

# Nonlinear optical investigation of (E)-1-(4-fluorobenzylidene)urea using theoretical calculations

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## Abstract

The FT-IR and FT-Raman spectra of (E)-1-(4-fluorobenzylidene)urea (4FBU) was recorded and analyzed. The optimized geometrical parameters were calculated. The complete vibrationally assignments were performed based on PED analysis with the help of SQM method. NBO analysis was carried out to explore the various conjugative/hyperconjugative interactions within the molecule and their second-order stabilization energy. The HOMO and LUMO energy gap was studied. All theoretical calculations were performed based on B3LYP/6-31G (d,p) level of theory. The first order hyperpolarizability ( $\beta_0$ ) and related properties ( $\beta$ ,  $\alpha_0$ ,  $\Delta\alpha$ ) of 4FBU were calculated. Besides, FMOs, MEP, Mulliken atomic charges and various thermodynamic parameters such as entropy, heat capacity and enthalpy were also calculated.

**Keywords:** DFT; FT-IR; FT-Raman; NLO; NBO; FMO.

## 1. Introduction

The >C=NH-group is present in Schiff base organic molecules are of fundamental importance. They have got extensive application in biological and industrial fields. Schiff bases with a potential pharmaceutical use were synthesized (Charles, 1955; Compagnic Franosise Dereaffinage, 1956). Schiff bases have been reported for their biologic properties, such as anti-bacterial, anti-fungal, anti-inflammatory, analgesic, anti-convulsant, anti-tubercular, anti-cancer, anti-oxidant and anti-helminthic activities (Mounika et al. 2010; Venkatesh, 2011; Yıldız et al. 2004; Ünver et al. 2005; Yıldız et al. 2005; Yıldız, and Dülger, 2005; Yıldız et al. 2007; Kiraz et al. 2009; Sondhi, et al. 2006). Schiff base metal complexes have applications in the areas from material science to biological sciences. They have been widely studied because they have anticancer and herbicidal applications (Cozzi, 2004; Chandra and Sangeetika, 2004).

Numerous studies on Schiff base hydrazones of pyridoxal phosphate, and its analogous have been reported to understanding the mechanism of action for vitamin B6 containing free ligand. Furthermore, metal complexes of hydrazones proved to have potential applications as catalysts (Whitall et al., 2006), luminescent probes (Spek, 1998), and molecular sensors (Pérez-Rebolledo et al., 2006). Moreover, it has been recently observed that hydrazone's iron chelators in vivo and in vitro, and may be of potential value for the treatment of iron overload (Buss et al. 2002). Kaya & Kamaci, 2012, synthesized novel low band gap and thermally stable poly (azomethine-urethane)s to investigate aliphatic and aromatic group effects on some physical properties such as thermal stability, optical and electrochemical properties.

Dincalpa et al. 2010 synthesized a series of new azo dyes containing salicylal dimine with different electron-withdrawing groups. They studied the absorption and emission spectra of the synthesized salicylal dimine-based azo ligands in five solvents of different polarities. The optical and electrochemical properties were studied, and photovoltaic performance of DSSCs based on these new type salicylal dimine compounds was also investigated. In our study, focus of the above factors, we have chosen a simple organic molecule (E)-1-(4-fluorobenzylidene) urea for the present investigation. The synthesized molecule is confirmed structurally by the spectral studies. Further the molecule is subjected to the theoretical investigation to study the nonlinear property of the synthesized molecule. In addition to that, the light harvesting efficiency has been calculated to find out its sensitizing property on the application to DSSC. Moreover, the intra-molecular studies are made over to interpret the properties of the molecule.

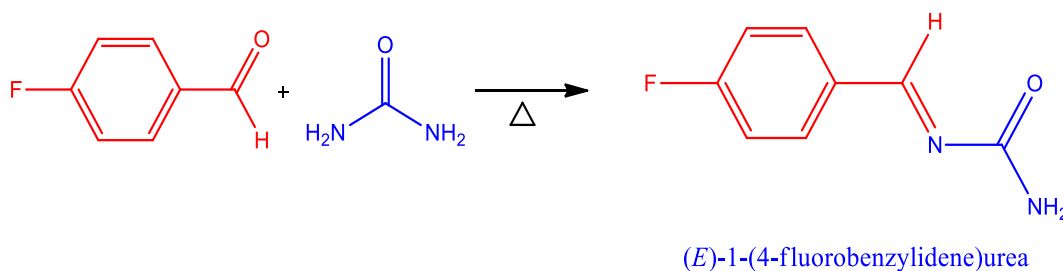
## 2. Experimental details

### 2.1. Synthesis of (E)-1-(4-fluorobenzylidene) urea

Equimolar amount of 4-fluorobenzaldehyde and urea were dissolved in 30 ml of absolute ethanol. The mixture was shaken to make homogenous solution. Few drops of catalyst acetic acid were added to increase the rate of reaction. The content was refluxed at 90°C for 3 hours. The completion of the reaction was monitored by thin layer chromatography. After the reaction was completed, the content was cooled the mixture was poured into water. The solid product obtained was filtered and purified using absolute ethanol.

Melting point = 174°C

Yield = 78%



## 2.2. Spectral measurements

### 2.2.1. FT-IR spectrum

The FT-IR spectrum of the synthesized 4FBU was measured in the 4000–400  $\text{cm}^{-1}$  region at the spectral resolution of 4  $\text{cm}^{-1}$  using on SHIMADZU FT-IR affinity Spectrophotometer (KBr pellet technique) in Faculty of Marine Biology, Annamalai University, Parangipettai.

### 2.2.2. FT-Raman spectrum

The FT-Raman spectrum was recorded on BRUKER: RFS27 spectrometer operating at laser 100mW in the spectral range of 4000–50  $\text{cm}^{-1}$ . FT-Raman spectral measurements were carried out from Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (IIT), Chennai.

### 2.2.3. NMR spectra

NMR spectral studies were carried out using Bruker 400 MHz spectrometer, using TMS as an internal standard and DMSO- $d_6$  as solvent and recorded at Annamalai University, Annamalainagar, Chidambaram. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectrum were shown in Fig. 9.

## 3. Computational details

To prove complete information regarding to the structural characteristics and the fundamental vibrational modes of 4FBU

has been carried out using DFT method with B3LYP/6-31G (d,p) basis set. The calculations were performed using the Gaussian 03W program package (Frisch et al. 2004; Schlegel, 1982) with default convergence criteria without any constraint on the geometry. The Vibrational modes were assigned on the basis of TED analysis using VEDA4 program package (Jamróz et al. 2006). The Raman activity was calculated by using Gaussian 03W package and the activity was transformed into Raman intensity using Raint program (Michalska, 2003) by the expression:

$$I_i = 10^{-12} \times (v_0 - v_i)^4 \times \frac{1}{v_i} \times RA_i \quad (1)$$

Where  $I_i$  is the Raman intensity,  $RA_i$  is the Raman scattering activities,  $v_i$  is the wavenumber of the normal modes and  $v_0$  denotes the wavenumber of the excitation laser (Michalska & Wysockiński, 2005).

## 4. Results and discussion

### 4.1. Molecular geometry

The molecular structure along with the numbering of atoms of (E)-1-(4-fluorobenzylidene)urea is obtained from Gaussian programs and is shown in Fig. 1. The bond parameters such as bond lengths, bond angles and dihedral angles values are calculated at DFT/B3LYP/6-31G(d,p) level of basis set and are listed in Table 1.

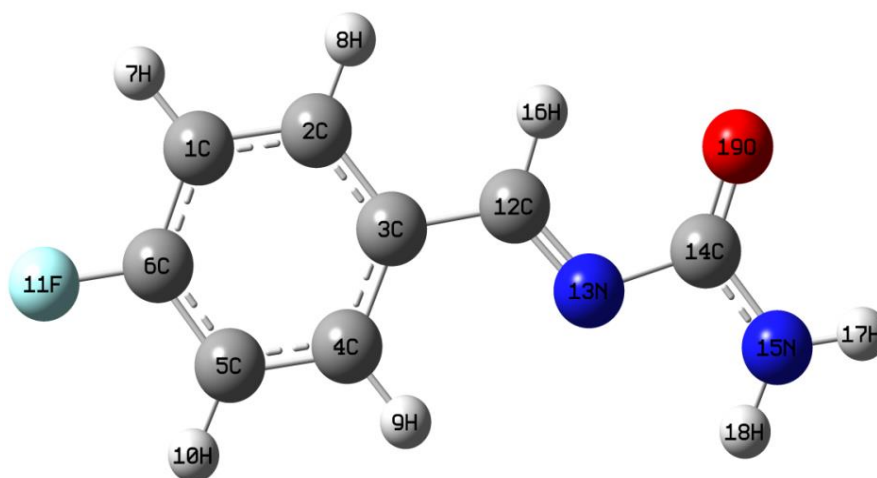


Fig. 1: The Optimized Molecular Structure of 4FBU.

**Table 1:** The Bond Parameters of 4FBU

| Bond Lengths (Å) | DFT    | Bond Angles (°) | DFT      | Dihedral Angles (°) | DFT       |
|------------------|--------|-----------------|----------|---------------------|-----------|
| R(1,2)           | 1.3922 | A(2,1,6)        | 118.3148 | D(6,1,2,3)          | 0.0001    |
| R(1,6)           | 1.3905 | A(2,1,7)        | 122.0041 | D(6,1,2,8)          | 180       |
| R(1,7)           | 1.0841 | A(6,1,7)        | 119.6811 | D(7,1,2,3)          | 180.0001  |
| R(2,3)           | 1.4045 | A(1,2,3)        | 120.9037 | D(7,1,2,8)          | 0         |
| R(2,8)           | 1.0865 | A(1,2,8)        | 119.6746 | D(2,1,6,5)          | 0         |
| R(3,4)           | 1.4074 | A(3,2,8)        | 119.4217 | D(2,1,6,11)         | 180.0001  |
| R(3,12)          | 1.4618 | A(2,3,4)        | 119.1403 | D(7,1,6,5)          | -180      |
| R(4,5)           | 1.388  | A(2,3,12)       | 119.2886 | D(7,1,6,11)         | 0.0001    |
| R(4,9)           | 1.0844 | A(4,3,12)       | 121.5712 | D(1,2,3,4)          | -0.0001   |
| R(5,6)           | 1.3947 | A(3,4,5)        | 120.6185 | D(1,2,3,12)         | 180.0001  |
| R(5,10)          | 1.0844 | A(3,4,9)        | 118.4749 | D(8,2,3,4)          | -180.0001 |
| R(6,11)          | 1.3458 | A(5,4,9)        | 120.9066 | D(8,2,3,12)         | 0.0001    |
| R(12,13)         | 1.2839 | A(4,5,6)        | 118.6305 | D(2,3,4,5)          | 0.0001    |
| R(12,16)         | 1.0973 | A(4,5,10)       | 121.9439 | D(2,3,4,9)          | -179.9995 |
| R(13,14)         | 1.4381 | A(6,5,10)       | 119.4255 | D(12,3,4,5)         | -180.0001 |
| R(14,15)         | 1.359  | A(1,6,5)        | 122.3922 | D(12,3,4,9)         | 0.0003    |
| R(14,19)         | 1.2226 | A(1,6,11)       | 118.8863 | D(2,3,12,13)        | -180.0021 |
| R(15,17)         | 1.0065 | A(5,6,11)       | 118.7215 | D(2,3,12,16)        | -0.0056   |
| R(15,18)         | 1.0062 | A(3,12,13)      | 122.7784 | D(4,3,12,13)        | -0.0019   |
|                  |        | A(3,12,16)      | 117.1783 | D(4,3,12,16)        | 179.9945  |
|                  |        | A(13,12,16)     | 120.0432 | D(3,4,5,6)          | -0.0001   |
|                  |        | A(12,13,14)     | 114.3216 | D(3,4,5,10)         | 179.9999  |
|                  |        | A(13,14,15)     | 110.0043 | D(9,4,5,6)          | -180.0005 |
|                  |        | A(13,14,19)     | 126.0266 | D(9,4,5,10)         | -0.0005   |
|                  |        | A(15,14,19)     | 123.9691 | D(4,5,6,1)          | 0.0001    |
|                  |        | A(14,15,17)     | 119.192  | D(4,5,6,11)         | -180.0001 |
|                  |        | A(14,15,18)     | 119.9422 | D(10,5,6,1)         | 180       |
|                  |        | A(17,15,18)     | 120.8657 | D(10,5,6,11)        | -0.0001   |
|                  |        |                 |          | D(3,12,13,14)       | 179.9956  |
|                  |        |                 |          | D(16,12,13,14)      | -0.0008   |
|                  |        |                 |          | D(12,13,14,15)      | 179.9779  |
|                  |        |                 |          | D(12,13,14,19)      | -0.0198   |
|                  |        |                 |          | D(13,14,15,17)      | 179.9952  |
|                  |        |                 |          | D(13,14,15,18)      | 0.0276    |
|                  |        |                 |          | D(19,14,15,17)      | -0.0071   |
|                  |        |                 |          | D(19,14,15,18)      | -179.9747 |

## 4.2. Non-linear optics

The first hyperpolarizabilities ( $\beta_0$ ,  $\alpha_0$  and  $\Delta\alpha$ ) of 4FBU molecule is calculated using B3LYP/6-31G (d,p) basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components by Kleinman symmetry (Kleinman, 1962). It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3x3x3 matrixes is a tetrahedral. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_a F_a - 1/2 \alpha_{ap} F_a F_p - 1/6 \beta_{apq} F_a F_p F_q \quad (2)$$

Where  $E^0$  is the energy of the unperturbed molecules,  $F_a$  is the field at the origin, and  $\mu_a, \alpha_{ap}, \beta_{apq}$  are the components of the dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment  $\mu$ , the mean polarizability  $\alpha_0$ , the anisotropy of polarizability  $\Delta\alpha$  and the mean first hyperpolarizability  $\beta_0$ , using the x, y, z components (Alyaret al. 2007) are defined as

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (3)$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (4)$$

$$\Delta\alpha = 2^{-1/2} \left[ \frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{(\alpha_{xx} - \alpha_{yy})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2)} \right]^{1/2} \quad (5)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (6)$$

Many organic molecules, containing conjugated  $\pi$  electrons are characterized by large values of first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy (Castiglioni et al. 1995; Zuliani et al. 1995; Del Zoppo et al., 1995; Del Zoppo et al. 1998). The intra-molecular charge transfer from the donor to acceptor group through a single-double bondconjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time (Ravikumar et al. 2008).

Theoretical investigation plays an important role in understanding the structure property relationship, which is able to assist in designing novel NLO materials. It is well known that the higher values of dipole moment, molecular polarizability and hyperpolarizability are important for more active NLO properties. The present study reveals that the  $\pi$ - $\pi$  interaction can make larger intra-molecular interaction and hence the polarizability of the molecule increases. It is evident to Table (2), the molecular dipole moment ( $\mu$ ), molecular polarizability and hyperpolarizability are calculated about 2.0705 (D), 5.7250 and  $10.5890 \times 10^{-30}$ esu, respectively. The  $\beta_0$  value of the title compound is twenty eight times greater than that of reference urea. Hence, our title molecule is an interesting object for Non-linear Optics.

**Table 2:** The Non-Linear Optical Properties of 4FBU

| Parameters                        | B3LYP/6-31G(d,p)              |
|-----------------------------------|-------------------------------|
| Dipole moment ( $\mu$ )           | Debye                         |
| $\mu_x$                           | -0.5194                       |
| $\mu_y$                           | -2.0017                       |
| $\mu_z$                           | 0.1030                        |
| M                                 | 2.0705Debye                   |
| Polarizability ( $\alpha_0$ )     | $\times 10^{-30}$ esu         |
| $\alpha_{xx}$                     | 241.55                        |
| $\alpha_{xy}$                     | -23.64                        |
| $\alpha_{yy}$                     | 281.26                        |
| $\alpha_{xz}$                     | -7.02                         |
| $\alpha_{yz}$                     | 17.27                         |
| $\alpha_{zz}$                     | 149.10                        |
| A                                 | $5.7250 \times 10^{-30}$ esu  |
| Hyperpolarizability ( $\beta_0$ ) | $\times 10^{-30}$ esu         |
| $\beta_{xxx}$                     | 542.29                        |
| $\beta_{xxv}$                     | 271.19                        |
| $\beta_{xyv}$                     | 457.42                        |
| $\beta_{vvv}$                     | -1008.01                      |
| $\beta_{xxz}$                     | -105.22                       |
| $\beta_{xyz}$                     | 56.53                         |
| $\beta_{vyz}$                     | -11.69                        |
| $\beta_{xzz}$                     | -6.03                         |
| $\beta_{yzz}$                     | 38.61                         |
| $\beta_{zzz}$                     | -48.65                        |
| $\beta_0$                         | $10.5890 \times 10^{-30}$ esu |

Reference value of urea ( $\mu=1.3732$  Debye,  $\beta_0=0.3728 \times 10^{-30}$ esu):  
esu-electrostatic unit

### 4.3. NBO analysis

NBO analysis provides an efficient method for studying intra and inter-molecular bonding and interaction among bonds, and provides a convenient basis for investigation charge transfer or conjugative interactions in the molecular system. Another useful aspect of NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could

enhance the analysis of intra and inter-molecular interactions. The hyper conjugation may be given as stabilizing effect that arises from an overlap between an occupied orbital with another neighboring electron deficient orbital when these orbitals are properly orientation. This non-covalent bonding and anti-bonding interaction can be quantitatively described in terms of the NBO analysis, which is expressed by means of the second-order perturbation interaction energy ( $E^{(2)}$ ) (Reed&Weinhold, 1985; Reed et al. 1985; Reed&Weinhold, 1983; Foster&Weinhold, 1980). this energy represents the estimation of the off-diagonal NBO Fock matrix elements. It can be deduced from the second-order perturbation approach (Chocholoušová et al. 2004).

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\epsilon_j - \epsilon_i} \quad (7)$$

Where,  $q_i$  is the donor orbital occupancy,  $\epsilon_i$  and  $\epsilon_j$  are diagonal elements (orbital energies) and  $F(i, j)$  is off diagonal NBO Fock matrix elements.

NBO analysis was performed by the B3LYP level of theory with 6-31G (d,p) basis set for the molecule 4FBU. NBO theory allows the assignment of hybridization of atomic lone pairs and of the atoms involved in bond orbitals. These are important data in spectral interpretation as the frequency ordering is related to the bond hybrid composition. The second order perturbation energy values  $E^{(2)}$  collected in Table 3 reveals the important interactions between the Lewis and non-Lewis type NBO orbitals of 4FBU molecular system. In the present case, the intra-molecular hyperconjugative interactions are formed by the orbital overlap between bonding (C-C), (C-N) and anti-bonding (C-C), (C-O), (C-N) orbitals. The lone pair electrons from N, O and F atoms have also shown interactions with anti-bonding orbitals of (C-C), (C-O) and (C-N), which results in the stabilization of 4FBU molecular system.

**Table 3:** The Second Order Fock Matrix of 4FBU

| Type          | Donor (i) | ED (e) | Acceptor (j) | ED (e) | $E^{(2)}$ KJ/mol | $E^{(2)}$ Kcal/mol | $E(j)-E(i)$ a.u. | $F(i,j)$ a.u. |
|---------------|-----------|--------|--------------|--------|------------------|--------------------|------------------|---------------|
| $\pi-\pi^*$   | C1-C6     | 1.6439 | C2-C3        | 0.3792 | 92.97            | 22.22              | 0.3              | 0.073         |
|               |           |        | C4-C5        | 0.2888 | 68.07            | 16.27              | 0.3              | 0.063         |
| $\pi-\pi^*$   | C2-C3     | 1.6273 | C1-C6        | 0.3671 | 77.61            | 18.55              | 0.27             | 0.063         |
|               |           |        | C4-C5        | 0.2888 | 87.82            | 20.99              | 0.28             | 0.07          |
|               |           |        | C12-N13      | 0.1278 | 83.47            | 19.95              | 0.28             | 0.071         |
| $\pi-\pi^*$   | C4-C5     | 1.6844 | C1-C6        | 0.3671 | 100.92           | 24.12              | 0.27             | 0.074         |
|               |           |        | C2-C3        | 0.3792 | 70.63            | 16.88              | 0.28             | 0.063         |
| $\pi-\pi^*$   | C12-N13   | 1.8904 | C2-C3        | 0.3792 | 33.56            | 8.02               | 0.34             | 0.05          |
|               |           |        | C14-O19      | 0.3321 | 87.86            | 21                 | 0.34             | 0.08          |
| n- $\sigma^*$ | F11       | 1.9680 | C1-C6        | 0.0275 | 27.74            | 6.63               | 0.96             | 0.071         |
|               |           |        | C5-C6        | 0.0280 | 27.74            | 6.63               | 0.96             | 0.071         |
| n- $\pi^*$    | F11       | 1.9098 | C1-C6        | 0.3671 | 88.41            | 21.13              | 0.42             | 0.091         |
| n- $\sigma^*$ | N13       | 1.9226 | C3-C12       | 0.0310 | 7.24             | 1.73               | 0.85             | 0.035         |
|               |           |        | C12-H16      | 0.0408 | 45.35            | 10.84              | 0.82             | 0.085         |
|               |           |        | C14-O19      | 0.0226 | 39.92            | 9.54               | 0.97             | 0.087         |
| n- $\pi^*$    | N15       | 1.7363 | C14-O19      | 0.3321 | 268.78           | 64.24              | 0.28             | 0.121         |
| n- $\sigma^*$ | O19       | 1.8431 | N13-C14      | 0.0916 | 114.14           | 27.28              | 0.62             | 0.118         |
|               |           |        | C14-N15      | 0.0678 | 101.34           | 24.22              | 0.71             | 0.12          |
| $\pi^*-\pi^*$ | C1-C6     | 0.3671 | C4-C5        | 0.2888 | 922.91           | 220.58             | 0.01             | 0.081         |

The strong delocalization of lone pair electrons were observed in the interactions of LP N15 $\rightarrow\pi^*(C14-O19)$ , LP O19 $\rightarrow\sigma^*(N13-C14)$  and LP O19 $\rightarrow\sigma^*(C14-N15)$  have shown stabilization energies of 268.78, 114.14 and 101.34 KJ/mol, respectively. A moderate stabilization energy of about 88.41 KJ/mol was shown by LP F11 $\rightarrow\pi^*(C1-C6)$  interaction. The orbital overlap between the donors  $\pi$  (C1-C6), (C2-C3), (C4-C5) and acceptors  $\pi^*$  (C2-C3), (C4-C5), (C1-C6) orbitals leads to the stabilization energy of ~74 KJ/mol. The intra-molecular interactions were observed an increase in electron density (ED) in (C-C) anti-bonding orbital that weakens the respective bonds. The electron density of conjugated bonds of aromatic ring (1.64e) clearly demonstrates strong delocalization for 4FBU molecule. The bonding orbitals of  $\pi$  (C2-C3) transfer the energy of 83.47 KJ/mol to the anti-bonding orbital

of  $\pi^*$  (C12-N13). Thus, the  $\pi$ -electron cloud movement from donor to acceptor can make the molecule highly polarized and causes ICT, which is responsible for the NLO activity of 4FBU molecule.

### 4.4. Energy gap analysis

Frontier molecular orbitals are nothing but the highest occupied molecular orbitals and lowest unoccupied molecular orbitals of the molecule. The LUMO as an electron acceptor represents the ability to obtain an electron; donor represents the ability to donate an electron. The energy gap of HOMO-LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. The positive and negative phases are represented in red and green colour

respectively. The energy of the two important FMOs such as the highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO) have been calculated. The frontier molecular orbitals of the title molecule are mapped in Fig (2). The frontier molecular orbitals play an important role in the electric and optical properties, as well as in UV-Vis spectra and chemical reactions. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. However, the intra-molecular charge transferred from the donor to accepter group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman's activity strong at the same time.

As seen from Fig. (2), the HOMO is localized over the Fluorine, phenyl and nitrogen atoms within the title molecule, while the LUMO localized all over the title molecule. The analysis of the wave function indicates that the electron absorption corresponds with the transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to the LUMO. The energy of HOMO orbital level is 7.2254 eV, and the energy of LUMO orbital level is 2.3371 eV. Hence, the energy gap of the 4FBU molecule is calculated as 4.84835 eV. The lowering of HOMO-LUMO energy gap (4.84835 eV) reflects the possibility of the intra-molecular charge transfer from HOMO to LUMO. The frontier molecular orbital values are presented in Table 4.

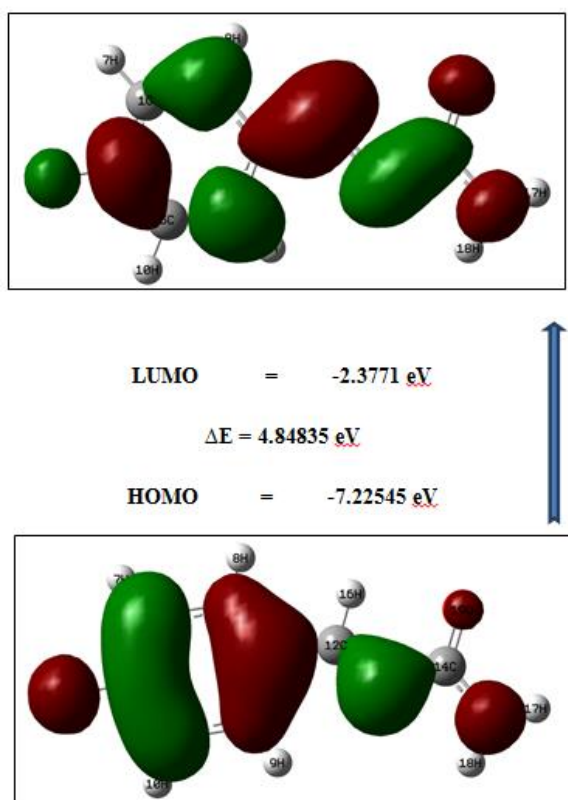


Fig. 2: The Frontier Molecular Orbitals of 4FBU.

Table 4: The Frontier Molecular Orbitals of 4FBU

| Orbitals | Energies (a.u) | Energies (eV) |
|----------|----------------|---------------|
| 39O      | -0.312672      | -8.50812      |
| 40O      | -0.289459      | -7.87647      |
| 41O      | -0.285295      | -7.76316      |
| 42O      | -0.265776      | -7.23203      |
| 43O      | -0.265534      | -7.22545      |
| 44V      | -0.087358      | -2.3771       |
| 45V      | -0.043228      | -1.17628      |
| 46V      | -0.012498      | -0.34008      |
| 47V      | -0.00469       | -0.12762      |
| 48V      | -0.00091       | -0.02476      |

#### 4.5. MEP analysis

MEP and electrostatic potential are useful quantities to illustrate the charge distributions of molecules and used to visualize variably charged regions of a molecule. Therefore, the charge distributions can give information about how the molecules interact with another molecule. The reactive behavior of the 4FBU molecule is visualized with the help of three-dimensional MEP surface. The molecular electrostatic potential and the electrostatic potential and contour mapped surface of the 4FBU are shown in Fig (3). The total electron density and MEP surface of the molecule under investigation is constructed by using B3LYP/6-31G (d,p) method. MEP surface describes the charge distribution in the molecule and helps in predicting the sites for nucleophilic and electrophilic attack in the molecule. The region of negative charge is pictured out by red colour, which indicates the electrophilic attack sites of our molecule. The red region localized over the carbonyl group of the thio moiety. The region of positive charge is pictured out by blue colour, which indicates the nucleophilic attack sites were localized over two hydrogen atoms of the thiourea side chain. The green colour corresponds to a potential half-way between the two extremes red and blue region and represents the neutral charge. The contour map of 4FBU has shown the electron density rich surface in closed curves, which regions are located over the imine group and the thio moiety present in the title molecule. Which are responsible regions for the activity of the 4FBU molecule.

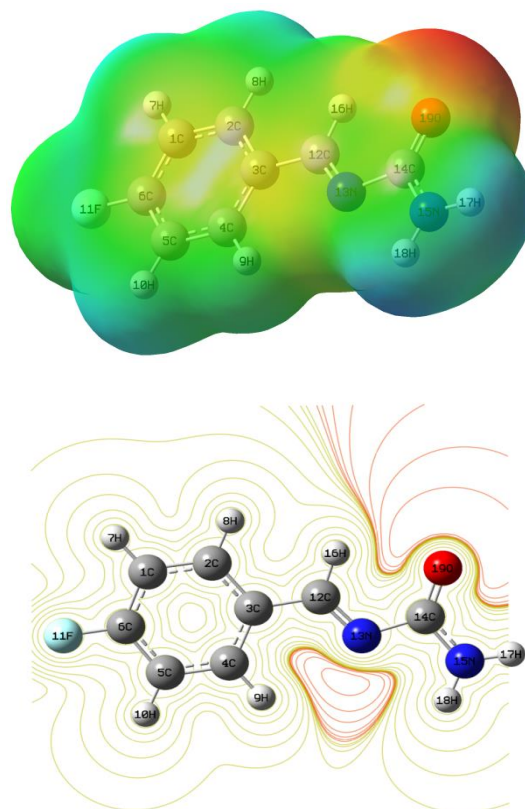


Fig. 3: The Molecular Electrostatic Potential and Contour Mapped Surfaces of 4FBU.

#### 4.6. Vibrational spectral studies

The full description of observed IR and Raman's spectra is presented in Table 5, along with detailed assignment as stipulated by the PED calculation. The observed FT-IR, FT-Raman spectra and the simulated spectra refined by DFT theory are given in Figs. 4 and 5. The theoretical and experimental wavenumbers are in fair agreement and the assignments of wavenumbers for different functional groups are discussed below.

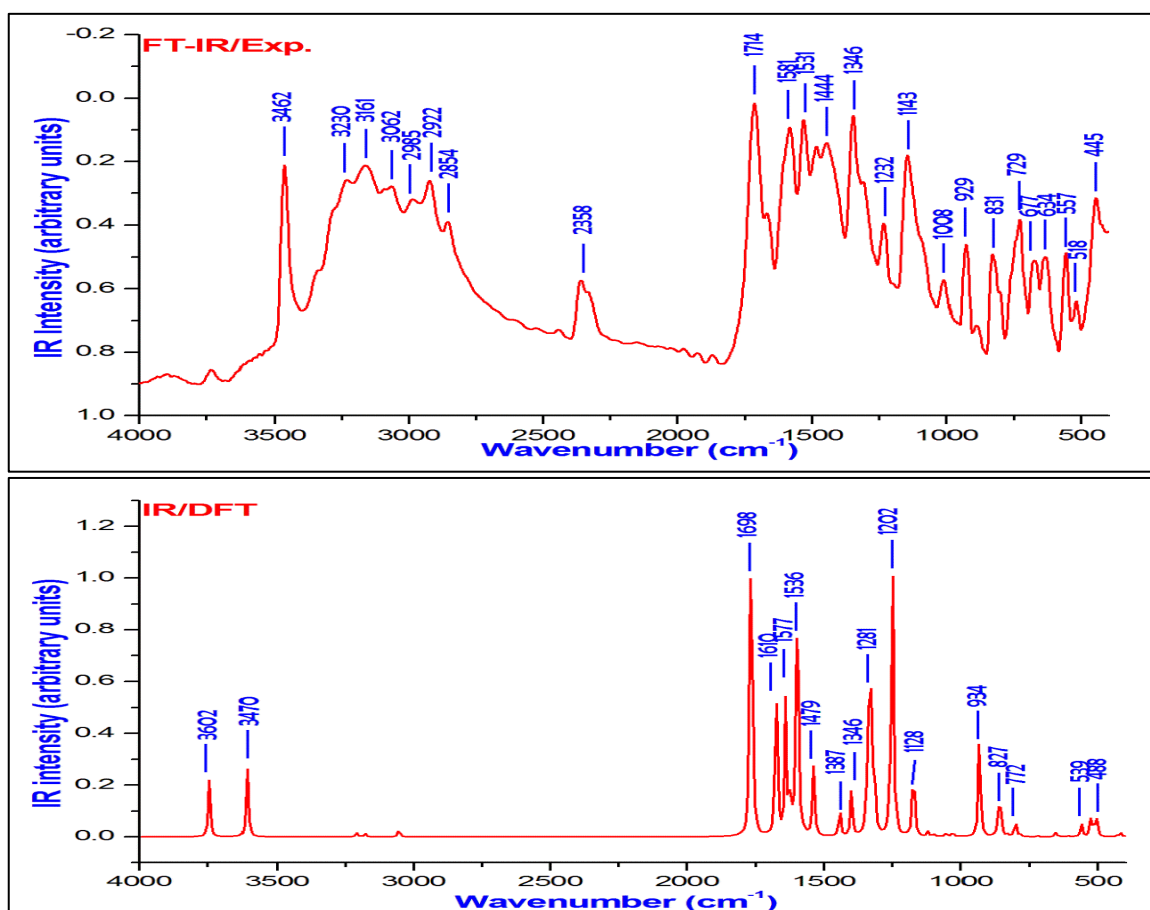


Fig. 4: The Recorded and Simulated FT-IR Spectra of 4FBU.

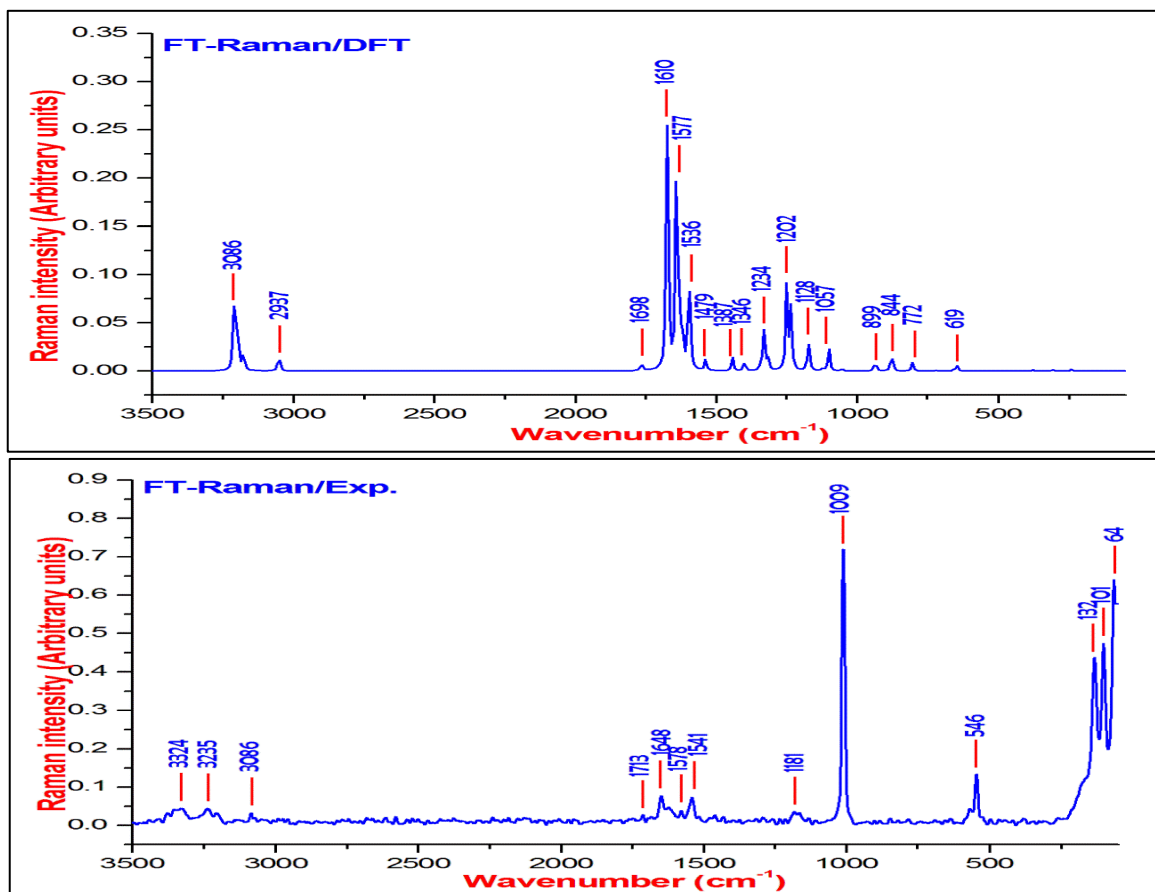


Fig. 5: The Recorded and Simulated FT-Raman Spectra of 4FBU.

**Table 5:** The Fundamental Vibrational Assignments of 4FBU

| Mode No | Theoretical             |        | Experimental     |       | IR    | Raman | PED $\geq$ 10%                                                                                                                 |
|---------|-------------------------|--------|------------------|-------|-------|-------|--------------------------------------------------------------------------------------------------------------------------------|
|         | Wavenumber<br>Un Scaled | Scaled | Wavenumber<br>IR | Raman |       |       |                                                                                                                                |
| 1       | 3744                    | 3602   |                  |       | 15.2  | 1.7   | $\nu_{N_{15}H_{17}}(100) + \nu_{N_{15}H_{18}}(100)$                                                                            |
| 2       | 3607                    | 3470   | 3462             | 3324  | 18.5  | 5.1   | $\nu_{N_{15}H_{17}}(100) + \nu_{N_{15}H_{18}}(100)$                                                                            |
| 3       | 3208                    | 3086   | 3089             | 3086  | 0.7   | 5.8   | $\nu_{C_4H_9}(99) + \nu_{C_5H_{10}}(98)$                                                                                       |
| 4       | 3205                    | 3083   |                  |       | 0.4   | 5.9   | $\nu_{C_1H_7}(92)$                                                                                                             |
| 5       | 3195                    | 3074   | 3062             |       | 0.2   | 2.8   | $\nu_{C_4H_9}(99) + \nu_{C_5H_{10}}(98)$                                                                                       |
| 6       | 3175                    | 3055   |                  |       | 0.8   | 2.2   | $\nu_{C_2H_8}(94)$                                                                                                             |
| 7       | 3053                    | 2937   | 2922             |       | 2.3   | 2.3   | $\nu_{C_{12}H_{16}}(100)$                                                                                                      |
| 8       | 1765                    | 1698   | 1714             | 1713  | 100.0 | 3.0   | $\nu_{O_{19}C_{14}}(87) + \nu_{N_{15}C_{14}}(53)$                                                                              |
| 9       | 1674                    | 1610   | 1666             | 1648  | 41.3  | 90.2  | $\nu_{N_{13}C_{12}}(62) + \nu_{C_1C_2}(41) + \nu_{C_4C_5}(34)$                                                                 |
| 10      | 1639                    | 1577   | 1581             | 1578  | 36.3  | 100.0 | $\nu_{C_4C_5}(68) + \nu_{C_1C_2}(71) + \nu_{C_3C_3}(51)$                                                                       |
| 11      | 1622                    | 1560   |                  |       | 10.7  | 19.5  | $\nu_{C_5C_6}(67) + \nu_{C_3C_4}(52) + \beta_{C_2C_1C_6}(64)$                                                                  |
| 12      | 1596                    | 1536   | 1531             | 1541  | 92.3  | 41.8  | $\beta_{H_{17}N_{15}H_{18}}(82)$                                                                                               |
| 13      | 1538                    | 1479   | 1483             | 1460  | 21.2  | 4.4   | $\beta_{C_1C_6C_5}(51) + \beta_{H_7C_1C_2}(69) + \beta_{H_8C_2C_1}(79) + \beta_{H_9C_4C_5}(67) + \beta_{H_{10}C_5C_4}(72)$     |
| 14      | 1442                    | 1387   |                  |       | 7.8   | 6.1   | $\nu_{C_4C_5}(68) + \nu_{C_1C_2}(71)$                                                                                          |
| 15      | 1399                    | 1346   | 1346             |       | 12.6  | 5.5   | $\beta_{H_{16}C_{12}N_{13}}(68)$                                                                                               |
| 16      | 1343                    | 1292   | 1309             | 1292  | 8.1   | 1.3   | $\nu_{C_5C_6}(67) + \nu_{N_{15}C_{14}}(53)$                                                                                    |
| 17      | 1332                    | 1281   |                  |       | 67.4  | 24.3  | $\nu_{C_5C_6}(67) + \nu_{N_{15}C_{14}}(53) + \beta_{H_{17}N_{15}C_{14}}(57) + \beta_{H_{16}C_{12}N_{13}}(68)$                  |
| 18      | 1316                    | 1266   |                  |       | 22.0  | 8.0   | $\beta_{H_7C_1C_2}(69) + \beta_{H_8C_2C_1}(79) + \beta_{H_9C_4C_5}(67) + \beta_{H_{10}C_5C_4}(72)$                             |
| 19      | 1250                    | 1202   | 1201             |       | 78.8  | 47.6  | $\nu_{C_4C_5}(38) + \nu_{C_1C_2}(31) + \nu_{C_3C_{12}}(48) + \nu_{F_{11}C_6}(67)$                                              |
| 20      | 1235                    | 1188   |                  | 1181  | 2.3   | 36.4  | $\nu_{C_3C_{12}}(48) + \nu_{F_{11}C_6}(67) + \beta_{H_8C_2C_1}(79)$                                                            |
| 21      | 1172                    | 1128   | 1143             |       | 24.1  | 20.2  | $\beta_{H_7C_1C_2}(69) + \beta_{H_8C_2C_1}(79) + \beta_{H_9C_4C_5}(67) + \beta_{H_{10}C_5C_4}(72)$                             |
| 22      | 1119                    | 1077   |                  |       | 1.4   | 1.8   | $\nu_{C_4C_5}(68) + \nu_{C_1C_2}(71) + \beta_{H_7C_1C_2}(69) + \beta_{H_8C_2C_1}(79) + \beta_{H_9C_4C_5}(67)$                  |
| 23      | 1099                    | 1057   |                  |       | 0.9   | 14.5  | $\nu_{O_{19}C_{14}}(87) + \beta_{H_{17}N_{15}C_{14}}(57)$                                                                      |
| 24      | 1053                    | 1013   |                  |       | 1.3   | 1.7   | $\Gamma_{H_{16}C_{12}N_{13}C_{14}}(84)$                                                                                        |
| 25      | 1028                    | 989    | 1008             | 1009  | 1.4   | 0.2   | $\beta_{C_1C_6C_5}(51) + \beta_{C_2C_1C_6}(64) + \beta_{C_4C_5C_6}(65)$                                                        |
| 26      | 990                     | 953    |                  |       | 0.0   | 0.0   | $\Gamma_{H_7C_1C_2H_8}(84) + \tau_{C_4C_3C_5H_9}(75) + \Gamma_{H_{10}C_5C_6F_{11}}(83)$                                        |
| 27      | 961                     | 925    | 929              |       | 0.0   | 0.0   | $\Gamma_{H_7C_1C_2H_8}(84)$                                                                                                    |
| 28      | 934                     | 899    | 891              |       | 29.4  | 8.3   | $\nu_{N_{13}C_{14}}(51) + \beta_{C_3C_{12}N_{13}}(76)$                                                                         |
| 29      | 877                     | 844    | 831              |       | 0.5   | 16.2  | $\nu_{C_2C_3}(51) + \nu_{C_3C_4}(52) + \nu_{C_5C_6}(67)$                                                                       |
| 30      | 860                     | 827    |                  |       | 15.5  | 0.1   | $\Gamma_{H_7C_1C_6F_{11}}(82) + \tau_{C_4C_3C_5H_9}(75) + \Gamma_{H_{10}C_5C_6F_{11}}(83) + \Gamma_{C_1C_6C_4C_5}(77)$         |
| 31      | 831                     | 799    | 804              |       | 0.5   | 0.0   | $\Gamma_{H_7C_1C_6F_{11}}(82) + \tau_{C_4C_3C_5H_9}(75) + \Gamma_{H_{10}C_5C_6F_{11}}(83)$                                     |
| 32      | 803                     | 772    |                  |       | 4.7   | 8.4   | $\nu_{F_{11}C_6}(67) + \beta_{C_2C_3C_4}(64)$                                                                                  |
| 33      | 782                     | 753    |                  |       | 0.6   | 0.2   | $\Gamma_{C_3C_{12}N_{13}C_{14}}(80) + \tau_{O_{19}N_{13}N_{15}C_{14}}(82)$                                                     |
| 34      | 718                     | 691    | 677              |       | 0.4   | 0.9   | $\Gamma_{C_1C_6C_2C_3}(89) + \Gamma_{C_1C_6C_4C_5}(77) + \tau_{O_{19}N_{13}N_{15}C_{14}}(82) + \tau_{F_{11}C_1C_5C_6}(88)$     |
| 35      | 655                     | 631    | 634              |       | 1.1   | 1.7   | $\beta_{N_{13}C_{14}O_{19}}(65) + \beta_{C_4C_5C_6}(65)$                                                                       |
| 36      | 644                     | 619    |                  |       | 0.3   | 7.7   | $\beta_{C_1C_6C_5}(51) + \beta_{N_{13}C_{14}O_{19}}(65) + \beta_{C_4C_5C_6}(65)$                                               |
| 37      | 608                     | 585    |                  |       | 0.3   | 0.1   | $\Gamma_{H_{17}N_{15}C_{14}N_{13}}(92)$                                                                                        |
| 38      | 561                     | 539    |                  | 546   | 3.3   | 0.8   | $\beta_{C_3C_{12}N_{13}}(76) + \beta_{N_{13}C_{14}N_{15}}(73) + \beta_{C_2C_3C_{12}}(65)$                                      |
| 39      | 525                     | 505    | 518              |       | 6.8   | 0.3   | $\Gamma_{C_3C_2C_4C_5}(83) + \tau_{F_{11}C_1C_5C_6}(88)$                                                                       |
| 40      | 507                     | 488    |                  |       | 7.2   | 0.6   | $\beta_{C_1C_6C_5}(51) + \beta_{N_{13}C_{14}N_{15}}(73)$                                                                       |
| 41      | 429                     | 413    |                  |       | 0.4   | 0.2   | $\Gamma_{C_1C_6C_2C_3}(89) + \Gamma_{C_3C_2C_4C_5}(83)$                                                                        |
| 42      | 417                     | 401    |                  |       | 1.0   | 0.2   | $\beta_{C_2C_1C_6}(64) + \beta_{C_5C_6F_{11}}(67)$                                                                             |
| 43      | 377                     | 363    |                  |       | 2.2   | 3.2   | $\Gamma_{C_1C_6C_4C_5}(77) + \tau_{F_{11}C_1C_5C_6}(88) + \Gamma_{C_5C_4C_3C_{12}}(87)$                                        |
| 44      | 309                     | 297    |                  |       | 2.2   | 4.8   | $\beta_{N_{13}C_{14}N_{15}}(73) + \beta_{C_2C_3C_{12}}(65)$                                                                    |
| 45      | 243                     | 234    |                  |       | 52.5  | 0.8   | $\tau_{N_{15}H_{17}C_{14}H_{18}}(89)$                                                                                          |
| 46      | 240                     | 231    |                  |       | 0.7   | 6.8   | $\nu_{C_3C_{12}}(48) + \beta_{N_{13}C_{14}O_{19}}(65) + \beta_{C_2C_3C_4}(64) + \beta_{C_{12}N_{13}C_{14}}(62)$                |
| 47      | 202                     | 194    |                  |       | 0.5   | 2.0   | $\Gamma_{C_4C_3C_{12}N_{13}}(79) + \Gamma_{C_1C_6C_4C_5}(77) + \Gamma_{C_3C_2C_4C_5}(83) + \Gamma_{C_3C_{12}N_{13}C_{14}}(80)$ |
| 48      | 152                     | 146    |                  | 132   | 1.3   | 0.6   | $\Gamma_{C_4C_3C_{12}N_{13}}(79) + \Gamma_{C_{12}N_{13}C_{14}N_{15}}(96) + \Gamma_{C_3C_{12}N_{13}C_{14}}(80)$                 |
| 49      | 95                      | 91     |                  | 101   | 0.3   | 3.0   | $\beta_{C_3C_{12}N_{13}}(76) + \beta_{C_2C_3C_{12}}(65) + \beta_{C_{12}N_{13}C_{14}}(62)$                                      |
| 50      | 64                      | 62     |                  |       | 0.2   | 1.2   | $\Gamma_{C_1C_6C_4C_5}(77) + \Gamma_{C_3C_{12}N_{13}C_{14}}(80) + \Gamma_{C_5C_4C_3C_{12}}(87)$                                |
| 51      | 32                      | 31     |                  |       | 2.2   | 3.0   | $\Gamma_{C_4C_3C_{12}N_{13}}(79) + \Gamma_{C_{12}N_{13}C_{14}N_{15}}(96)$                                                      |

#### 4.6.1. C=O Vibrations

The C=O stretching vibration band can be easily identified from the IR and Raman spectrum. Because of the degree of conjugation, the strength and polarizations are also increasing. The carbonyl vibrations bands in ketones normally show strong intensity and are expected in the region 1715–1680  $\text{cm}^{-1}$  (Smith, 1998). The strong band observed at 1714  $\text{cm}^{-1}$  in FT-IR and a weak band observed at 1713  $\text{cm}^{-1}$  in FT-Raman spectrum are assigned to the carbonyl stretching vibration of the 4FBU molecule. The theoretical wavenumber at 1698  $\text{cm}^{-1}$  corresponds to the same vibration with 87% of PED contribution along with  $\nu_{CN}$  stretching vibration. The both observed and calculated values are coincides well with each other. The intensity of the carbonyl group can increase by the conjugation or formation of hydrogen bonds.

#### 4.6.2. C=N and C-N Vibrations

The identification of C=N and C–N stretching in the side chain is a rather difficult task since there are problems in identifying these frequencies from other vibrations. Clougherty et al. 1957, have

assigned the C=N stretching frequency in benzylidene anilines to the region 1610–1630  $\text{cm}^{-1}$ . In our present study, the C=N stretching vibration observed as a weak band at 1666  $\text{cm}^{-1}$  in FT-IR and at 1648  $\text{cm}^{-1}$  in FT-Raman spectrum. The wavenumber calculated at 1610  $\text{cm}^{-1}$  shown deviation with experimental wavenumber due to the mixing of  $\nu_{CC}$  vibrations of the phenyl ring. Silverstein et al. 1981 assigned C–N stretching vibrations in the region 1382–1266  $\text{cm}^{-1}$  for the aromatic amines. Herein, the C–N stretching vibrations are identified as weak bands in both FT-IR (1309  $\text{cm}^{-1}$ ) and FT-Raman (1292  $\text{cm}^{-1}$ ) spectrum. The calculated wavenumber at 1292  $\text{cm}^{-1}$  shows very good agreement with each other. The vibration observed at 1346  $\text{cm}^{-1}$  in FT-IR spectrum and its corresponding harmonic wavenumber computed at 1346  $\text{cm}^{-1}$  are assigned to  $\beta_{CNH}$  bending vibration.

#### 4.6.3. N-H Vibrations

The N–H stretching vibration appears strongly and broadly in the region 3500–3300  $\text{cm}^{-1}$  (Erdoğdu et al. 2008). In this study, the amino group stretching vibration is observed at very strong band at 3462  $\text{cm}^{-1}$  in FT-IR spectrum and as weak band at 3324  $\text{cm}^{-1}$  in

FT-Raman spectrum, respectively. The wavenumber calculated at  $3470\text{ cm}^{-1}$  assigned to the N-H vibration of the title molecule. The PED corresponding to this vibration is a pure mode and is exactly contributes about to 100%. The symmetric deformation of  $\text{NH}_2$  usually occurs as a strong band in the region  $1580\text{--}1650\text{ cm}^{-1}$ . The strong deformation observed at  $1531$  and  $1541\text{ cm}^{-1}$  in FT-IR and FT-Raman spectrum is assigned to  $\text{NH}_2$  deformation vibration of the title molecule and its corresponding theoretical wavenumber shows good covenant with  $1536\text{ cm}^{-1}$ .

#### 4.6.4. C-F Vibrations

The C-F group gives rise to its stretching wavenumber in the region  $1000\text{--}1450\text{ cm}^{-1}$  and usually appears with strong intensity in both Raman and infrared spectra (Páez Jerez et al. 2015). For the title compound the band observed at  $1201\text{ cm}^{-1}$  is assigned for the C-F stretching vibration and this vibration mixed with the C-C vibrations of the phenyl ring with considerable PED contribution  $\sim 38\%$ . The wavenumber computed at  $1202\text{ cm}^{-1}$  is corresponds to the C-F stretching vibration of the title molecule. The C-F in-plane bending wavenumber appears in the region  $700\text{--}850\text{ cm}^{-1}$ . The FT-IR bands at  $831$  and  $804\text{ cm}^{-1}$  are corresponds to the in-plane bending vibrations of the fluorine atom. The theoretical wavenumber at  $827$  and  $799$  agree well with the experimental findings. The C-F out-of-plane bending vibrations are computed at  $505\text{ cm}^{-1}$  and the band observed at  $501\text{ cm}^{-1}$  in FT-IR spectrum are assigned appropriately.

#### 4.6.5. Ring Vibrations

The aromatic CH-stretching vibrations absorb weakly to moderately between  $3120$  and  $3000\text{ cm}^{-1}$  (Roeges, 1994). The DFT calculations gives the bands at  $3086\text{--}3055\text{ cm}^{-1}$  are assigned to the C-H stretching vibrations of the phenyl ring. The experimental wavenumbers observed  $3089$ ,  $3062\text{ cm}^{-1}$  in FT-IR and at  $3086\text{ cm}^{-1}$  in FT-Raman spectrum are corresponds to the C-H vibrations. In this region, the TED calculations show that all the C-H stretching vibrations are pure modes. The C-H vibration of azomethine group is observed as strong band at  $2922\text{ cm}^{-1}$  in FT-IR spectrum and its theoretical wavenumber computed at  $2937\text{ cm}^{-1}$  shows good agreement with each other. The carbon-carbon stretching modes of the phenyl group are expected in the range of  $1620$  to  $1320\text{ cm}^{-1}$  (Faniran&Shurvell, 1968). In the present study, the carbon-carbon stretching vibrations of the 4FBU have been observed at  $1581$ ,  $1483$ ,  $1309\text{ cm}^{-1}$  in FT-IR and at  $1578$ ,  $1460$ ,  $1292\text{ cm}^{-1}$  in FT-Raman are corresponding bands for the C-C vibrations of the aromatic ring. The wavenumbers at  $1577$ ,  $1560$ ,  $1479$  and  $1292\text{ cm}^{-1}$  from the B3LYP calculations are assigned to the ring C-C vibrations of the title molecule. The ring-breathing mode for the para substituted benzenes with entirely different substituents has been reported to be strongly IR active with typical bands in the interval  $780\text{--}840\text{ cm}^{-1}$  (Varsanyi, 1974). The ring breathing mode and trigonal bending vibration of the phenyl were observed at  $1008$ ,  $831\text{ cm}^{-1}$  in FT-IR and  $1009\text{ cm}^{-1}$  in FT-Raman spectrum. The theoretical wavenumber corresponds to these vibrations obtained at  $989$  and  $844\text{ cm}^{-1}$ .

#### 4.7. Light harvesting efficiency calculations

The excitation energies, absorbance and oscillator strengths for the title molecule at the optimized geometry were computed and tabulated in Table 6. The highest band observed at  $305\text{ nm}$  with an oscillator strength of  $f=0.5055$  corresponds to the transition of HOMO-1 to LUMO. From the three excitations predicted by TD-DFT, two have non-negligible oscillator strengths  $f>0.1$ . The oscillator strength  $G$  reflects the strength of the particular transition; in other words, the light harvesting efficiency (LHE). The values of  $f$  determine the usefulness of sensitizer in DSSC (Wang et al. 2013; Heera&Cindrella, 2009). Relationship of LHE to  $f$  is expressed as:

$$\text{LHE} = 1 - 10^{-f} \quad (8)$$

**Table 6:** The Oscillator Strength, Excitation Energies and Transitions of 4FBU

| Excited States  | CI expansion coefficient | Energy gap | Gas phase | Oscillator strength |
|-----------------|--------------------------|------------|-----------|---------------------|
| Excited State1: |                          |            |           |                     |
| 43→44           | 0.6967                   | 3.6503 eV  | 339.66 nm | $f=0.0003$          |
| Excited State2: |                          |            |           |                     |
| 40→44           | 0.1141                   |            |           |                     |
| 42→44           | 0.6842                   | 4.7268 eV  | 262.30 nm | $f=0.5055$          |
| Excited State3: |                          |            |           |                     |
| 40→44           | 0.6029                   | 4.7859 eV  | 259.06 nm | $f=0.0267$          |
| 42→44           | -0.1101                  |            |           |                     |
| 42→45           | -0.3471                  |            |           |                     |

The light harvesting efficiency of 4FBU is calculated as 0.6877, which shows the capability to capture photons and exhibiting the photon-energy conversion efficiency. The light harvesting efficiency 0.6877 reveals that 4FBU have sensitizing application in dye sensitized solar cells. The theoretical absorption maximum peak of the 4FBU is shown in Fig. 6.

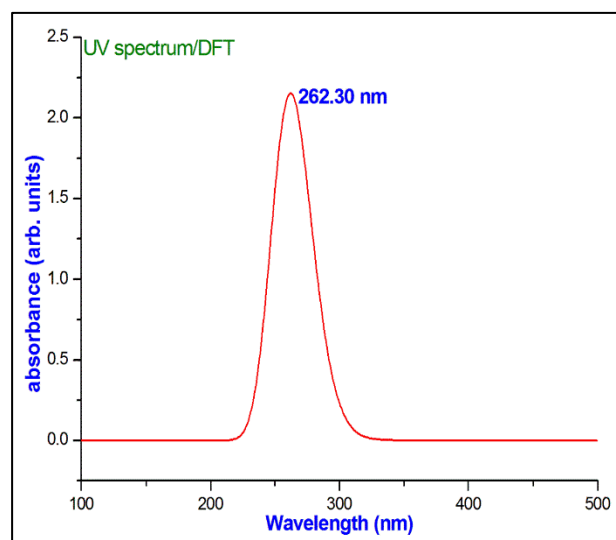


**Fig. 6:** The Absorption Maximum Peak of 4FBU Calculated by DFT Method.

#### 4.8. Mulliken atomic charges

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system, since atomic charges affect the dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems. The Mulliken charges were calculated by DFT/B3LYP/6-31G(d,p) basis set. The calculated Mulliken charge values are listed in Table 7 and are plotted in Fig. 7. In our study, the carbon atoms have most positive (C3: 0.74847) and most negative charge (C2: -1.09447). The lone pair atoms such as N, O and F have negative charges. All the hydrogen atoms have positive charge.

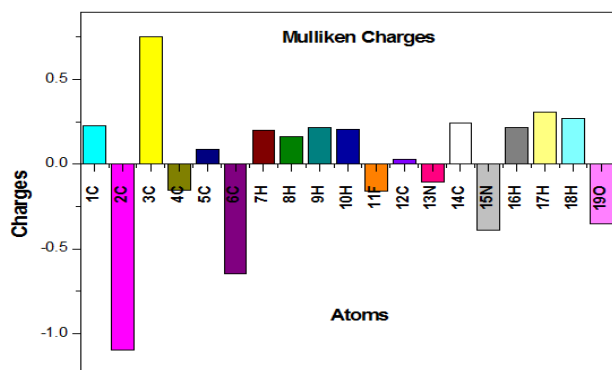


**Table 7:** The Mulliken Atomic Charges of 4FBU  
**Fig. 7:** The Mulliken Atomic Charges Plot of 4FBU.

| Atoms | Charges   | Atoms | Charges   |
|-------|-----------|-------|-----------|
| 1C    | 0.224137  | 11F   | -0.15987  |
| 2C    | -1.09447  | 12C   | 0.027733  |
| 3C    | 0.74847   | 13N   | -0.105321 |
| 4C    | -0.154701 | 14C   | 0.240205  |
| 5C    | 0.086297  | 15N   | -0.389476 |
| 6C    | -0.647069 | 16H   | 0.217425  |
| 7H    | 0.201226  | 17H   | 0.30784   |
| 8H    | 0.161171  | 18H   | 0.266044  |
| 9H    | 0.214749  | 19O   | -0.349516 |
| 10H   | 0.205125  |       |           |

#### 4.9. Thermodynamic properties

On the basis of vibrational analysis, the statistical thermodynamic functions heat capacity ( $C_{p,m}^0$ ), entropy ( $S_m^0$ ), and enthalpy changes ( $\Delta H_m^0$ ) for the 4FBU were obtained from the theoretical harmonic frequencies listed in Table 8. It can be seen from Table 8, the thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures were fitted by quadratic formulas and the corresponding fitting factors ( $R^2$ ) for these thermodynamic properties are 0.99895, 0.99997 and 0.99946, respectively. The comparative thermodynamical graphs of 4FBU are shown in Fig. 8. The corresponding fitting equations are as follows:

$$C_{p,m}^0 = 5.42703 + 0.02291T + 2.0243 \times 10^{-5} T^2 \quad (R^2 = 0.99895)$$

$$S_m^0 = 1.24898 + 0.00527T + 4.65873 \times 10^{-5} T^2 \quad (R^2 = 0.99997)$$

$$\Delta H_m^0 = 3.05729 + 0.01291T + 1.14038 \times 10^{-5} T^2 \quad (R^2 = 0.99946)$$

All the given thermodynamic data are the helpful information for further study on 4FBU. It can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field. All the thermodynamic calculations were done in gas phase and they could not be used in solution.

**Table 8:** Thermodynamic Properties of 4FBU at Different Temperatures

| T (K)  | S (J/mol.K) | C <sub>p</sub> (J/mol.K) | ΔH (KJ/mol) |
|--------|-------------|--------------------------|-------------|
| 100    | 341.24      | 97.36                    | 6.77        |
| 200    | 425.36      | 153.35                   | 19.22       |
| 298.15 | 498.26      | 216.68                   | 37.35       |
| 300    | 499.6       | 217.89                   | 37.75       |
| 400    | 570.98      | 279.98                   | 62.71       |
| 500    | 639.27      | 332.23                   | 93.41       |
| 600    | 703.68      | 374.06                   | 128.81      |
| 700    | 763.94      | 407.38                   | 167.94      |
| 800    | 820.16      | 434.28                   | 210.07      |
| 900    | 872.62      | 456.34                   | 254.64      |
| 1000   | 921.68      | 474.68                   | 301.21      |

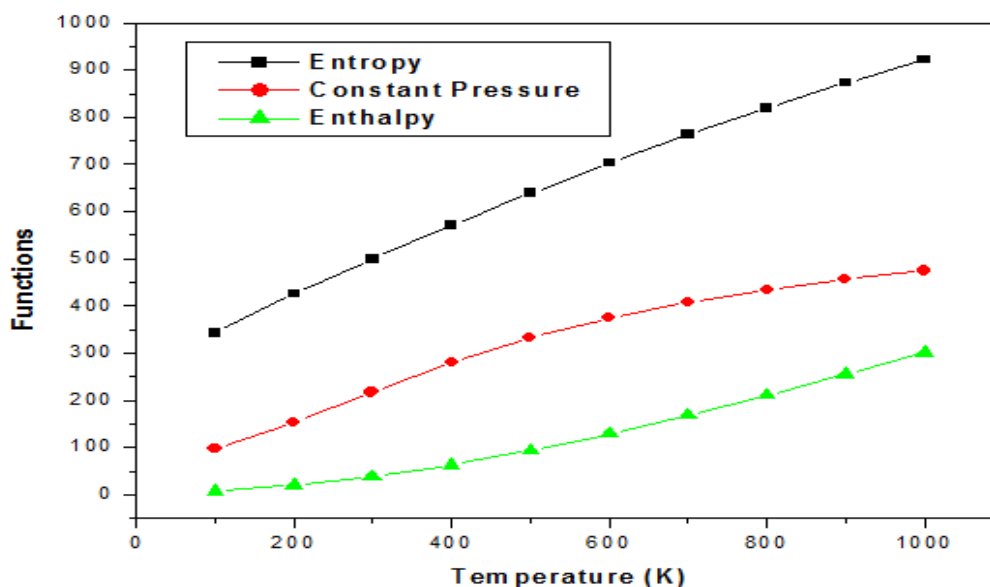


**Fig. 8:** The Thermodynamic Properties of 4FBU at Different Temperatures.

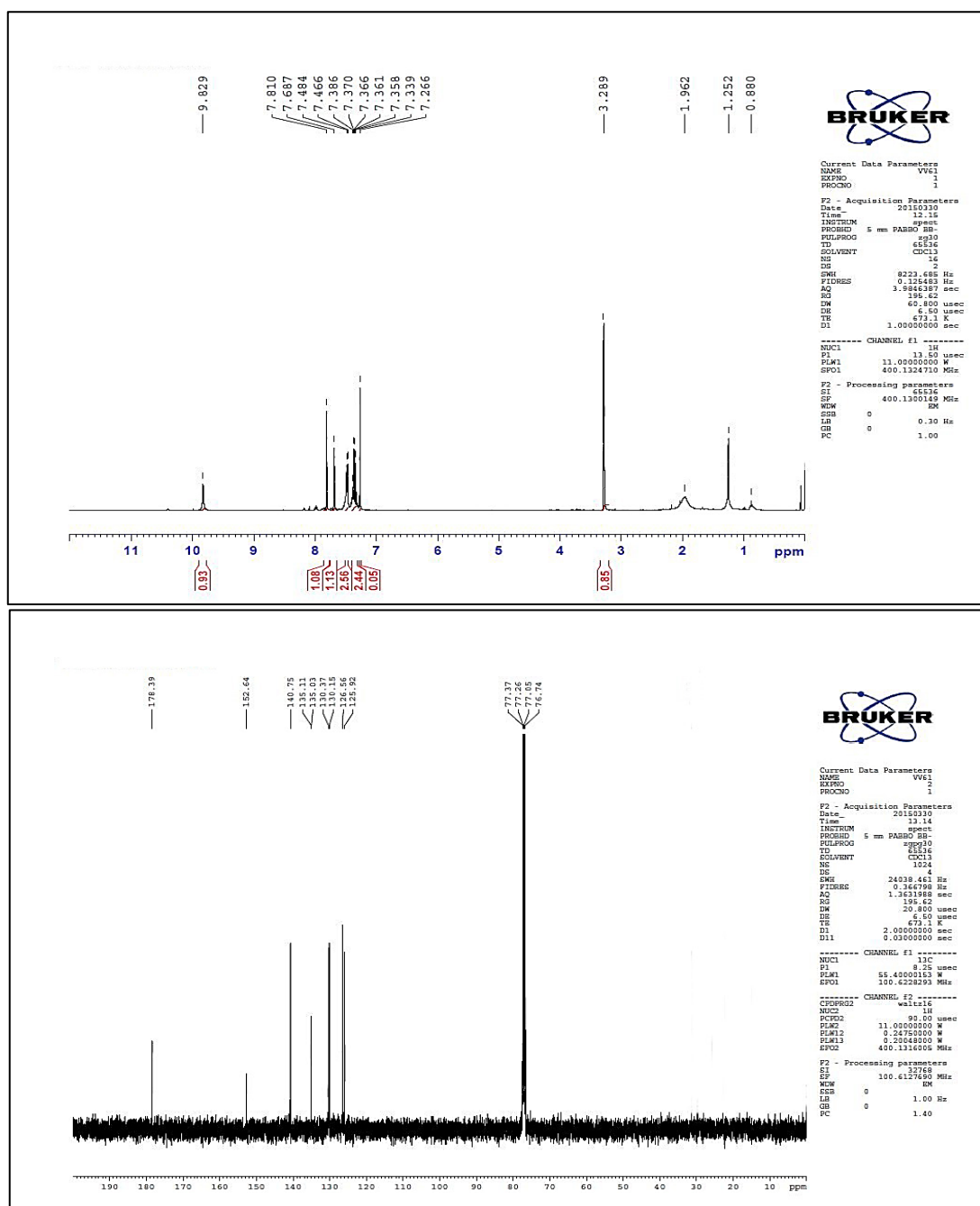


Fig. 9: The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR Spectra of 4FBU.

## 5. Conclusion

A complete vibrational analysis was carried out for the first time to the molecule 4FBU. The optimized bond parameters were calculated at DFT/B3LYP/6-31G (d,p) method. The observed FT-IR and FT-Raman spectral values were in good agreement with the calculated values. The first order hyperpolarizability ( $\beta_0=10.5890 \times 10^{-30}$  esu) of 4FBU was calculated and found to be twentyeight times greater than that of urea and hence the molecule possesses considerable NLO activity. NBO study reveals that the  $\pi$ -electron cloud movement from donor to acceptor can make the molecule highly polarized and causes ICT, which is responsible for the NLO activity of 4FBU molecule. The light harvesting efficiency 0.6877 reveals that 4FBU have sensitizing application in dye sensitized solar cells. MEP surface analysis mentioned the active charge sites of the molecule 4FBU. In addition, Mulliken charges and thermodynamic properties were also reported.

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