

**ChemTech****International Journal of ChemTech Research**CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.1, pp 362-371, 2015**FT-IR, FT-Raman and DFT Investigation, NBO Analysis, HOMO and LUMO Analysis of 2-Furoyl Chloride****J. Daisy Magdaline¹, T. Chithambarathanu^{2*}****¹Department of Physics, Rani Anna Government College for Women, Tirunelveli, TamilNadu, India****²Department of Physics, S.T. Hindu College, Nagercoil, Tamil Nadu, India**

Abstract: A combined experimental and theoretical study on the molecular structure and the vibrational spectra of 2-furoyl chloride (2FCL) is reported. The FT-IR and FT-Raman experimental spectra are recorded in the region 4000-450 cm^{-1} and 4000-50 cm^{-1} respectively. The molecular geometry and vibrational frequencies are calculated using DFT/ B3LYP with 6-31G** basis set. On the basis of B3LYP calculations, the normal coordinate analysis is performed to assign the vibrational fundamental frequencies according to potential energy distribution. The overestimations of the calculated wave numbers are corrected by the aid of scaled quantum mechanical force field methodology. The computational frequencies are in good agreement with the observed results. The stability of the molecule arising from hyper conjugative interactions and charge delocalization have been analyzed using natural bond orbital analysis (NBO). The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule.

Keywords: 2- furoyl chloride, DFT, IR, Raman, NBO.

Introduction

Furan is a five membered heterocyclic oxygen- containing unsaturated ring compound. Furan shows aromatic properties because the resulting π molecular orbital satisfies the Huckel's rule ($n=1$ in $4n + 2$). The furan nucleus is also found in a large number of biologically active materials. Furan ring is an important constituent in synfuel products that are of major interest in the coal conversion industry [1]. Synthesis of furan co-polymers from renewable vegetable resources have extensive applications in the paint industry [2]. Furan and its derivatives exhibit a wide spectrum of biological activities such as cytotoxic and anti tumour properties, antispasmodic and antifeeding activities [3-5]. Despite the significant role of furan and its derivatives in the field of science and technology, studies on furan derivatives are still scarce.

Until recently the vibrational spectrum of 2-furoyl chloride (2FCL), a furan derivative has been the subject of little research. In organic chemistry, furoyl chloride is used primarily for the introduction of furoyl group into alcohols and phenols and is a vigorous lachrymator which must be handled with care [6]. Spectroscopic studies on 2FCL were reported by a few authors [7-9]. Hagen has performed the electron diffraction study of the molecular structure and conformation of gaseous 2FCL [10]. Recently Ankur Saha et al., has investigated the photo dissociation dynamic of 2FCL at 235nm employing resonance-enhanced multi photon ionization technique and time-of-flight mass- spectrometry [11]. In spite of the above studies on 2FCL, no theoretical density functional calculations or detailed vibrational infrared and Raman analyses have been performed on 2FCL. Hence, in this work, an attempt has been made to interpret the vibrational spectra of 2-furoyl chloride(2FCL) using density functional theory (DFT) at B3LYP level employing 6-31G** basis sets and the observed bands are assigned based on the results of normal coordinate analysis. The redistribution of electron density in various bonding and antibonding orbitals and the stabilization resonance energy (E2) were

systematically calculated by natural bond orbital (NBO) analysis using DFT computation with B3LYP/ 6-31G** basis set. The HOMO and LUMO analysis have been used to elucidate information regarding charge transfer within the molecule.

Experimental Details

The sample of liquid 2FCL with 99% purity was purchased from Sigma –Aldrich chemical Company (USA). The FT-IR spectrum of 2FCL was recorded using Perkin Elmer RXI spectrometer in the region 4000-450 cm^{-1} using TIBr Cell method. The resolution of the spectrum is 4 cm^{-1} . The FT-Raman spectrum of 2FCL was recorded using 1064nm line of Nd:YAG laser as exciting wavelength in the region 4000-50 cm^{-1} on a Bruker RFS 27 model FT-Raman spectrometer having a spectral resolution 2 cm^{-1} .

Computational Details

The quantum chemical computation of 2FCL was performed using Gaussian'03W software package [12] at Becke-3-Lee-Yang- Parr (B3LYP) level [13,14] with standard 6-31G** basis set. The geometries were fully optimized without any constraint with the help of analytical procedure implemented with Gaussian'03 program. Multiple scaling of force field has been performed by Scaled Quantum Mechanical (SQM) procedure [15,16] in the natural internal coordinate representation [17] to offset the systematic errors caused by the basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. Transformations of the force field and the subsequent normal coordinate analysis including least square refinement of scale factors, calculation of potential energy distribution (PED) and the prediction of IR intensities were done using MOLVIB program version 7.0 written by Sundius [18, 19]. For plots of simulated IR spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm^{-1} . By combining GAUSSVIEW [20] program with symmetry considerations, vibration frequency assignments were made with high degree of accuracy. However, the defined coordinates form complete set and matches quite well with the motions observed using the program. Natural Bond Orbital (NBO) [21] analysis was performed by the NBO 3.1 program, included in Gaussian 03 package of programs to understand the intramolecular delocalization or hyper conjugation.

Results and Discussion

Molecular Geometry

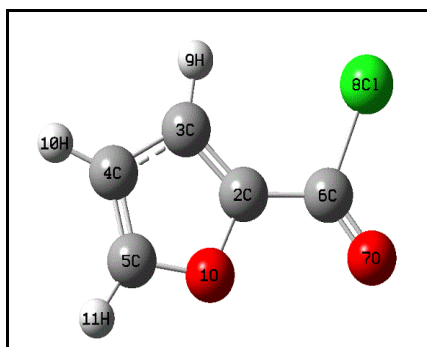


Fig.1. The optimized molecular structure of 2FCL calculated at B3LYP/6-31G**

The optimized molecular structure of 2FCL is shown in Fig 1. The global minimum energy obtained by the DFT structure optimization is found to be -802.9632680 hartree. The optimized values of bond length and bond angle are shown in Table 1. 2FCL molecule has an acid halide group attached to the second position of the furan ring. In COCl the carbonyl group is attached to a highly electronegative chlorine atom and the high electro negativity of chlorine makes it hard for the oxygen in C=O to draw electrons and thereby weakens the resonance. Hence the inductive effect predominates resulting in an increase in the C=O force constant and a decrease in the corresponding bond length [22]. The bond length C6-O7 (1.194 Å) is shortened by 0.02Å from the standard C=O bond length (1.220 Å) [23]. Due to the inductive effect (-I) of the electron withdrawing substituent, the furan ring appears a little distorted and the angles are slightly deviated from the pentagonal structure. When compared with the bond angles of the furan[24] molecule (O1-C2-C3=110.20 °, C3-C4-C5=106.60 °, O1-C5-C4=110.20 °), in 2FCL the valence angles O1-C2-C3 (109.84 °) and C3-C4-C5 (105.94°) show a shrink by ~1° and there is a corresponding widening of 1° in the bond angle O1-C5-C4 (111.14°).

Table -1: Optimized geometrical parameters of 2FCL obtained by B3LYP/6-31G density functional calculations.**

Bond Length / Å		Bond Angle / °	
O1-C2	1.372	C2-O1- C5	106.723
O1-C5	1.349	O1-C2-C3	109.839
C2-C3	1.375	O1-C2-C6	115.646
C2-C6	1.450	C3-C2-C6	134.515
C3-C4	1.421	C2-C3-C4	106.358
C3-H9	1.079	C2-C3-H9	125.830
C4-C5	1.369	C4-C3-H9	125.812
C4-H10	1.080	C3-C4-C5	105.940
C6-O7	1.194	C3-C4-H10	127.468
C6-CL8	1.831	C5-C4-H10	126.592
		O1-C5-C4	111.140
		O1-C5-H11	115.800
		C4-C5-H11	133.060
		C2-C6-O7	125.339
		C2-C6-CL8	111.928
		O7-C6- CL8	120.733

NBO analysis

The NBO calculations give information about interactions between both filled and virtual orbital spaces which is a measure of intermolecular delocalization or hyper conjugation [25]. NBO analysis has been performed on 2FCL molecule by DFT/B3LYP/6-31G** level in order to elucidate intramolecular charge transfer (ICT), rehybridization and delocalization of electron density within molecule. In NBO analysis, the donor- acceptor (bond-antibond) interactions are taken into consideration by examining the possible interactions between ‘filled’ (donor) Lewis-type NBOs and ‘empty’ (acceptor) non-Lewis NBOs and then estimating their energies by second-order perturbation theory.

For each donor NBO (i) and acceptor NBO (j), the stabilization energy associated with the i→j is estimated as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{E_i - E_j}$$

where q_i is the i^{th} donor orbital occupancy, E_j , E_i are diagonal element (orbital energies) and $F(i,j)$ is the off diagonal NBO Fock matrix element. The stabilizing orbital interaction is high when the energy difference between the interacting orbitals is low and therefore the strongest stabilizing interaction will take place between the most effective donors and acceptors [21]. The delocalization effects can be identified from the presence of off-diagonal elements (overlap integral) of the Fock matrix in NBO basis. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital, hence the new orbitals are more stable than pure Lewis orbitals. The strength of the delocalized interactions $E(2)$ is estimated by second order perturbation theory. The larger the $E(2)$ value, more intense is the interaction between the electron donors and acceptors and greater is the extent of conjugation of the whole system. The results of second order perturbation theory analysis of Fock matrix at B3LYP/6-31G** level of theory are presented in Table 2. The intramolecular interactions are formed by the orbital overlap between bonding C-C, C=C, C-O, C-H and C-Cl to the antibonding orbitals, which results in intramolecular transfer (ICT) causing stabilization of the system. The interaction energy related to the resonance in 2FCL molecule are electron withdrawing to the ring through $\pi^*(\text{C2-C3}, \text{C4-C5})$ bond from $n_2(\text{O1})$ which leads to moderate stabilization energy of approximately 26 and 31 kcal/mol. In 2FCL, the stabilization energy related to $n \rightarrow \sigma^*$ interactions between the lone pair oxygen atom (O7) to the antibonding $\sigma^*(\text{C2-C6}, \text{C2-Cl8})$ are of 16.61 and 54.86 kcal/mol respectively. This interaction is responsible for the decrease of the lone pair occupancy of approximately 1.8e of O7 in 2FCL. The intra molecular hyper conjugative interaction of the $\pi(\text{C2-C3})$ distribute to the $\pi^*(\text{C6-O7})$ have a stabilization of 25.73 kcal/mol. This enhanced $\pi^*(\text{C6-O7})$ NBO further conjugates with $\pi^*(\text{C2-C3})$ of the furan ring leads to a stronger delocalization of 112.41 kcal/mol. This large energy indicates the hyperconjugation of the carbonyl group with the aromatic ring. The stronger stabilization denotes larger

delocalization. The lone pair donor orbital n_3 (C18) $\rightarrow \pi^*$ (C6-O7) between the chloride lone pair orbital and the antiperiplanar orbital (C6-O7) gives a stabilization of 16.88 kcal/mol.

Table -2: Second order perturbation theory analysis of Fock matrix in NBO basis for 2 FCL

Donor (i)	ED (i) (e)	Acceptor (j)	ED (j) (e)	E (2) ^a (Kcalmol ⁻¹)	E(j)-E(i) ^b (a.u)	F(i,j) ^c (a.u)
σ (O ₁ -C ₂)	1.98758	σ^* (C ₃ -H ₉)	0.01162	1.97	1.39	0.048
		σ^* (C ₅ -H ₁₁)	0.01402	2.26	1.38	0.050
		σ^* (C ₆ -Cl ₈)	0.19657	2.03	0.98	0.042
σ (O ₁ -C ₅)	1.98908	σ^* (C ₂ -C ₆)	0.07163	3.30	1.37	0.061
		σ^* (C ₄ -H ₁₀)	0.01192	2.26	1.40	0.050
σ (C ₂ -C ₃)	1.98244	σ^* (C ₂ -C ₆)	0.07163	3.57	1.19	0.059
		σ^* (C ₃ -C ₄)	0.01096	1.55	1.25	0.039
		σ^* (C ₃ -H ₉)	0.01162	1.54	1.22	0.039
		σ^* (C ₄ -H ₁₀)	0.01192	3.57	1.21	0.059
		σ^* (C ₆ -O ₇)	0.01771	1.69	1.34	0.043
π (C ₂ -C ₃)	1.80454	π^* (C ₄ -C ₅)	0.26723	14.76	0.29	0.059
		π^* (C ₆ -O ₇)	0.27728	25.73	0.28	0.076
σ (C ₃ -C ₄)	1.97093	σ^* (C ₂ -C ₆)	0.07163	6.89	1.13	0.080
		σ^* (C ₅ -H ₁₁)	0.01402	4.75	1.15	0.066
σ (C ₂ -C ₆)	1.97828	σ^* (O ₁ -C ₅)	1.98908	1.91	1.11	0.041
		σ^* (C ₂ -C ₃)	0.01968	3.90	1.31	0.064
σ (C ₄ -C ₅)	1.98800	σ^* (C ₃ -H ₉)	0.01162	3.70	1.21	0.060
π (C ₄ -C ₅)	1.82932	π^* (C ₂ -C ₃)	0.30902	18.96	0.30	0.30
		π^* (C ₄ -C ₅)	0.26723	1.19	0.29	0.29
σ (C ₆ -O ₇)	1.99459	σ^* (C ₂ -C ₃)	0.02778	1.17	1.71	0.040
		σ^* (C ₂ -C ₆)	0.07163	1.52	1.59	0.045
σ (C ₆ -Cl ₈)	1.98638	σ^* (O ₁ -C ₂)	0.07163	3.81	1.16	0.059
n1(O ₁)	1.97163	σ^* (C ₂ -C ₃)	0.01968	3.59	1.17	0.058
		σ^* (C ₄ -C ₅)	0.01442	26.06	0.36	0.086
n2(O ₁)	1.68217	π^* (C ₂ -C ₃)	0.30902	30.78	0.35	0.094
		π^* (C ₄ -C ₅)	0.26723	30.21	0.35	0.093
n1(O ₇)	1.97809	σ^* (C ₂ -C ₆)	0.07163	0.07163	3.60	1.15
		σ^* (C ₆ -Cl ₈)	0.19657	1.43	0.77	0.031
n2(O ₇)	1.83759	σ^* (C ₂ -C ₆)	0.07163	16.61	0.73	0.103
		σ^* (C ₆ -Cl ₈)	0.19657	54.86	0.35	0.126
n2(Cl ₈)	1.96854	σ^* (C ₂ -C ₆)	0.07163	2.51	0.76	0.039
		σ^* (C ₆ -O ₇)	0.01771	5.18	0.92	0.062
		σ^* (O ₁ -C ₂)	0.03493	1.03	0.64	0.023
n3(Cl ₈)	1.91203	π^* (C ₆ -O ₇)	0.24034	16.58	0.30	0.066
π (C ₆ -O ₇)	1.98212	π^* (C ₂ -C ₃)	0.30902	5.20	0.42	0.045
π^* (C ₆ -O ₇)	0.27728	π^* (C ₂ -C ₃)	0.30902	112.41	0.02	0.079
σ^* (C ₆ -Cl ₈)	0.19657	σ^* (O ₁ -C ₂)	0.03493	1.94	0.37	0.034

^a E(2) means energy of hyper conjugative 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.

Table -3: Natural atomic charges of FCL calculated at B3LYP/6-31G level of theory**

Atoms	Atomic charges /e
O ₁	-0.42125
C ₂	0.15180
C ₃	-0.23709
C ₄	-0.33839
C ₅	0.15040
C ₆	0.50332

O ₇	-0.46889
Cl ₈	-0.11453
H ₉	0.27319
H ₁₀	0.26215
H ₁₁	0.23928

The atomic charges of 2FCl calculated by NBO analysis using B3LYP/6-31G** method are presented in Table-3. Among the ring carbon atoms C3 and C2 have positive charge while C3 and C2 have negative charge. The high positive charge on C2 is due to the attachment of the highly electronegative chlorine atom and also due to the polar nature of the C=O group.

Vibrational analysis

Table 4: Definition of local symmetry coordinates for 2FCL.

Sl.No	Symmetry Coordinates ^a	Description ^b
In-Plane Vibrations		
1	$S_1 = r_{54}$	ν_{C5C4}
2	$S_2 = r_{32}$	ν_{C3C2}
3	$S_3 = r_{43}$	ν_{C4C3}
4	$S_4 = r_{26}$	ν_{C2C6}
5	$S_5 = r_{51}$	ν_{C5O1}
6	$S_6 = r_{12}$	ν_{O1C2}
7	$S_7 = r_{67}$	ν_{C6O7}
8	$S_8 = r_{68}$	ν_{C6Cl8}
9	$S_9 = r_{511}$	ν_{C5H11}
10	$S_{10} = r_{410}$	ν_{C4H10}
11	$S_{11} = r_{39}$	ν_{C3H9}
12	$S_{12} = \beta_{239} - \beta_{439}$	β_{C3H9}
13	$S_{13} = \beta_{3410} - \beta_{5410}$	β_{C4H10}
14	$S_{14} = \beta_{4511} - \beta_{1511}$	β_{C5H11}
15	$S_{15} = \beta_{126} - \beta_{326}$	β_{C2C6}
16	$S_{16} = \beta_{762} - \beta_{862}$	β_{COCl}
17	$S_{17} = \beta_{512} + a(\beta_{123} + \beta_{451}) + b(\beta_{234} + \beta_{345})$	$\beta_{ring 1}$
18	$S_{18} = (a-b)(\beta_{123} - \beta_{345}) + (1-a)(\beta_{234} - \beta_{451})$	$\beta_{ring 2}$
19	$S_{19} = 2\beta_{867} - \beta_{762} - \beta_{862}$	δ_{COCl}
Out-of-Plane Vibration		
20	$S_{20} = \gamma_{11514}$	γ_{C5H11}
21	$S_{21} = \gamma_{9324}$	γ_{C3H9}
22	$S_{22} = \gamma_{10435}$	γ_{C4H10}
23	$S_{23} = \gamma_{6213}$	γ_{C6C2}
24	$S_{24} = \gamma_{2687}$	γ_{COCl}
25	$S_{25} = b(\gamma_{5123} + \gamma_{2345}) + a(\gamma_{1234} + \gamma_{3451}) + \gamma_{4512}$	$\gamma_{ring 1}$
26	$S_{26} = (a-b)(\gamma_{3451} + \gamma_{1234}) + (1-a)(\gamma_{4512} + \gamma_{5123})$	$\gamma_{ring 2}$
27	$S_{27} = \tau_{8621} + \tau_{7621} + \tau_{8623} + \tau_{7623}$	τ_{COCl}

For numbering of atoms refer Fig 1

^aDefinitions are made interms of the valence coordinates: r_{ij} is the bond length between atoms i and j ; β_{ijk} is the valence angle between i, j, k where j is the central atom; γ_{ijkl} is the out-of-plane angle between the $i-j$ bond and the plane defined by the j, k, l atoms; τ_{ijkl} is the torsion (dihedral) angle between the plane defined by i, j, k and j, k, l atoms

^b(ν)stretching; (β) in-plane-bending; (γ)out-of-plane-bending (τ)torsion.

2FCL has 11 atoms with 27 normal modes of vibrations. All vibrations are active both in Raman and infrared spectrum. The vibrational band assignments have been made by means of normal coordinate analysis (NCA). Non-redundant set of local symmetry coordinates constructed by suitable linear combinations of internal coordinates chosen according to the recommendations of Pulay et al., [17] are summarized in Table 4. In order to reproduce the observed frequencies, refinement of scale factors are applied and optimized via least

square refinement algorithm which resulted in a weighted RMS deviation of 10 cm^{-1} between the experimental and scaled frequencies. Root mean square value is obtained in this study using the following expression

$$\text{RMS} = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{\text{cal}} - v_i^{\text{exp}})^2}$$

Table -5: Assignments of fundamental vibrations of 2 FCL by normal coordinate analysis by SQM force field calculations using selectively scaled B3LYP/6-31G**

Observed wavenumbers (cm^{-1})		B3LYP/631G** Calculated Wavenumbers (cm^{-1})	IR intensity	Raman Activity	Characterisation of normal modes with PED(%) ^a
IR	Raman	Scaled			
	3153	3155	0.58	166.37	$\nu\text{CH}(97)$
-	-	3148	0.88	23.61	$\nu\text{CH}(96)$
-	3141	3131	0.79	90.65	$\nu\text{CH}(97)$
1749	1741	1755	381.82	134.92	$\nu\text{C}=\text{O}$ (80), $\nu\text{C}-\text{C}_{\text{ar}}$ (10)
1557		1564	10.95	3.50	$\nu\text{C}=\text{C}$ (48), $\beta\text{ring 2}$ (43)
1461	1461	1455	89.78	135.81	$\nu\text{C}=\text{C}(76)$, $\beta\text{CH}(10)$
1387	1387	1399	37.51	43.14	$\beta\text{CH}(31)$, $\nu\text{C}-\text{C}$ (26), $\nu\text{C}-\text{O}$ (12)
1256	1255	1238	67.41	6.8	$\nu\text{C}-\text{C}$ (27), $\beta\text{CH}(26)$, $\nu\text{C}-\text{C}_{\text{ar}}$ (21), $\nu\text{C}-\text{O}$ (18)
1233	1232	1221	16.47	4.87	βCH (44), $\nu\text{C}-\text{O}$ (27), $\nu\text{C}=\text{C}$ (12)
1160	1163	1172	6.45	4.50	$\nu\text{C}-\text{O}(48)$, $\nu\text{C}=\text{C}(22)$, $\beta\text{CH}(17)$, $\beta\text{ring2}(11)$
1080	1082	1086	19.13	11.41	$\nu\text{C}-\text{O}(30)$, $\nu\text{C}=\text{C}(24)$, $\beta\text{ring2}(21)$, $\beta\text{CH}(18)$
1026	1026	1023	53.63	3.30	$\beta\text{CH}(58)$, $\nu\text{C}-\text{C}$ (26)
947	946	948	56.99	5.23	$\beta\text{ring2}(55)$, $\nu\text{C}-\text{O}(24)$
-	-	892	17.43	7.81	$\beta\text{ring1}(57)$, $\beta\text{ring 2}(20)$, $\nu\text{C}=\text{C}$ (19)
886	887	885	1.07	1.71	γCH (84), τ ring 1(15)
820	823	830	2.81	2.81	γCH (84)
-	-	795	47.21	1.11	γCH (84)
770	-	762	307.41	6.59	$\nu\text{C}-\text{Cl}(36)$, βCOCl (24), $\beta \text{C}_{\text{ar}}\text{OCl}$ (12),
695	-	699	1.41	1.06	τ ring 2(35), $\gamma\text{C}-\text{COCl}(31)$, $\gamma\text{CC}_{\text{ar}}$ (28)
590		605	23.11	1.89	τ ring 2(51), τ ring 1(20), $\gamma\text{C}-\text{COCl}(31)$
578		576	0.12	0.12	ring 1(τ 73), $\gamma\text{C}-\text{COCl}(12)$
	532	526	17.1	0.8	$\beta \text{C}_{\text{ar}}\text{OCl}$ (21), $\nu\text{C}-\text{Cl}(18)$, $\beta \text{C}_{\text{ar}}\text{C}(16)$, $\nu\text{C}=\text{C}(16)$, $\nu\text{C}-\text{C}_{\text{ar}}$ (13),
-	428	390	6.63	6.67	$\nu\text{C}-\text{Cl}(54)$, βCOCl (22)
	334	313	9.52	3.70	βCOCl (22), $\beta \text{C}_{\text{ar}}\text{C}(16)$
	187	174	0.00	2.52	$\gamma\text{CC}_{\text{ar}}$ (79), $\gamma\text{C}-\text{COCl}$ (11)
	154	164	0.56	1.08	$\beta \text{C}_{\text{ar}}\text{OCl}$ (56), $\beta \text{C}_{\text{ar}}\text{C}(37)$
-	-	78	0.01	0.72	$\tau\text{CCL}(91)$

^a PED values greater than 10% are given

The observed and calculated frequencies, IR intensity, Raman activity and potential energy distribution (PED) are presented in Table 5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra are shown in Figs. 2 and 3 respectively.

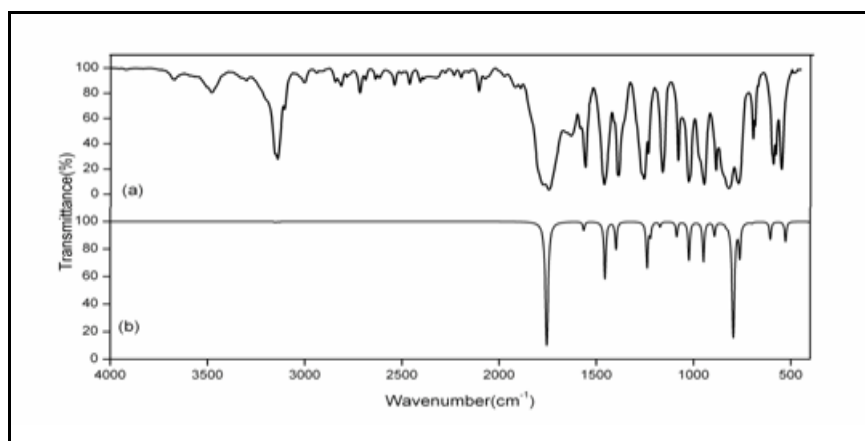


Fig.2: FT-IR spectra of 2FCL (a) observed (b) simulated

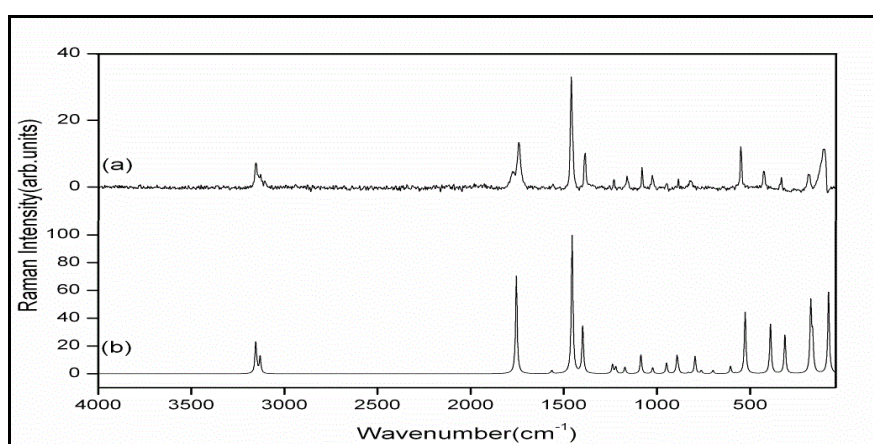


Fig.3 FT-Raman spectra of 2FCL (a) observed (b) simulated

COCl vibrations

Almost all carbonyl compounds have a very intense and narrow peak in the range $1800\text{-}1600\text{ cm}^{-1}$. The position of the C=O stretching is determined by the physical state, electronic and mass effects of neighboring substituents, conjugation, hydrogen bonding and ring strain. Generally acid halides absorb at much higher frequencies ($1870\text{-}1770\text{ cm}^{-1}$) than ketones or acids because of the electrical effects of the halogen atom. The direct attachment of halogen to the carbonyl group results in a shift of C=O frequency to a higher value because the high electro negativity of chlorine makes it hard for the oxygen to draw electrons. Consequently, inductive effect predominates the resonance effect causing an increase in the C=O force constant and its stretching frequency. In strained rings (ring size decreases) also, C=O stretching frequency is shifted upwards, they absorb near 1780 cm^{-1} . The C=O stretching frequency is found in the range $1715\text{-}1706\text{ cm}^{-1}$ in five membered ring ketones and $1686\text{-}1680\text{ cm}^{-1}$ in six and seven membered ring lactones. Conjugated acid halides absorb at a slightly lower frequency because the double bond character of C=C and C=O bonds decrease due to conjugation. The factors like the inductive effect and ring strain tend to increase the carbonyl frequency of 2FCL, whereas conjugation of the C=O bond with C=C lowers the value of the carbonyl stretching wave numbers [22, 27, 28]. For the title compound, a very strong band observed in the FT-IR and FT-Raman spectrum at $1749\text{ and }1749\text{ cm}^{-1}$ are assigned to C=O stretching vibration. The computed wave number for this mode of vibration at 1755 cm^{-1} shows good agreement with the experimental data.

The C-Cl stretching vibrations give generally strong bands in the region $730\text{-}580\text{ cm}^{-1}$ [29]. Mooney [30] assigned vibrations of the C-X group (X= Cl, Br, I) in the frequency range $1127\text{-}480\text{ cm}^{-1}$. In the present investigation the medium strong band identified in IR spectrum at 770 cm^{-1} is attributed to C-Cl stretching vibration and is in good agreement with theoretically computed value at 762 cm^{-1} . The deformations bands of C-O-Cl are also identified (Table 5). The C=O in-plane and out-of-plane bending vibrations are reported to appear in the region around $700\text{ and }540\text{ cm}^{-1}$ [28, 31, 32]. Govindarajan et al., assigned the wave numbers of the C-Cl in-plane and out-of-plane bending vibrations at $405\text{ and }195\text{ cm}^{-1}$ [33,34]. The C-O-Cl deformation

bands for 2FCL are assigned in the region below 800 cm^{-1} . All these modes are not pure but contain significant contribution from other modes.

Ring vibrations

Hetero aromatics exhibit C-H stretching bands in the region $3100\text{-}3000\text{ cm}^{-1}$, but in five membered ring heterocycles the C-H stretching frequencies are observed at little higher range. These bands are not strong in the infra red spectrum and the intensity is further reduced when an oxygen atom is present [35, 36]. In 2FCL the FT-Raman bands observed at 3153 and 3141 cm^{-1} are assigned to C-H stretching vibration. The C-H in-plane and out-of-plane bending vibration in aromatic heterocyclic compounds are characterized by several medium to strong intensity bands in the region $1300\text{-}1000$ and $1000\text{-}700\text{ cm}^{-1}$ respectively [28, 37,38]. The observed IR and Raman lines in the range $1387\text{-}1026\text{ cm}^{-1}$ are due to C-H in-plane bending of 2FCL. The corresponding calculated modes are dominated by C-H in-plane bending vibrations and are coupled mostly with ring stretching vibrations. In the present study the C-H out-of-plane bending cause strong to medium intensity bands at 886 and 820 cm^{-1} in the FT-Raman spectrum. The same vibrations appear in the FT-Raman at 887 and 823 cm^{-1} with weak intensity. An analysis by PED calculations show that the CH out-of-plane bending vibrations are pure modes with a contribution of 84 %.

The aromatic ring stretching vibrations occur in the region $1600\text{-}1300\text{ cm}^{-1}$, whereas five membered rings show three bands around 1590 , 1480 and 1400 cm^{-1} . The band pattern and the relative intensities depend on the substitution pattern and the nature of substituents. The bands are quite intense if the substituents are electron withdrawing in nature [22,27]. The carbon- carbon stretching vibrations of 2FCL are found at 1557 , 1461 and 1256 cm^{-1} in the IR spectrum as very strong bands and in the Raman spectrum at 1461 and 1256 cm^{-1} . Klots et al., reported C-O stretching vibration for the furan molecule at 1181 and 1067 cm^{-1} [39]. Hence the C-O stretching mode of 2FCL are identified as strong bands at $1160,1080\text{ cm}^{-1}$ in FT-IR spectrum and at $1163, 1082\text{ cm}^{-1}$ in the FT- Raman spectrum. The peaks observed at $1082, 947, 946\text{ cm}^{-1}$ are due to ring in-plane vibrations and the bands at $695, 590$ and 578 cm^{-1} are due to ring out-of-plane bending vibrations. The theoretically computed ring in-plane and out-of-plane bending vibrational modes have been found to be consistent with the spectral data.

HOMO-LUMO energy gap

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in chemical stability [40]. Molecular orbitals can provide insight into the nature of reactivity and some of the structural and physical properties of molecules. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor, represents the ability to obtain an electron. The electronic transition absorption corresponds to the transition from ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital [41, 42]. The HOMO is located over the C=C bond and LUMO is delocalized over the C-C bond. HOMO \rightarrow LUMO transition implies an electron density transfer from the C=C bond of the heterocyclic ring. The energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer [42]. The frontier molecular orbitals are mainly composed of p atomic orbital, so electronic transitions from the HOMO to the LUMO are mainly derived from the electronic transition of $\pi \rightarrow \pi^*$. The energy gap measures the kinetic stability of the molecules. A molecule with a small frontier orbital gap is more polarizable and it implies high chemical reactivity and low kinetic stability. The energies of HOMO, LUMO, LUMO+1, HOMO-1 and their orbital energy gaps are calculated using B3LYP/6-31G** method and their pictorial representation of the frontier molecular orbitals are shown in Fig. 4 for 2FCL. The green and red solid region represents the molecular orbitals with completely opposite phases [43, 44].

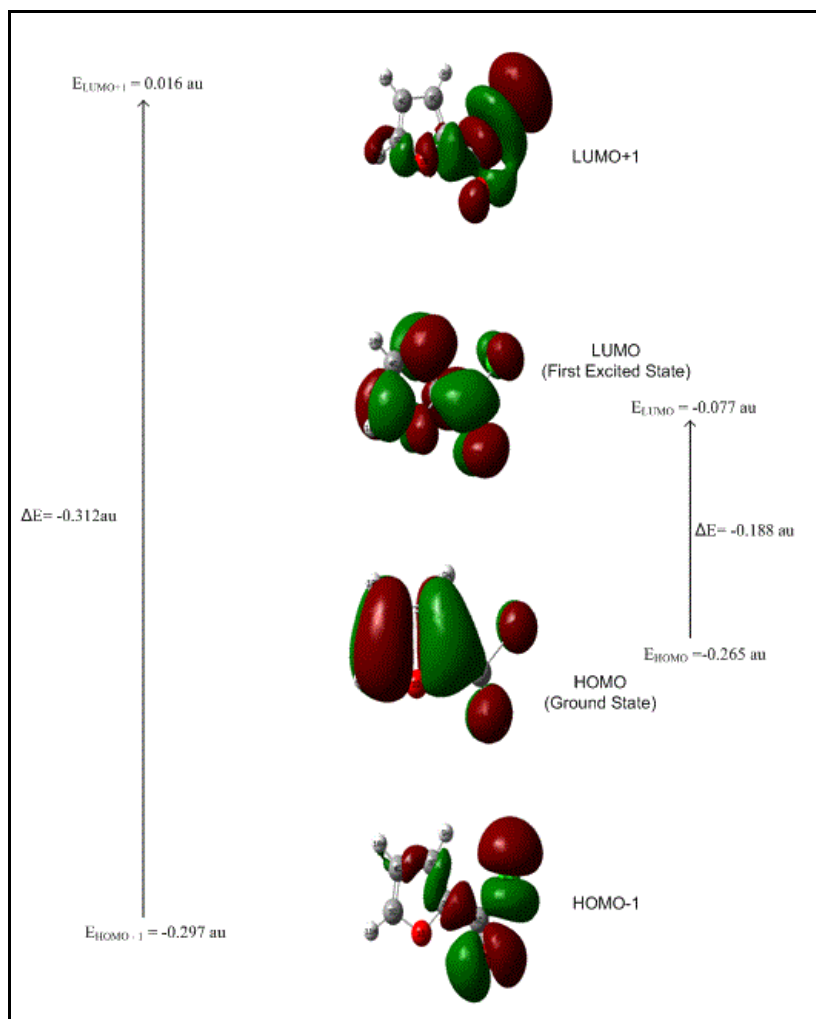


Fig. 4. The molecular orbitals and energies for the HOMO-1, HOMO, LUMO and LUMO-1 of 2FCL

Conclusions

The FT-IR and FT-Raman spectra have been recorded and the vibrational assignment has been presented for the title compound 2FCL. The ground state geometry, vibrational wave numbers and NBO analysis are determined and analyzed using the B3LYP with 6-31G** basis set. The geometrical structure shows a little distortion due to the substitution of the acid halide group and a shortening of C=O bond indicates the influence of the highly electro negative chlorine atom on the carbonyl bond. The dependence of C=O stretching mode on factors like inductive effect, ring strain and conjugation have been studied. HOMO-LUMO studies are presented in this study for better understanding of intra molecular charge transfer within the molecule.

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