδ
14	A		685.8	700.6038	0.7185	2.4935	γC-C-C+t C≡N
15	A	753.2	754	713.601	1.7294	0.3961	γC-C-C+t C≡N
16	A	768.3		769.1046	5.0664	24.505	βC-C-C+t C-F
17	A	831.4		836.704	23.2161	0.1268	17bγC-H
18	A	886.4	867	896.4401	24.4011	0.1313	γC-H+τ C≡N
19	A	951.45	936	950.8395	21.1946	4.5349	10aγC-H
20	A	993.8		970.5941	0.0134	0.0512	Ring breathing
21	A	1007.4	1006	1019.558	18.0624	0.9225	Trigonal bending
22	A	1069		1060.461	2.6859	0.0411	ρCH$_3$
23	A	1142.5	1132	1130.859	36.0379	19.7862	βCH+υC-F
24	A	1194.9		1171.555	0.575	3.0025	βCH
25	A	1214.5	1200	1216.88	3.7437	1.9298	βCH+υC-F
26	A	1270.4	1277	1276.279	78.5627	76.1255	βCH
27	A		1285	1295.275	1.0495	1.5283	υC-F
28	A		1332	1329.431	0.409	2.3016	γC-CH$_3$
29	A	1429.5	1410	1419.072	3.2555	20.0889	CH$_3$ asym. deform
30	A	1469.5		1439.191	29.835	0.7039	CH$_3$ asym. deform
31	A	1472	1487	1480.588	8.2457	9.5451	14υC-C
32	A	1499		1492.38	8.7334	13.1925	βCH$_3$
33	A	1572.6	1584.7	1531.799	50.2532	1.5091	19aυC-C
34	A	1600		1601.005	40.2309	2.2114	8bυC-C (semi-circle stretch)
35	A	1668.6	1658	1656.248	2.154	172.8537	8aυC-C
36	A	2338	2338	2333.982	43.5827	557.747	γC≡N
37	A	3000	2986	3035.594	15.3871	306.9231	υsym CH$_3$
38	A	3078	3053	3086.357	8.4141	99.1312	20a** arom. υC-H
39	A	3117	3108	3118.279	12.3515	65.7333	υC-H
40	A	3178		3177.419	5.5481	75.475	υC-H
41	A	3203	3207	3203.313	1.539	102.9211	υC-H
42	A	3221		3212.26	0.7115	88.4629	υC-H

υ-stretching; υ$_{sym}$-symmetrical stretching; υ$_{asy}$- asymmetrical stretching; β-in plane bending; γ-out-of-plane bending; ω-wagging; t-twisting; δ-scissoring; τ-torsion; ρ-rocking; *-wilson's notion; IR int-IR intensities.

Mulliken atomic Charges

The scope of bonding of a molecule depend on the number of unpaired electrons in the atoms and hence the atomic charges has been retrieved by Mulliken population assay (A. A. Popov, 2004). Mulliken atomic Charges calculation plays an important part in applying quantum chemistry calculation to molecular systems because atomic charge affects dipole moments, polarizability, electronic structures and other properties of molecular systems (R. S. Mulliken, 1985). Mulliken charges obtained using B3LYP 6-311++G (d,p) are shown in Table 3. Mulliken atomic charges graph is shown in Fig.2. All hydrogen atoms exhibits positive charge, nitrogen and fluorine atom exhibit negative charge. This suggests the creation of intermolecular interaction in solid forms(Isa Sidir, 2010). From the charge calculation it is clear that nitrogen atom having negative charge acts as donor atom and the ring hydrogen atom having positive charge acts as acceptor atoms.

Table 3: Mulliken Population Analysis of 3--fluoro-4-methylbenzonitrile

Sl.No	Atoms	B3LYP
1	C	-0.38354
2	C	1.303938
3	C	-0.85876
4	C	-0.53413
5	C	2.179886
6	C	-0.15444
7	C	-0.68165
8	F	-0.17206
9	C	-1.58496
10	N	-0.1711
11	H	0.178828
12	H	0.17881
13	H	0.157086
14	H	0.143043
15	H	0.190491
16	H	0.208561

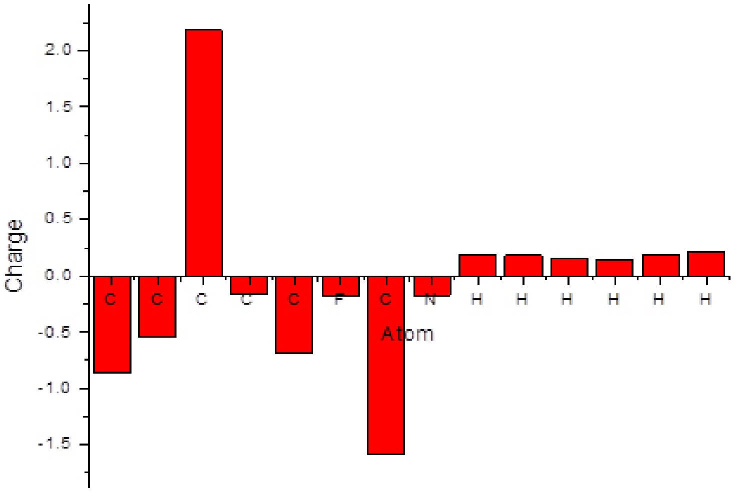

Fig. 2. A plot of Mulliken atomic charges of 3--fluoro- 4-methylbenzonitrile

Polarizability and Hyperpolarizability

The reaction of systems in applied electric fields has been explained by its Polarizability and hyperpolarizability. The non linear optical property of a compound can be studied using these parameters. The investigated first order hyperpolarizability of investigated compound is 2.768x10^{-30} esu which is 9 times urea (0.2991x10^{-30} esu) a standard NLO material (Li Xiao-Hong, 2011). Calculated dipole moment, polarizability and hyperpolarizability are given in Table 4.

HOMO LUMO analysis

HOMO stands for highest occupied molecular orbital which represents the ability of a molecule to donate an electron and LUMO stands for lowest unoccupied molecular orbital which represents the ability of a molecule to accept an electron. HOMO and LUMO are the major orbitals that take part in the chemical stability of the molecule (J. A. Alanso, 2004). The calculated HOMO LUMO gap using B3LYP 6-311++G(d,p) is 5.61eV. The HOMO LUMO energy gap explain that the title compound is experiencing charge transfer interactions and it reflects its NLO property (Basak Kosar, 2011). The calculated energy values are shown in Table 5.

Table 4: Electric dipole moment, polarizability and hyperpolarizability of 3--fluoro-4-methylbenzonitrile

Parameters	B3LYP 6-311++G(d,p)
μ_x	0.5802156
μ_y	0.010185
μ_z	-1.7797845
μ=	1.87200Debye
α_{xx}	92.0760016
α_{xy}	-0.0391977
α_{yy}	54.1494
α_{xz}	0.300154
α_{yz}	-0.5182233
α_{zz}	145.5895464
α_0	194.7552x10^{-33} esu
α=	1682.549x10^{-33} esu
β_{xxx}	103.2968388
β_{xxy}	-7.7277807
β_{xyy}	34.3821757
β_{yyy}	6.763047
β_{xxz}	24.3731807
β_{xyz}	0.135037
β_{yyz}	-18.6541887
β_{xzz}	28.6181066
β_{yzz}	5.1407
β_{zzz}	268.1870903
β_0	2768.5784x10^{-33} esu

Table 5: Calculated energies of 3--fluoro-4-methylbenzonitrile

LUMO	-1.79
HOMO	-7.4
Energy Gap	5.61
Electronegativity (χ)	-4.595
Chemical Potential (μ)	4.595
Global Hardness (η)	2.805
Global softness (s)	0.356506239
Electrophilicity Index (ω)	6.4444875
EHOMO-1(eV)	-7.82
ELUMO+1(eV)	-1.36
EHOMO-1 - ELUMO+1(eV)	-6.46

Thermodynamic parameters

Several thermodynamical parameters has been calculated and are listed in Table 6. Scale factors were recommended (Zeynep Demircioglu, 2014) for calculating zero point vibrational energy and entropy accurately. Changes in total energy and entropy at normal temperature are presented in Table. 6. These changes seems to be insignificant.

Table 6: Thermodynamic parameters

Thermodynamic functions of DMAP	B3LYP 6-311++G(d,p)
Self-consistent field energy (a.u)	-463.132
Zero point vibrational energy (kcal/mol)	74.043
Rotational constant (GHz)	3.021
	0.880
	0.684
Rotational temperature (K)	0.145
	0.042
	0.033
Thermal energy (kcal/mol)	
Total	79.491
Translational	0.889
Rotational	0.889
Vibrational	77.714
Specific heat capacity at constant volume (cal/mol K)	
Total	32.233
Translational	2.981
Rotational	2.981
Vibrational	26.271
Dipole moment (Debye)	4.7644
Lumo(eV)	-1.79
Homo(eV)	-7.4
Energy gap(eV)	-5.61
Entropy(S)(cal/mol K)	
Total	91.514
Translational	40.614
Rotational	29.559
Vibrational	21.342
Gibbs Free Energy	0.084
Enthalpy	0.128

Non linear optical activity

NLO activity give key function for properties like the frequency shifting, optical modulation, optical swaping, optical logic for the extending technology in the field of communications, signal processings and optical inter-connections (Mauricio Alcolea Palafox, 2000). Molecules that exhibit asymmetric polarization which is induced because of electron donars and acceptors in the pi-electron conjugatedsystems are efficient materials for electro-optics and NLO applications (I. Khan, 2013). In order to find the non linear activity of the material, first order hyperpolarizability of the investigated compound was calculated and compared with urea, a standard NLO material. It was found that the first order hyperpolarizability of our investigated compound is 9 times than urea. Hence we propose that the investigated compound under study is an efficient material for future NLO applications.

CONCLUSION

Detailed investigation of the structural and electronic property of the compound under study has been performed by DFT using suitable basis set. Calculated first order hyperpolarizability and HOMO-LUMO energy gap confirmed the NLO property of the compound. First order hyperpolarizability calculated for the compound is 9 times greater than urea. Hence the compound under study is an efficient material for future NLO applications. Mulliken atomic charge calculation suggests that there is charge transfer from N, F to H.

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