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Molecular geometry, spectroscopic and NLO studies of 1-(chloromethyl)-4-fluorobenzene – A DFT study

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The vibrational spectra of 1-(chloromethyl)-4-fluorobenzene have been studied in the 4000 - 400 cm^{-1} and 3500 - 50 cm^{-1} range, by FTIR and FT-Raman, respectively. In this work, structural analysis and vibrational frequencies are performed utilizing the GAUSSIAN 09W program with DFT/B3LYP strategy with basis set 6-311++G (d, p). Least differences are noted between the measured and scaled wavenumbers. The molecular vibrational assignments are confirmed by the PED (potential energy distribution) percentage. Frontier molecular orbital, natural bond orbital and Mullikan charge examinations are employed to explain the reason for intra and intermolecular charge exchange of the molecule. Reactive sites and chemical shifts are investigated by molecular electrostatic potential map and nuclear magnetic resonance analysis. Besides, the polarizability, the first hyperpolarizability, and total dipole moment of the molecule have been computed for describing its NLO activity.

Keywords: 1-(Chloromethyl)-4-fluorobenzene; HOMO, LUMO, Polarizability; MEP; NBO

A benzene derivative such as 1-(chloromethyl)-4-fluorobenzene (CMFB) is an aromatic compound, colourless, explosive liquid and broadly used in making pesticides. Particularly, the chloro and fluorobenzene derivatives are critical industrial material and utilized as intermediates in the generation of dyestuffs, and paint solvents[1]. Further, several heterocyclic derivatives covering chlorine and fluorine atoms serve as a special and flexible framework for experimental drug plans[2]. Many spectroscopic works of halogen relating compounds has been detailed in the previous report[3-5]. Vijisha *et al*[6] reported that the halogen contained benzene derivative possesses nonlinear optical (NLO) properties.

For polyatomic atoms, the DFT strategies lead to the expectation of more exact molecular structure and frequencies. In DFT approaches, Becke's three-parameter hybrid function combined with the Lee-Yang–Parr relationship (B3LYP) expects best calculation for structural analysis[7]. Due to greater industrial significance of CMFB, an attempt has been opted to perform its geometry, spectroscopic and NLO studies along with density computational theory (DFT) computation using 6-311++G (d, p) sets[8,9]. The present work has been also focused to recognize the frontier molecular orbitals, Mullikan charges, NLO property and natural bond orbitals (NBO) of CMFB.

Experimental Details

The CMFB (99% purity) has been purchased from Sigma Aldrich, USA. Perkin Elmer Fourier transform infrared (FT-IR) spectrometer of CMFB was recorded by employing a KBr pellet method at room temperature with a 1.0 cm^{-1} resolution. Stand-alone FT-Raman spectrum of CMFB was taken by using BRUKER RFS 27 model spectrometer at room temperature with a resolution of 2 cm^{-1}. The FT-IR and FT-Raman spectra have been established in the wavenumber range 4000-400 cm^{-1} and 4000-50 cm^{-1}, respectively.

Computational Details

The GAUSSIAN 09W program[10] exploiting Becke-3-Lee-Yang-Parr (B3LYP) hybrid functional[11,12] with the standard 6-311++G (d,p) basis set have been utilized for DFT calculations. Initially, the structure of CMFB is optimized by the DFT/B3LYP strategy with a 6-311++G (d,p), then the vibrational wavenumbers and intensities are calculated. The scaled quantum mechanical (SQM)[13] strategy ensures between the experimental data and DFT computed results. Subsequently, the computed wavenumbers were scaled by employing a scaling value of 0.9613 for the B3LYP strategy[14]. The frontier molecular orbitals (FMOs) of CMFB have been visualized using Gaussview *05* visualization program[15]. The UV-visible range of CMFB have been computed (without any solvation) by time-dependent (TD)-DFT/B3LYP method. The ^{13}C and ^{1}H NMR shielding was recreated using the Gauge-Invariant-atomic orbital (GIAO) method. The vibrational wavenumbers of each functional group of CMFB have been confirmed from potential energy dispersion (PED) using MOLVIB program[16].

Results and Discussion

Molecular geometry

The optimized structure of CMFB having C_1 point group is shown in Fig. 1. The CMFB contains fluorine, chlorine atoms and methyl group in the benzene ring. By using the B3LYP strategy with 6-311++G (d, p) premise set, the computed optimized parameters of CMFB along with XRD data are recorded in Table 1. From the computational results, most of the bond distances are slightly bigger than the

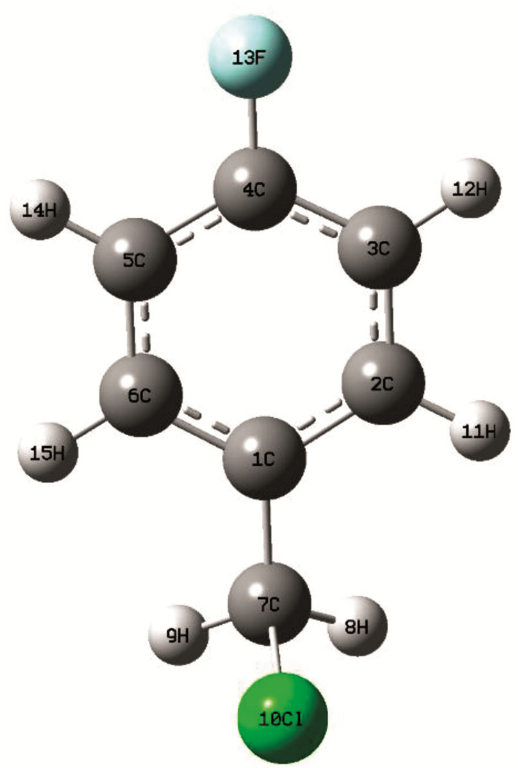

Fig. 1 — Optimized molecular structure of 1-(chloromethyl)-4-fluorobenzene

Table 1 — Optimized geometrical parameters of 1-(chloromethyl)-4-fluorobenzene

Parameters	Method/Basis set B3LYP/6-311++G(d,p)	Experimental[26]
Bond length		
C1-C2	1.399	1.391
C1-C6	1.399	1.382
C1-C7	1.495	1.491
C2-C3	1.391	1.377
C2-H11	1.084	0.930
C3-C4	1.386	1.372
C3-H12	1.082	0.930
C4-C5	1.386	1.380
C4-F13	1.354	1.359
C5-C6	1.391	1.383
C5-H14	1.082	0.930
C6-H15	1.084	0.930
C7-H8	1.087	0.970
C7-H9	1.087	0.970
C7-Cl10	1.841	1.795
Bond angles		
C2-C1-C6	118.84	119.43
C2-C1-C7	120.57	120.64
C1-C2-C3	120.99	120.69
C1-C2-H11	119.68	120.00
C3-C2-H11	119.32	120.00
C2-C3-C4	118.39	118.48
C2-C3-H12	121.76	121.00
C4-C3-H12	119.84	122.51
C3-C4-C5	122.37	122.51
C3-C4-F13	118.81	118.26
C5-C4-F13	118.81	118.09
C4-C5-C6	118.39	118.22
C4-C5-H14	119.84	121.00
C6-C5-H14	121.76	121.00
C1-C6-C5	120.99	120.65
C1-C6-H15	119.68	120.00
C5-C6-H15	119.32	120.00
C1-C7-H8	112.19	110.00
C1-C7-H9	112.19	110.00
C1-C7-Cl10	112.28	109.58
H8-C7-H9	109.64	108.00
H8-C7-Cl10	105.02	110.00
H9-C7-Cl10	105.02	110.00
Dihedral angles		
C6-C1-C2-C3	-0.076	-1.0
C7-C1-C2-C3	179.789	178.30
C2-C1-C6-C5	0.076	1.2
C7-C1-C6-C5	-179.789	-178.1
C2-C1-C7-C110	90.084	83.2
C6-C1-C7-C110	-90.052	-95.5
C1-C2-C3-C4	0.071	-0.2
C2-C3-C4-C5	-0.068	1.3
C2-C3-C4-F13	-179.863	-179.58
C3-C4-C5-C6	0.068	-1.1
C4-C5-C6-C1	-0.072	-0.2

experimental values, due to that the DFT calculations carried out in gaseous stage whereas the observed results carried out in different state[17]. The global least energy obtained for CMFB is calculated as -830.5292674 Hartrees. The C-H bond length changes from 1.082 to 1.087 Å. The C-C bond distances extend from 1.386 to 1.495 Å by the B3LYP/6-311G++ (d, p) strategy, which are good assertion with those experimental XRD (1.372-1.491Å) report[18]. The benzene ring shows a slightly out of the hexagonal region. It is due to the fluorine, chlorine and methyl groups of CMFB. From the DFT calculations, the C2-C1-C7, C4-C5-C6 and C1-C2-H11 bond angles are computed as 120.57°, 118.39°, 119.68°, individually, (Experimental values: 120.64°, 118.22°, 120.0°). All the tetrahedral angles of the CMFB ring are nearly 0°or 180° which represents its planar nature. The variety in bond angles depends on the electronegativity of the fluorine atom, the present of lone pair electrons, and the coupling of the double bonds. In benzenes, the ring carbon atoms shows a huge involvement on the outermost electron of the H atoms which results an increment in the C-H force constant and a diminish its bond distance. The C-H would be affected by the impacts of the inductive-mesomeric interactions[19]. The C-X (X; F, Cl, Br, I) bond length demonstrates a significant increment when substituted in a place of C-H. In calculation, the effect of conjugation between the chloro and benzene ring can be understood from the rise in bond length of C7-Cl10 (1.841 by B3LYP and 1.795 Å by experimental)[20]. Bond arrangement could be a valuable tool for depicting bond type and analyzing bond quality.

The thermodynamic parameters of CMFB are accounted in Table 2. As the interaction between the atoms within the molecule is very stronger, then the dipole moment will be most extreme. Here, the calculated dipole moment and total energy of CMFB are evaluated as 1.8940 D and 74.554 kcal mol^{-1}. The irrelevant vibrational energy (zero-point) is obtained (69.69292 kcal mol^{-1}) for CMFB. These thermodynamic parameters can be utilized in the assessment of chemical responses and to discover the extra thermodynamic energies of CMFB.

Vibrational assignments

The computed and test FTIR and FT-Raman spectra of CMFB have been represented in the Figs. 2 and 3. The IR and Raman peak intensities and the vibrational wavenumbers of CMFB are given in Table 3. The CMFB molecule comprises of 15 atoms and its leads to 39 typical vibrational modes.

C-H Vibrations—The C-H vibrations[21] are found within the range 3100-3000 cm^{-1}. Subsequently, for CMFB, the infrared bands that showed up at 3112,

Table 2 — The thermodynamic parameters of 1-(chloromethyl)-4-fluorobenzene

Parameters	Method/Basis set
	B3LYP/6-311++G(d.p)
Optimized global minimum Energy (Hartrees)	-830.418205
Total energy (thermal) E_{total} (kcal mol^{-1})	74.554
Heat capacity C_v(cal mol^{-1}k^{-1})	28.789
Entropy S (cal mol^{-1}k^{-1})	89.566
Total	
Translational	40.805
Rotational	29.707
Vibrational	19.054
Vibrational energy E_{vib} (kcal mol^{-1})	72.777
Zero point vibrational energy (kcal mol^{-1})	69.69292
Rotational constants (GHz)	
A	3.96359
B	0.65014
C	0.60852
Dipole moment (D)	1.8940

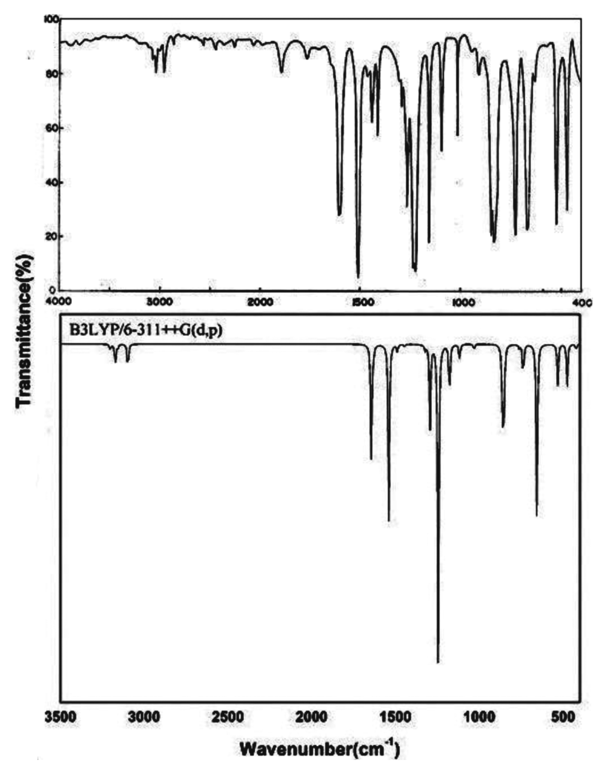

Fig. 2 — Comparison of experimental and computed FTIR spectra of 1-(chloromethyl)-4-fluorobenzene

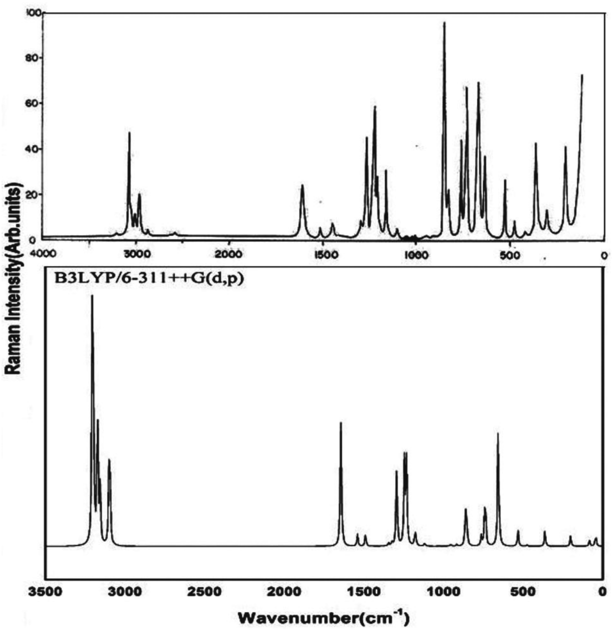

Fig. 3 — Comparison of observed and calculated FT-Raman spectra of 1-(chloromethyl)-4-fluorobenzene

3082, 3058, 3046, 2991, 2963 cm^{-1} and Raman frequencies at 3122, 3088, 3063, 2983, 2961 cm^{-1} have been assigned as stretching C-H vibrations. The scaled DFT values have been found at 3080, 3078, 3059, 3051, 3034, 2978 cm^{-1} are well supported with the total energy distribution (99-94% TED). The computed and experimental C-H bending vibrations have also been assigned well and found to be in good support with the literature data[22] as given in Table 3.

C-Cl Vibrations—The C-Cl[23] is generally built up in between the frequencies 850 and 550 cm^{-1}. Therefore, the computed wavenumber of CMFB at 408 cm^{-1} and the corresponding Raman peak absorbed at 401 cm^{-1} have been designated for stretching C-Cl vibrations (75% TED). In most of the chloro aromatic compounds, the band of various intensities in the 385–265 cm^{-1} region have been designated to C-Cl bending in-plane vibration[24]. Hence, the C-Cl in-plane deformation for CMFB has been set up at 293 cm^{-1} as strong Raman peak. The out-of-plane C–Cl deformation of CMFB is also listed in Table 3.

C-F Vibrations—The observed C-F[25] bands are found to be very solid in the region 1000-1300 cm^{-1}. Moreover, the C-F vibrations in the mono fluorinated are noted in between 1100 and 1000 cm^{-1}. For CMFB, the C-F stretching vibration have been found as strong wavenumber at 1294 cm^{-1} in Raman and 1299 cm^{-1} in FTIR. These frequencies are in fine match with the computed values at 1272 cm^{-1} (85% TED). The C-F in plane bending deformation is established at 352 cm^{-1} in Raman and C-F out-of-plane wavenumber is also coincided with the literature[26].

C-C Vibrations—The C-C vibrations are usually shown in between 1430 and 1650 cm^{-1} for the hetero aromatic compounds[27]. Appropriately, in the present examination, the C-C (84-92% TED) vibrations of CMFB are observed at 1599, 1517, 1488, 1412, 1394, 1321, 1242 cm^{-1} in FTIR and at 1594, 1521, 1483, 1417, 1388, 1319, 1233 cm^{-1} in FT-Raman. The corresponding computed values have been noted at 1581, 1570, 1480, 1432, 1391, 1292, 1243 cm^{-1}. The C-C in-plane vibration of CMFB is found at 851cm^{-1} in IR and out-of plane at 181 cm^{-1} in Raman. Further, the ring modes of vibrations for CMFB are also represented in Table 3.

Frontier molecular orbital (FMO) analysis

The electronic excitations in FMOs are extremely valuable for electric and optical studies. In molecular interface, donor and acceptor electron orbitals are represented as HOMO and LUMO. The stabilization and destabilization of the molecule can increase because of the HOMO and LUMO orbitals[28,29.] The HOMO-LUMO of CMFB has been computed at the DFT levels and energy gap is found to be 4.402 eV, which reflects the chemical activity of CMFB by using Koopman's theorem[30] and are illustrated in Table 4. The most notable (E_{HOMO-2}= -9.782 eV) HOMO energy permits to be the excellent electron giver (chlorine and fluorine atoms) and the LUMO (E_{LUMO+2}= -2.529 eV) implies the leading electron acceptor (C-C bond of ring). The corresponding energy gap is obtained as 7.253eV. The various frontier orbitals of CMFB are plotted in Fig. 4. The frequency of oscillation (f), excitation energies (E), electronic transition and UV-visible spectrum studies of CMFB are computed by TD-DFT method[31]. The energizing state of CMFB is computed at 239 nm with energy E=5.1754 eV and oscillator frequency of 0.0068. For that, the $\pi \rightarrow \pi^*$ transition is calculated from H→L (65%). Another energize state has been computed at 216 nm with frequency f = 0.0920, E = 5.7360 eV from H→ L+1 ($\pi \rightarrow \pi^*$ type) leading to contributions of 76%. For CMFB, a solid peak has been observed at 205nm with oscillator quality f = 0.0002 and energy = 6.0422 eV as exposed in Fig. 5. For this strong peak, the transition of charges from HOMO to LUMO describes $\pi \rightarrow \pi^*$. This has the most raised transition by 98% contribution from

Table 3 — The vibrational frequencies (cm^{-1}), IR intensity ($km\ mol^{-1}$) and Raman Activity ($Å^4\ amu^{-1}$) for 1-(chloromethyl)-4-fluorobenzene

Observed wavenumber		Wavenumber		IR Intensity	Raman activity	Reduced mass	Force constant	Assignment with PED (%)
FT-IR	FT- Raman	Calculated	Scaled					
3112(vw)	3122(vw)	3204	3080	1.9328	233.3755	1.0943	6.6160	ν C-H (99)
3082(vw)	3088(s)	3202	3078	1.4809	53.6595	1.0938	6.6116	ν C-H (98)
3058(vw)	3063(ms)	3174	3059	5.1405	53.8948	1.0897	6.4657	ν C-H (96)
3046(w)	-	3173	3051	6.4908	68.0088	1.0899	6.4663	ν C-H (95)
2991(w)	2983(m)	3157	3034	1.7931	42.9556	1.1115	6.5277	ν C-H (96)
2963(vw)	2961(vw)	3098	2978	14.1367	105.8958	1.0574	5.9788	ν C-H (94)
1599(ms)	1594(ms)	1645	1581	55.3737	66.3018	5.9731	9.5273	ν C-C (92)
1517(vs)	1521(w)	1634	1570	6.6485	5.0335	7.0284	11.0612	ν C-C (90)
1488(ms)	1483(m)	1540	1480	86.5241	6.3198	2.6541	3.7103	ν C-C (89)
1412(ms)	1417(w)	1490	1432	1.4629	6.3729	1.1190	1.4629	ν C-C (88)
1394(ms)	1388(s)	1447	1391	1.4396	0.2620	2.9849	3.6811	ν C-C (87)
1321(w)	1319(s)	1345	1292	0.0182	1.6205	3.7012	3.9434	ν C-C (86)
1299(vw)	1294(s)	1324	1272	3.1015	1.7821	1.5232	1.5725	ν C-F (85)
1242(vw)	1233(s)	1294	1243	42.4185	38.2854	1.2053	1.1894	ν C-C (84)
1202(vw)	1200(ms)	1246	1197	155.2062	42.1043	5.6878	5.1998	b C-H (82)
1194(w)	1183(ms)	1233	1185	0.0568	44.6051	2.3612	2.1148	b C-H (84)
1131(vw)	1139(vw)	1179	1133	28.6047	7.4428	1.2234	1.0015	b C-H (80)
1124(vs)	1116(vw)	1173	1127	0.0002	1.9864	1.0985	0.8906	b C-H (79)
1093(s)	1084(vw)	1118	1074	8.4031	1.5832	1.2844	0.9459	b C-H (75)
998(ms)	991(vw)	1032	992	3.1191	0.1750	2.5652	1.6090	b C-H (72)
951(vw)	-	973	935	0.0287	0.0614	1.3529	0.7539	Rtrigd (70)
-	912(vw)	955	918	0.1852	1.1288	1.3479	0.7246	Rasymd (69)
884(vw)	879(vs)	916	880	0.0385	0.9418	1.5532	0.7685	Rsymd (68)
851(ms)	-	862	828	38.4947	17.0370	2.6854	1.1769	b C-C (73)
819(vw)	822(ms)	853	819	34.4276	9.5201	2.6996	1.1564	ω C-H (65)
788(vs)	792(s)	827	794	0.0025	0.0766	1.2456	0.5013	ω C-H (66)
731(vs)	-	763	762	1.9804	4.6392	4.5983	1.5752	ω C-H (64)
719(vs)	714(s)	739	710	18.2610	26.9383	4.1424	1.3325	ω C-H (63)
691(vw)	-	657	631	85.0083	48.3679	4.8298	1.2298	ω C-H (62)
643(vw)	641(s)	650	624	0.0110	5.7487	6.8156	1.6942	ω C-H (64)
514(vs)	517(s)	533	512	21.0532	6.8941	3.1073	0.5196	tRtrigd (61)
488(vs)	483(w)	476	457	20.6671	0.5444	5.7366	0.7671	tRasymd (63)
-	401(vw)	425	408	0.8241	0.0177	3.2567	0.3469	ν C-Cl (75)
407(vw)	399(s)	422	405	2.0432	0.0207	3.8739	0.4069	tRsymd (62)
-	352(ms)	363	348	0.7100	6.3271	7.5396	0.5861	b C-F (71)
-	293(s)	299	287	0.0004	0.0286	2.7462	0.1442	b C-Cl (72)
-	181(vs)	202	194	3.0108	4.2479	10.2906	0.2475	ω C-C (65)
-	-	84	80	1.1555	2.2650	12.8216	0.0535	ω C-F (62)
-	-	45	43	1.8264	4.8562	4.5486	0.0054	ω C-Cl (61)

ν-stretching; b-bending; ω-out-of-plane bending; R-ring; trigd-trigonal deformation; symd-symmetric deformation; asymd-antisymmetric deformation; s-strong; vs-very strong; ms-medium strong; w-weak; vw-very weak

H→L+2 as given in Table 5. Hence, the CMFB has been unsaturated due to the π →π* type transition arises with interface in the aromatic ring. These properties of CMFB reflect the eigen values of HOMO and LUMO.

Mulliken atomic charges

The reactive charges[32] show the dynamic application in quantum calculation, since they affect the electronic properties of the molecule. The Mullikan analysis plot utilizing B3LYP with 6-311++G (d, p) basis sets for CMFB is given in Fig. 6 and values are recorded in Table 6. The positive values (0.1911, 0.1921, 0.1573, 0.2065, 0.2075 and 0.1573) of H8, H9, H11, H12, H14, and H15 represents that CMFB is more acidic. The partial charges of C1, C2, C3, C4, C5, C6, and C7 are highly influenced by their substituents. Further, the two electronegative chlorine and fluorine (Cl 10 and F13) dominate the largest negative charge of CMFB (-0.1505 and -0.1677). Also, the Mullikan charge has been utilized to explain the forms of electronegativity balance and exchange in chemical responses[33] to exterior molecular surfaces. The Mullikan charge of chlorine is bigger than the fluorine. It signifies that chlorine is more acidic than the fluorine.

Table 4 — Chemical parameters of 1-(chloromethyl)-4-fluorobenzene

Molecular Properties	B3LYP/6-311++G(d,p)
HOMO (eV)	-9.196
LUMO (eV)	-4.794
ΔE (E_{HOMO} –E_{LUMO}) (eV)	4.402
Ionization potential (I) (eV)	9.196
Electron affinity (A) (eV)	4.794
Global hardness (η) (eV)	2.201
Global softness (s) (eV^{-1})	0.227
Electronegativity (χ) (eV)	6.995
Chemical potential (μ) (eV)	-6.995
Global electrophilicity (w) (eV)	11.117

Natural bonding orbital analysis [NBO]

NBO gives an exact method for examining the interaction bonds and exploring charge exchange in several molecular frameworks. In general, greater the stabilization energy value, there will be more tendency to donate electrons to acceptor orbitals and causes more prominent degree of conjugation in any system as[34]

$$E_2 = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i - \varepsilon_j}$$

Where F(i,j) is the Fock matrix NBO element, ε_i and ε_j are diagonal elements and q_i is the donor orbital occupancy. NBO investigation has been completed for CMFB at the DFT/B3LYP 6-311++G (d, p) level to explain the molecular stabilization and are recorded in Table 7. The solid interaction (E (2) = 10.82 kcal/mol) is gotten between the π (C2-C3) orbital and π * (C4 – C5) orbital, and another

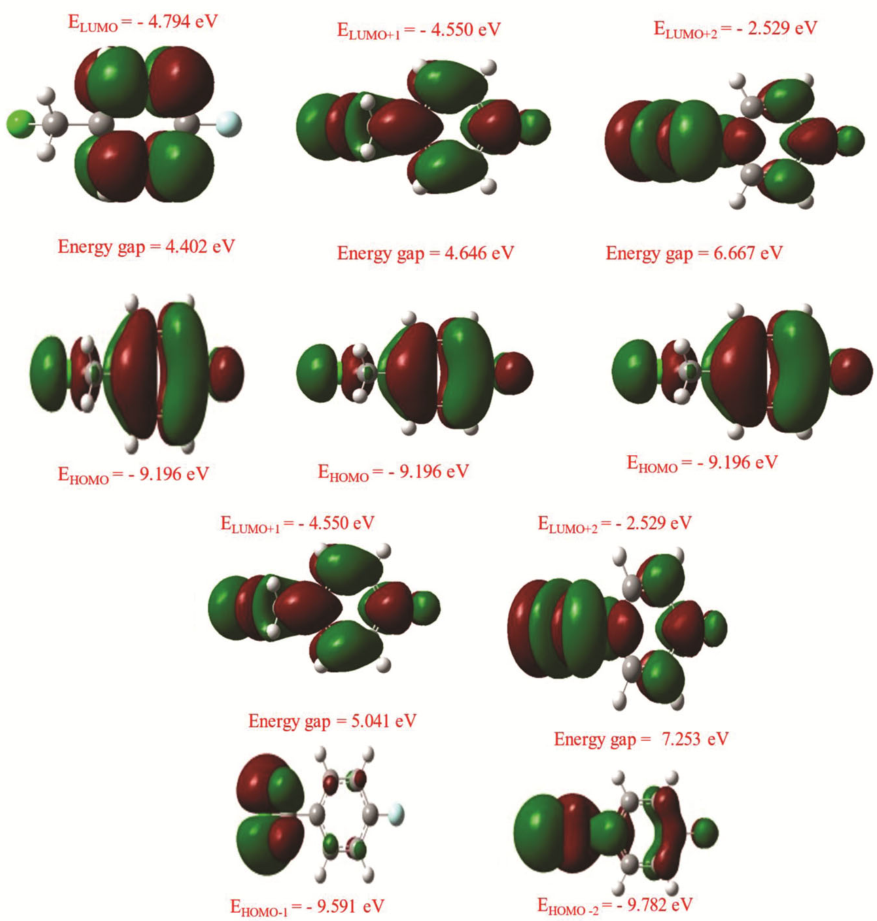

Fig. 4 — Contribution of HOMO-LUMO energy gap for 1-(chloromethyl)-4-fluorobenzene

Table 5 — Molecular orbital contributions of 1-(chloromethyl)-4-fluorobenzene

TDDFT/ B3LYP/6-311++G(d,p) Method				
Energy (eV)	Oscillator strength	Wavelength (nm)	Major contributions	Assignment
5.1754	0.0068	239.56	H → L (65%)	π→π*
5.7360	0.0920	216.15	H → L+1(76%)	π→π*
6.0422	0.0002	205.20	H → L+2(98%)	π→π*

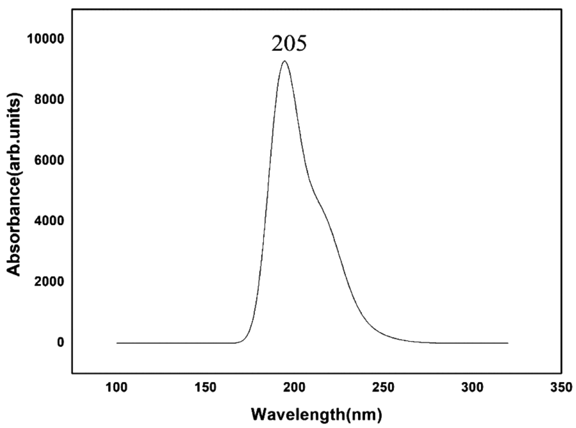

Fig. 5 — Absorption spectrum of 1-(chloromethyl)-4-fluorobenzene

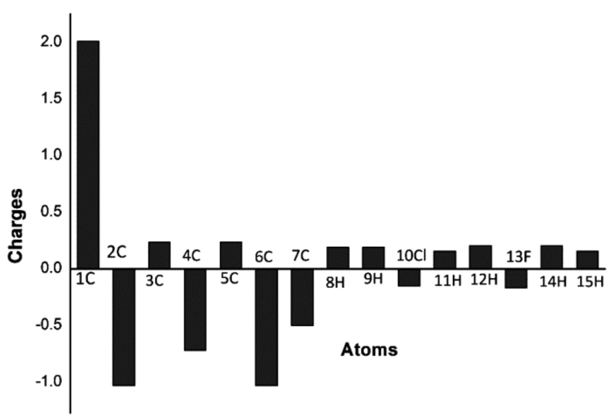

Fig. 6 — Mullikan charges of 1-(chloromethyl)-4-fluorobenzene

Table 6 — Mulliken's charge of 1-(chloromethyl)-4-fluorobenzene

Atom	Mulliken's atomic charges B3LYP/6-311++G(d.p)
1C	2.0115
2C	-1.0290
3C	0.2363
4C	-0.7181
5C	0.2362
6C	-1.0294
7C	-0.4994
8H	0.1911
9H	0.1921
10Cl	-0.1505
11H	0.1573
12H	0.2065
13F	-0.1677
14H	0.2075
15H	0.1573

E (2) = 10.09kcal/mol is observed between π (C1– C6) orbital and π * (C4 – C5) orbital. These are characteristic highlights of chemical activity of CMFB.

NMR spectral analysis

The optimized CMFB has been utilized in the ^{13}C and ^{1}H NMR spectra using DFT/ B3LYP 6-311++G (d, p) method employing the GIAO strategy. It is the effective way to interpret the structure of huge biomolecules[35]. The computational ^{13}C and ^{1}H isotropic shift values of the CMFB with tetramethyl silane (TMS) as a reference is recorded in Table 8. The ^{13}C calculated spectra have appeared in Fig. 7. In common, the chemical shift range of aromatic carbon molecules lies from 100 to 200 ppm[36]. In this case, the computational ^{13}C NMR values of the aromatic carbons are gotten in between 122.57 and 171.46 ppm. The high electronegative properties of the chlorine and bromine atoms deliver positive charges to the carbon atoms. Therefore, the highest shift of aromatic carbons C4 and C1 are found as 171.46 and 144.91 ppm, respectively. The carbon C7 gives the lowest shift at 48.47 ppm, since it is coupled to the two H atoms. The H9 protons linked with methyl group exhibits the lowest shift at 3.52 ppm. Hydrogens connected straight forwardly, their protecting diminishes shielding, and the resonance leads to higher wavenumber. Hydrogens put closer to electron donor the resonance moved to lower wavenumber. The computed chemical shifts of H11, H12, H14 and H15 attached directly to carbon atoms have the most extreme of 7.67, 7.27, 7.28 and 7.65 ppm and are given in Fig. 8.

Molecular electrostatic potential surface analysis

MEP surface can give responsive locales of electrophilic, nucleophilic, molecular shape as well as hydrogen holding reactions[37]. This MEP surface used to differentiate the electron - deficient, slightly

Table 7 — Natural bond orbital analyses for 1-(chloromethyl)-4-fluorobenzene

Donor(i)	ED(i) (e)	Acceptor (j)	ED (j) (e)	Stabilization energy E(2) (kJ mol^{-1})	Energy difference E(j) – E(i) (a.u.)	Fock matrix element F (I,j) (a.u.)
σ (C1-C2)	0.98747	σ*(C1-C6)	0.01169	1.83	1.28	0.061
σ (C1-C6)	0.98748	σ*(C1-C2)	0.01172	1.83	1.28	0.061
σ(C1-C6)	0.98748	σ*(C5-C6)	0.00642	1.47	1.28	0.055
σ (C1-C6)	0.98748	σ*(C5-H14)	0.00619	1.12	1.12	0.045
π (C1-C6)	0.82797	π*(C2-C3)	0.16787	10.7	0.28	0.069
π (C1-C6)	0.82797	π*(C4-C5)	0.18522	10.09	0.27	0.066
π (C1-C6)	0.82797	σ*(C7-Cl10)	0.01343	2.49	0.4	0.043
σ(C2-C3)	0.98682	σ*(C1-C2)	0.01172	1.66	1.28	0.058
σ (C2-C3)	0.98682	σ*(C1-C7)	0.01522	1.89	1.08	0.057
σ (C2-C3)	0.98682	σ *(C4-F13)	0.01538	2.01	0.97	0.056
π (C2-C3)	0.84003	π*(C1-C6)	0.17869	9.9	0.29	0.068
π (C2-C3)	0.84003	π*(C4-C5)	0.01357	10.82	0.27	0.07
σ(C3-C4)	0.99027	σ*(C4-C5)	0.18522	1.91	1.26	0.062
σ (C3-H12)	0.98896	σ*(C1-C2)	0.01172	1.78	1.1	0.056
σ (C3-H12)	0.98896	σ*(C4-C5)	0.01357	1.82	1.07	0.056
σ (C4-C5)	0.99028	σ*(C3-C4)	0.01359	1.91	1.26	0.062
σ (C4-C5)	0.99028	σ*(C5-C6)	0.00642	1.24	1.29	0.05
σ (C4-C5)	0.99028	σ*(C5-H14)	0.00619	0.42	1.13	0.028
π (C4-C5)	0.82708	π*(C1-C6)	0.17869	10.12	0.3	0.07
π (C4-C5)	0.82708	π*(C2-C3)	0.16787	9.54	0.29	0.067
σ (C5-C6)	0.98680	σ*(C1-C6)	0.01169	1.66	1.28	0.058
σ (C5-C6)	0.98680	σ*(C1-C7)	0.01522	1.89	1.08	0.057
σ (C5-C6)	0.98680	σ*(C4-C5)	0.01357	1.15	1.25	0.048
σ (C5-C6)	0.98680	σ*(C4-F13)	0.01538	2.02	0.97	0.056
σ (C5-H14)	0.98896	σ*(C1-C6)	0.01169	1.77	1.1	0.056
σ (C5-H14)	0.98896	σ*(C3-C4)	0.01359	1.82	1.07	0.056
σ (C6-H15)	0.98945	σ*(C1-C2)	0.01172	2.4	1.1	0.065
σ (C6-H15)	0.98945	σ*(C4-C5)	0.01357	1.6	1.07	0.052
σ (C7-H8)	0.99356	σ*(C1-C6)	0.01169	1.64	1.12	0.054
σ (C7-H9)	0.99366	σ* (C4-F13)	0.01538	1.68	1.12	0.055
LP(Cl10)	0.99838	σ*(C7-H8)	0.01031	2.13	0.72	0.05
LP(Cl10)	0.99838	σ*(C7-H9)	0.01023	2.03	0.72	0.048
LP(Cl10)	0.99838	σ*(C1-C7)	0.01522	2.05	0.68	0.047
LP(F13)	0.99472	σ*(C3-C4)	0.01359	3.12	0.96	0.069
LP(F13)	0.99472	σ*(C4-C5)	0.01357	3.12	0.97	0.069
LP(F13)	0.99472	π* (C4-C5)	0.18522	9.26	0.43	0.086

[a]E(2) means energy of hyperconjugative interactions.
[b]Energy difference between donor and acceptor i and j NBO orbitals.
[c]F(i,j) is the Fock matrix element between i and j NBO orbitals

deficient, rich, slightly rich by understanding its color codes as blue color, light blue color, red, and yellow, respectively. The MEP surface of CMFB has been portrayed in Fig. 9. The negative potential of CMFB is found over the chlorine (Cl10) and fluorine atoms (F13), which are due to the lone pair negative charges. The C6 atom is also electronegative since it is prepared to be held adjacent to chlorine. The positive locales are nucleophilic and are found in the hydrogens of methyl group (H8 and H9) and other hydrogens attached with the ring. Blue and red represents the region of hydrogen and chlorine has secured to be most attractive and repulsive regions, respectively. The MEP colour code of CMFB is ranging between -0.02949 a.u. (red) and +0.02949 a.u (blue). The MEP of CMFB explains that the methyl chloride and fluorine atoms are probably outbreak of the reactive sites.

Non-linear optical (NLO) effects

An expansive research about modern materials exhibiting NLO highlights have been of extraordinary interest, since of potential applications in modern communication innovation, media transmission, and optical flag processing[38-40]. Key significance of the polarizability and the primary hyperpolarizability

Table 8 — The ^{13}C and ^{1}H NMR chemical shifts with respect to TMS for 1-(chloromethyl)-4-fluorobenzene

Atom	Theoretical values (ppm)	
	Chemical shielding	Chemical shift
1C	37.55	144.91
2C	47.25	135.21
3C	59.88	122.57
4C	10.99	171.46
5C	59.98	122.48
6C	47.37	135.09
7C	133.98	48.47
8H	28.33	3.54
9H	28.36	3.52
11H	24.21	7.67
12H	24.60	7.27
14H	24.60	7.28
15H	24.22	7.65

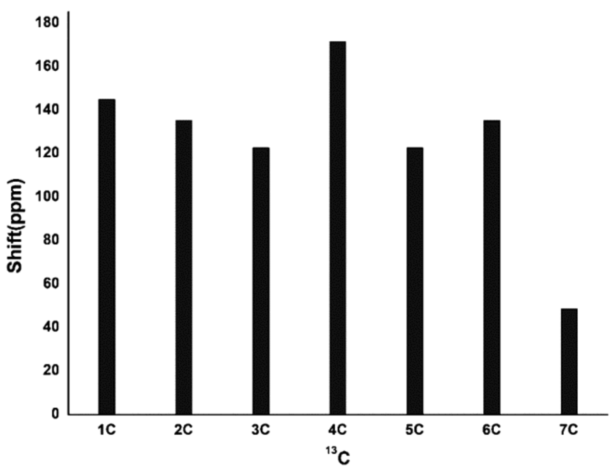

Fig. 7 — ^{13}C NMR of 1-(chloromethyl)-4-fluorobenzene

depend on acceptor and donor charge exchange of the molecule[41]. Particularly, organic systems are designed to have high NLO susceptibilities rising π-electron and fast responding time. The total static dipole moment μ, the average linear polarizability $\overline{\alpha}$, the anisotropy of the polarizability Δα, and the first hyperpolarizability β can be calculated by using the following equations[42]:

$$\overline{\alpha}=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$$

$$\Delta\alpha=\frac{1}{\sqrt{2}}\left[[(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2+6\alpha_{xx}^2]\right]^{1/2}$$

$$\mu=(\mu_x^2+\mu_y^2+\mu_z^2)^{1/2}$$

Table 9 — Calculated dipole moment μ (Debye), polarizability *(α)* and the first hyperpolarizability *(β)* components (a.u.) of 1-(chloromethyl)-4-fluorobenzene

Components	Values	Components	Values
μ_x	0.0985	β_{xxx}	0.5970732
μ_y	0.0008	β_{xxy}	-13.3211062
μ_z	1.8915	β_{xyy}	2.0227119
μ_{total}	1.8941	β_{yyy}	450.7415024
α_{xx}	92.3321118	β_{xxz}	-20.2389858
α_{xy}	0.1419273	β_{xyz}	-0.3652308
α_{yy}	124.281812	β_{yyz}	-21.2177669
α_{xz}	0.3409912	β_{xzz}	0.11446 82
α_{yz}	-1.703112	β_{yzz}	15.4286023
α_{zz}	64.687378	β_{zzz}	-45.2967076
$\overline{\alpha}$	13.881 Å^3	β_{total}	4.098×10^{-30} cm^5 e.s.u.$^{-1}$
Δα	24.941 Å^3		

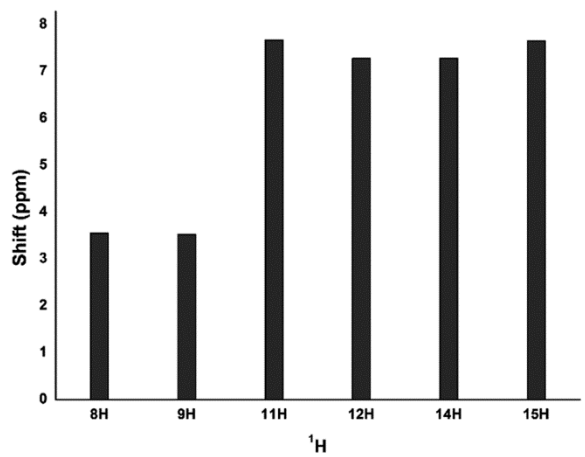

Fig. 8 — ^{1}H NMR of 1-(chloromethyl)-4-fluorobenzene

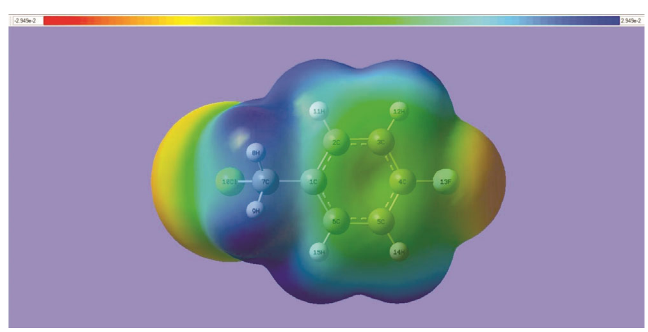

Fig. 9 — MEP of 1-(chloromethyl)-4-fluorobenzene

$$\beta=[(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{xxy}+\beta_{yzz})^2+(\beta_{zzz}+\beta_{xxz}+\beta_{yyz})^2]^{1/2}$$

The components of dipole moment (μ), polarizability *(α)* and the first hyperpolarizability *(β)* of CMFB are given in Table 9. The calculated values of total static dipole moment μ, the average linear polarizability $\overline{\alpha}$, the anisotropy of the polarizability Δα, and the first hyperpolarizability β of CMFB by DFT-B3LYP/6-311++G(d,p) method are 1.8941 D, 13.881 $Å^3$, 24.941 $Å^3$ and 4.098×10^{-30} cm^5 $e.s.u.^{-1}$, respectively, which is good comparable with the reported values of urea. Urea is a typical molecule with NLO properties and commonly used for relative purposes. The values of μ, $\overline{\alpha}$ and β attained bySun *et al*.[43] for urea are 1.373 D, 3.831 $Å^3$ and 0.3729×10^{-30} $e.s.u.^{-1}$, respectively. Therefore, the hyperpolarizability of CMFB is 11 bigger than of Urea and may found to be an interesting object for the development of NLO studies.

Conclusion

The optimized structural parameters and spectroscopic studies of the 1-(chloromethyl)-4-fluorobenzene (CMFB) have been investigated by DFT method. Frequencies of normal modes have been analyzed and agree well with the experimental values. MEP investigation shows the electrophilic and nucleophilic responsive locales of the molecule. The Mulliken distribution and FMOs analysis confirm the chemical activity of the molecule. The electronic spectra of CMFB are performed which reflects the frontier molecular orbitals. The computed chemical shifts of ^{13}C and ^{1}H NMR reflects the structural information of the molecule. The NBO indicates the intra and intermolecular charge exchange of the CMFB. The result of nonlinear optical studies indicates that the CMFB might have potential material in the development of NLO applications.

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