

Vibrational Spectra and Electronic Structural Studies of Some Coumarins

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ABSTRACT: Coumarin derivatives are used in a wide range of applications such as dye lasers, antioxidant agents, HIV inhibitors and anticoagulants and have attracted considerable research interest. The optimized geometric bond lengths, HOMO-LUMO energies and vibrational spectra are computed by DFT method employing B3LYP exchange correlation with the 6-311G** basis set. The vibrational spectra are also recorded experimentally in the region 4000- 400 cm⁻¹, which show good correlation with theoretical vibrational spectra. It is observed that UV-Vis peak absorption wavelength have a positive correlation with the resonance states of coumarin derivatives and it depends on the nature and position of the substituents.

Keywords: Coumarin, DFT, Vibrational spectra, HOMO-LUMO, Bond-length

I. INTRODUCTION

The excited states of coumarin derivatives have been studied extensively both experimentally and theoretically because of their interesting photophysical, photochemical and pharmaceutical properties. These molecules are highly fluorescent and thus widely used as laser dyes in the blue-green region, solar energy concentrators and nonlinear chromophores. The large state-dependent variation of the dipole moment causes a large Stokes shift for these molecules, which is sensitive to the polarity of solvents. Coumarins are used to produce liquid crystals as the coumarin can undergo photo alignment. Due to tunability of their absorbance and fluorescence (as fluorescence bands shifts due to change of substituents at the coumarin) they are used in light emitting diodes (LEDs).

Coumarin consists of a benzene ring fused together with a pyrone ring. The pyrone ring also contains a double bond such that it extends the conjugate π system across the molecule. We have defined the aromatic ring consisting of 6 carbon atoms as ring 1 and the pyrone ring as ring 2 as shown in Fig. 1 which shows the coumarin molecular structure, its position-numbering convention and atomic labeling used in this paper.

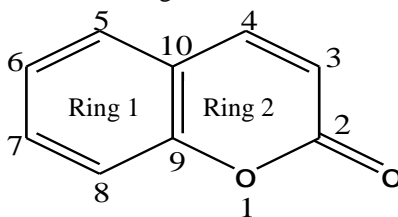


Fig. 1. Molecular structure of coumarin.

Various quantum chemical methods have been employed to study electronic and photophysical properties of coumarins derivatives. Recently, M Ebihara *et al* [1] studied the optoelectronic properties of coumarin dyes. J. Preat and co workers [2] studied the TD-DFT investigation of the UV spectra of pyranone derivatives. Semi-empirical excited state calculations of 7-aminocoumarins in the gas phase have been reported by McCarthy and Blanchard [3]. Ando [4] combined ab initio electronic structure calculations and molecular dynamics simulation to study the solvation dynamics of Coumarin 120 in methanol. A Car-Parrinello molecular dynamics (CPMD) simulation was carried out to study microsolvated Coumarin151, Coumarin 35 and Coumarin 153 [5] utilizing the QM/MM CPMD method. R. Cave *et al* [6] have performed TD-DFT, CASSCF and multistate CASPT2 calculations for coumarin 120 and Coumarin 151. Recently N. Kitamura [7] reported a systematic study of the synthesis, absorption and fluorescence of 17 coumarin derivatives. They discussed the effect of alkylation of the amino group at the seventh position, trifluoromethylation of the methyl group at the fourth position and the number ring structures on the absorption and fluorescence spectra. In the fluorescence spectra they found that pyrrolyl coumarins exhibit weak fluorescence while most of the other

coumarins showed strong fluorescence. So it is very important to study the different parameters of coumarin derivatives theoretically.

II. Materials and Methods

2.1 Experimental Details

All the coumarins derivatives 5, 7-dihydroxy-4-methyl coumarin (57DH4MC); 6,7-dihydroxy-4-trifluoromethyl coumarin (67DH4TFMC); 7-diethyl amino-4-methyl coumarin(7DEA4MC); 7-diethyl amino coumarin (7DEAC); 7-hydroxy-4-trifluoromethyl coumarin (7H4TFMC) and 7-methoxy-4-trifluoromethyl coumarin (7M4TFMC) respectively were purchased from Sigma Aldrich chemical Co., USA and were used as received. The FT infrared spectra of all the coumarin derivatives were recorded in the region 4000-400 cm^{-1} on Perkin Elmer Spektrum-BXII FTIR spectrometer using KBr pallet technique.

2.2 Geometry Optimization and Computational details

All the calculations were performed with the DFT study using Jaguar module of Schrödinger software. The structure optimization of the ground state of the coumarin derivatives have been performed with Becke's three parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) level, using 6-311G** basis set. The ground state geometry of each molecule has been fully optimized with default thresholds on residual forces and displacement [8,9]. Vibrational frequencies of five coumarin derivatives were calculated analytically to verify the optimized structure of the molecule. Frequency calculations were performed at the same levels of theory as geometry optimization to confirm that the stationary of all the optimized geometries by the B3LYP functional and 6-311G** basis set [10]. Jaguar application is used for calculating geometric optimization, vibrational frequency and bond length of coumarins.

III. Results and Discussion

DFT calculations were performed on Coumarin derivatives using jagaur module of Schrodinger software. The molecular structures of these coumarin derivatives are given in Fig.2 (a-f). Fig. 3(a-f) describes the numbering system adopted in the present paper.

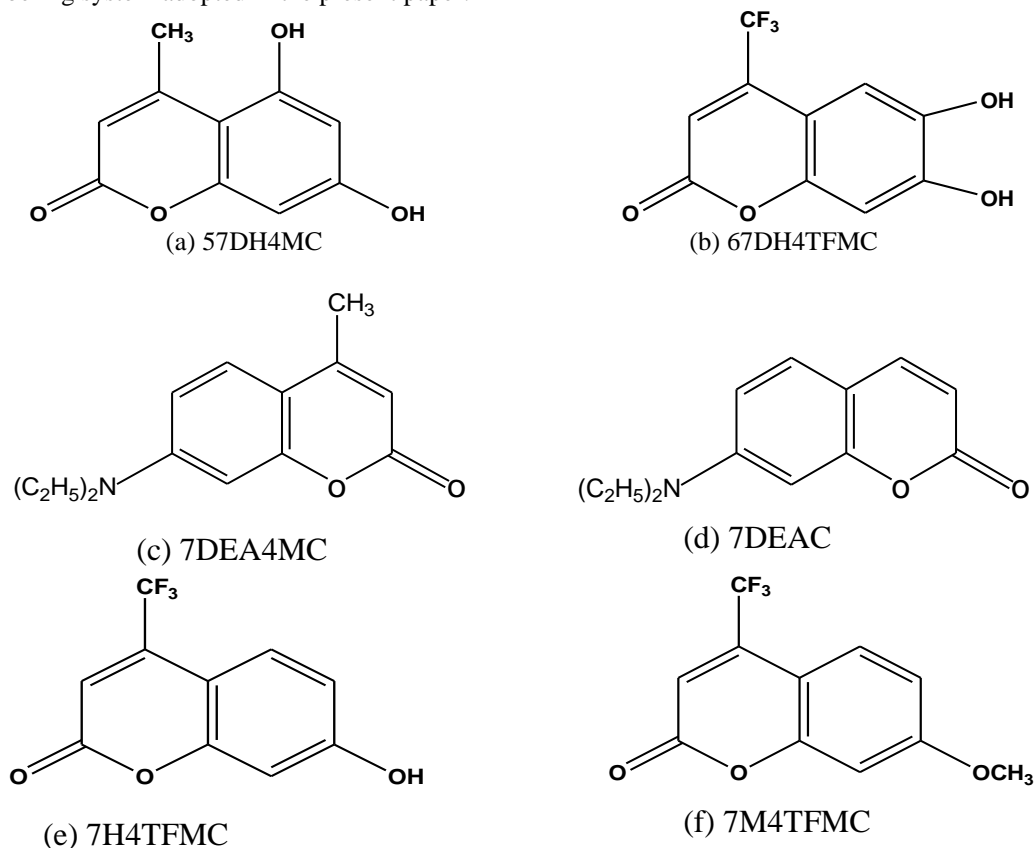


Fig. 2(a-f). Molecular structures of coumarin derivatives

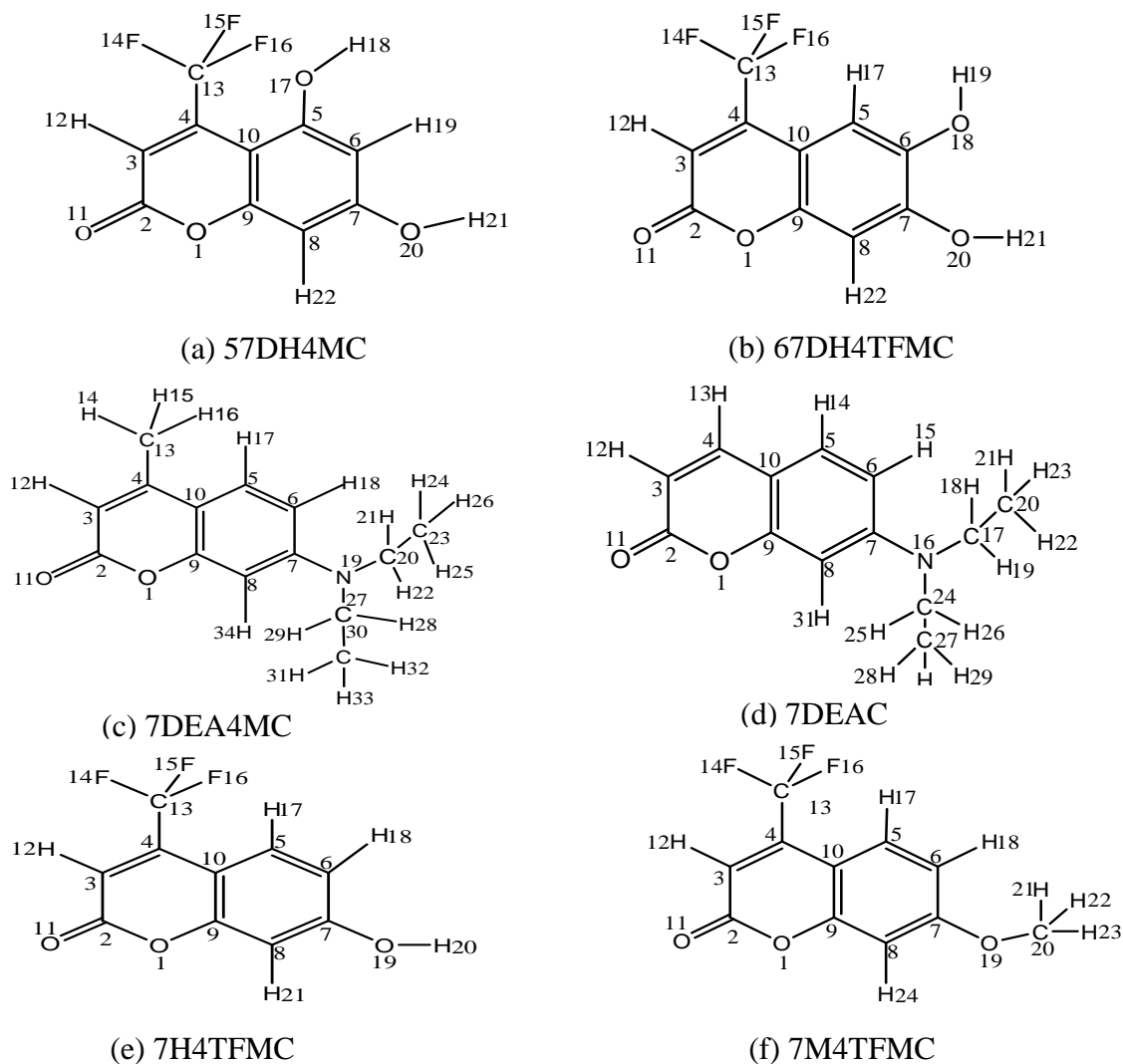


Fig. 3(a-f). Optimized structure and numbering system adopted for coumarin derivatives

1.1 Bond Length of Coumarins Derivatives

Bond length is determined by optimization of compound. By approximation the bond distance between two different atoms is the sum of the individual covalent radii. Bond length also depends on the bond order, orbital hybridization and resonance or delocalization of π -electrons of a molecule. Bond length decreases with increasing of bond order. e. g. C-C (1.54 Å) has largest bond length than C=C (1.34Å) and C≡C (1.20Å). Resonance is a reason of changes in bond lengths of coumarin derivatives. The bond lengths of some of the important bonds of different coumarin derivatives are presented in Table 1.

Table 1. Bond length of different bonds of coumarin derivatives

Molecule	Bond length (Å)			
	C4- C13	C2= O11	O1-C9	C6-C7
57DH4MC	1.512	1.201	1.361	1.395
67DH4TFMC	1.512	1.200	1.363	1.414
7DEA4MC	1.505 (1.48) ^a	1.210 (1.21) ^a	1.365 (1.37) ^a	1.423 (1.41) ^a
7DEAC	1.087*	1.208	1.365	1.413
7H4TFMC	1.514	1.207	1.364	1.407
7M4TFMC	1.514	1.207	1.365	1.408

* For molecule 7DEAC, there is C4- H13 bond instead of C4- C13. The numbering system is adopted according to the optimized structures given in Fig. 3(a-f)

^a The values are taken from Ref. [11].

The optimized bond length for C6-C13 (For 7DEAC; C6-H13) differs for coumarin derivatives because of their different functional groups. Bond length of C6-C13 for 7DEA4MC is about 1.505 Å, which is shorter than the length of a normal C-C single bond (1.540 Å) and longer than the length of a normal C-C double bond (1.340 Å). It indicates that bonds C-C bond lengths of 7-diethyl amino-4-methyl coumarin have partly the characteristic of single bond [12]. For 7DEAC, bond length for C6-H18 is 1.087 Å, which is approx C (sp³) – H bond (1.09). Bond lengths for C2-O11 bond of coumarin derivatives are approximately same because all seven compounds have bond length in the range of 1.183 – 1.210 Å. It is reported that the bond length between C-atom and O-atom for single bond is 1.42 Å and for double bond is 1.20 Å thus this bond is double bond between C=O bond of coumarin compound. Bond length for O1-C9 bond for coumarin derivatives are nearly same because all seven coumarin compounds have bond length of 1.342–1.365 Å. So this bond of coumarin compound is partly double bond. Bond length for C6-C7 bond for coumarin compounds is nearly same. Coumarin compounds have bond length in the range of 1.324–1.423 Å. It is reported that the bond length of aromatic compound at C-C bond for single bond is 1.54 Å, for double bond is 1.34 Å and for triple bond is 1.20 Å. Thus this is partially double bond.

3.2 HOMO-LUMO Energy Gap of Coumarin Derivatives

Frontier molecular orbitals (FMOs), highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are very important in quantum chemical parameters. The FMOs are important to determining molecular reactivity and the ability of a molecule to absorb light. The vicinal orbital of HOMO play the role of electron donor and LUMO play the same role of electron acceptor. The difference between HOMO and LUMO energy is termed the HOMO-LUMO energy gap. HOMO-LUMO gap are important for molecular reactivity and stability of the molecule to absorb light [13-18]. From the Table 2 we observed that 57DH4MC has highest HOMO-LUMO energy gap thus it is more stable molecule than other five coumarin molecules.

HOMO energy = -0.23226 hartrees

LUMO energy = -0.06669 hartrees

HOMO-LUMO energy gap (ΔE_g) = 0.16557 hartrees

Table 2. HOMO, LUMO energies and the energy gap of coumarin derivatives

Molecule	HOMO (hartrees)	LUMO (hartrees)	ΔE_g (hartrees)
57DH4MC	-0.23226	-0.06669	0.16557
67DH4TFMC	-0.23607	-0.0911	0.14497
7DEA4MC	-0.2134	-0.06251	0.15089
7DEAC	-0.19626	-0.04693	0.14933
7H4TFMC	-0.23897	-0.0815	0.15747
7M4TFMC	-0.23554	-0.08001	0.15553

3.3 UV/VIS Absorption Maxima Shift as Function of Electron-Donor/Acceptor Strength in Coumarins

When coumarins are excited by light absorption, intramolecular charge transfer (ICT) occurs. The ICT process can be assisted by the electron-donating group at the 7-position and/or an electron-withdrawing group either at the 3- or 4-position via resonance and inductive effect [19,20]. The absorption wavelength variation can be explained by considering coumarins with varying electron-donor/acceptor strengths. The ICT can be assisted by elevating the HOMO energy level of the donor in ring 1 and/or lowering the acceptor LUMO energy level in ring 2 [20]. These changes in energy levels can be explained by attaching different chemical substituents on both the rings. As the HOMO rises or the LUMO decreases, the UV-Vis absorption and emission wavelengths for coumarin compounds experienced a red shift (Bathochromic shift), as a less external energy is needed to

promote electrons from ring 1 to ring 2. So, to tune such wavelengths toward their blue region, electron-donating/-withdrawing substituents that widen the HOMO-LUMO energy difference (band gap) should be attached. Such conclusions can be equally extended to fluorescent and lasing wavelengths [19]. The influence of electron-donor/acceptor strength on the UV/Vis spectral wavelength is explained by the quantum chemical calculations discussed in this section. The effects of donor group are described by two coumarins 7DEAC and 7DEA4MC that have a common diethylamino [$-\text{N}(\text{C}_2\text{H}_5)_2$] group at their 7-position and 7DEA4MC has an additional methyl [$-\text{CH}_3$] group at 4-position. The ICT is pushed from ring 1 to ring 2, since $-\text{N}(\text{C}_2\text{H}_5)_2$ is more electron donating than $-\text{CH}_3$ group. This is because alkyl groups donate charge to the nitrogen atom via inductive effect: the more branched, the greater this charge transfer; likewise, the greater the number of saturated bonds in the alkyl chain, the larger the charge polarization. As the donor strength increases, the HOMO energy increases with respect to that of the LUMO, so causing the band gap to shrink (Table 2). Due to this corresponding UV/VIS absorption maxima experienced a red shift (bathochromic shift). As for 7DEAC experimental $\lambda_a(\text{max})$ in formamide is 386 nm whereas experimental $\lambda_a(\text{max})$ in formamide for 7DEA4MC is 381 nm [21]. The charge transfer from ring 1 to ring 2 is more in 7DEAC as in 7DEA4MC as methyl group is also electron donating which opposes the charge transfer via inductive effect. This result is explained in the Fig. 4.

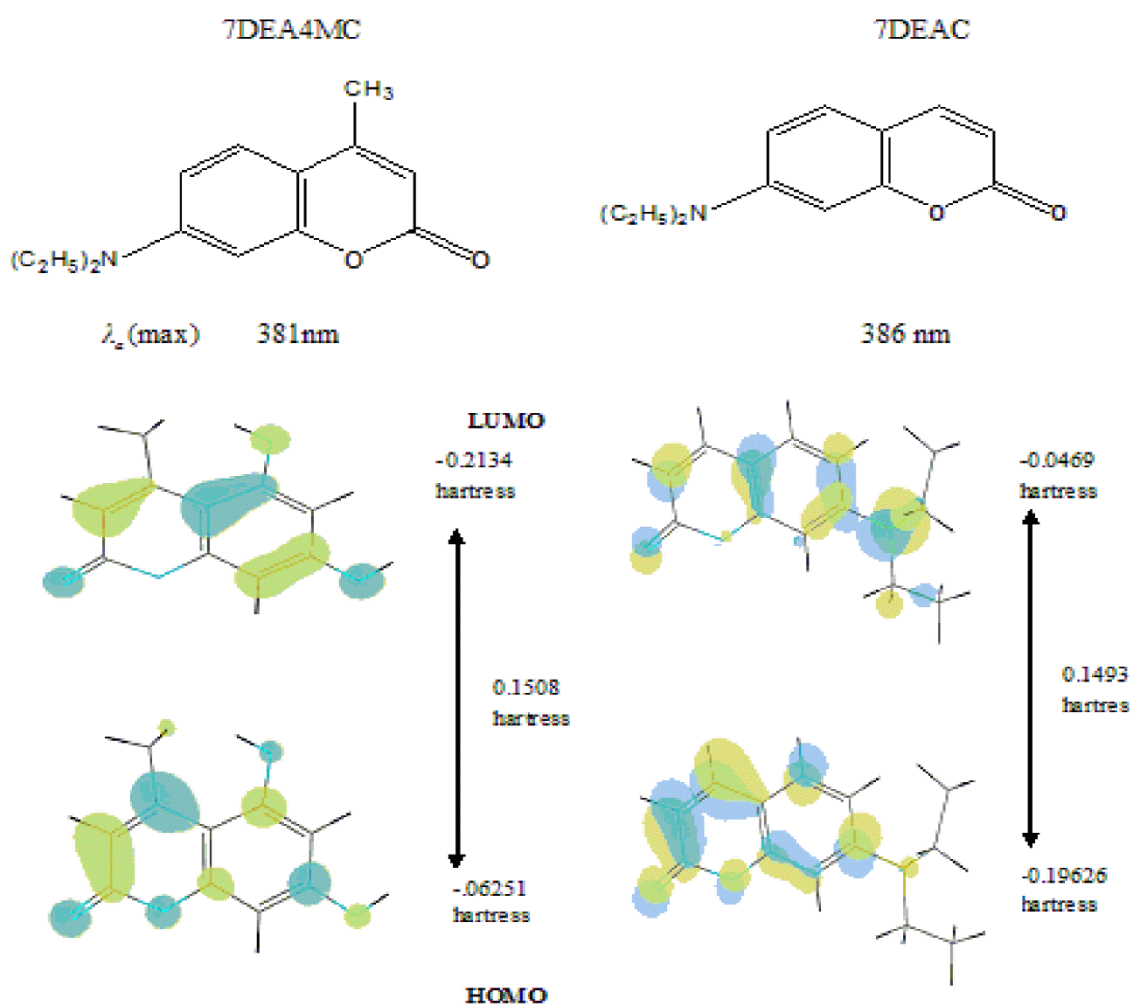


Fig. 4. 7DEAC and 7DEA4MC: Their molecular structure, UV-Vis peak absorption wavelengths in Formamide (Expt.), HOMO, LUMO and the corresponding band gaps of these molecules computed in the gas phase.

The effect of electron-donor/acceptor strength is further explored by three other coumarins derivatives namely 7M4TFMC, 7H4TFMC and 67DH4TFMC which have a common highly electron-withdrawing trifluoromethyl ($-\text{CF}_3$) group at the 4-position and a varying donor group at the 7-position (at 6,7- for 67DH4TFMC), which is a methoxy ($-\text{OCH}_3$) and hydroxyl ($-\text{OH}$) group for 7M4TFMC and 7H4TFMC respectively and two $-\text{OH}$ group at 6,7-position for 67DH4TFMC. As $-\text{CF}_3$ group is highly electron

withdrawing this induces a much stronger push-pull effect from the donor group in ring 1 to the acceptor group in ring 2. Substitution in the coumarin at various positions perturbs the electronic transitions of coumarin. The perturbation effect depends on the extent of the interaction between the substituent and the π -system of the coumarin nucleus. The methoxy group is a stronger electron donor than the hydroxyl group but the extent of their interaction with the π -electron system of the coumarin is nearly the same [22]. This can be explained as the experimental $\lambda_a(\text{max})$ in formamide for 7H4TFMC and 7M4TFMC is 339nm and 336nm respectively and their HOMO-LUMO band gap is 0.15747 and 0.15553 hartrees respectively. Substitution by another -OH group at 6-position facilitates the formation of the polar tautomer and this will show a larger red shift compared to 7M4TFMC and 7H4TFMC [22]. Due to this the experimental $\lambda_a(\text{max})$ in formamide for 67DH4TFMC is 373 nm (red shift compared to other two coumarins) [23] and the band gap is 0.14497 which is decreased as the donor strength increase as can be seen from Table 2.

The molecular orbital surfaces of the HOMO and LUMO for coumarin derivatives studied here are shown from Fig. 5 to Fig. 10. The localization of HOMO and LUMO can be seen from the figures of different coumarin derivatives.

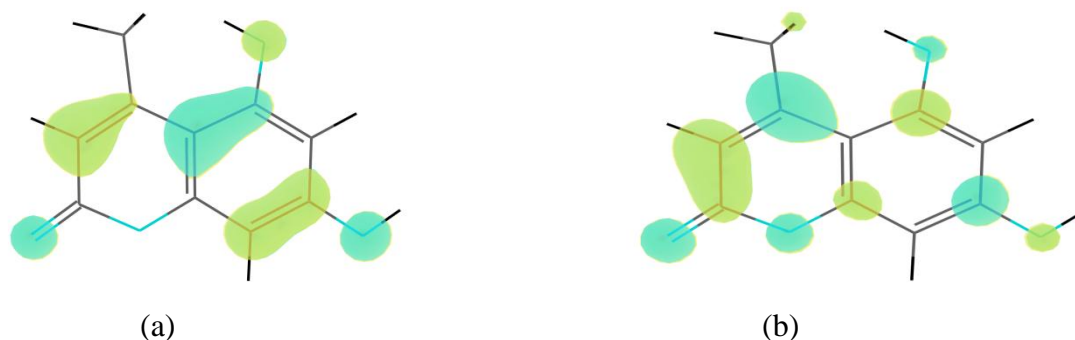


Fig. 5. Molecular orbital of the LUMO (a) and HOMO (b) for 57DH4MC by B3LYP/ 6- 311G** level

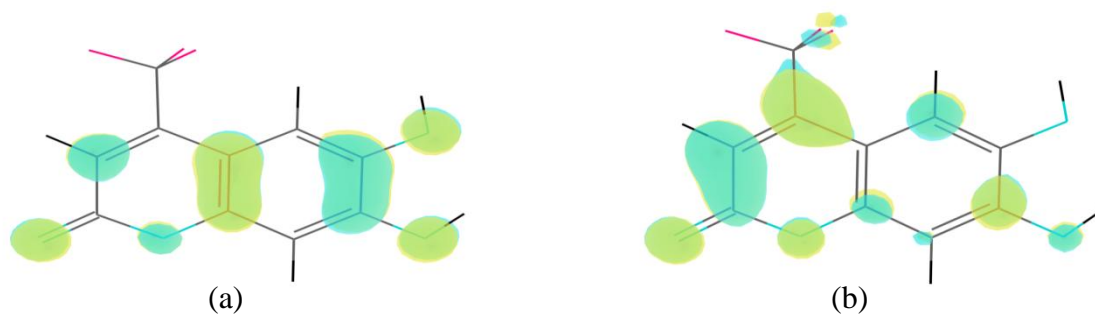


Fig. 6. Molecular orbital of the LUMO (a) and HOMO (b) for 67DH4TFMC by B3LYP/ 6-311G** level

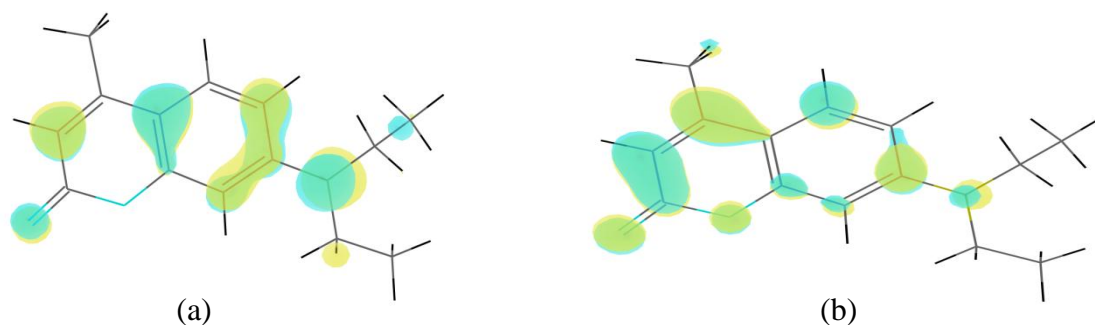


Fig. 7. Molecular orbital of the LUMO (a) and HOMO (b) for 7DEA4MC by B3LYP/ 6-311G** level

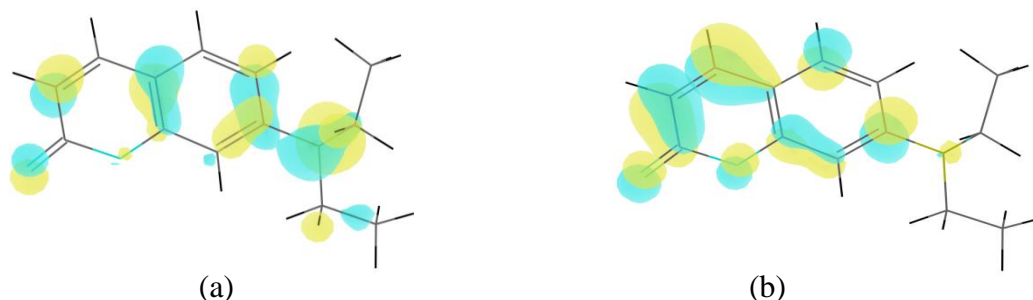


Fig. 8. Molecular orbital of the LUMO (a) and HOMO (b) for 7DEAC by B3LYP/ 6-311G** level

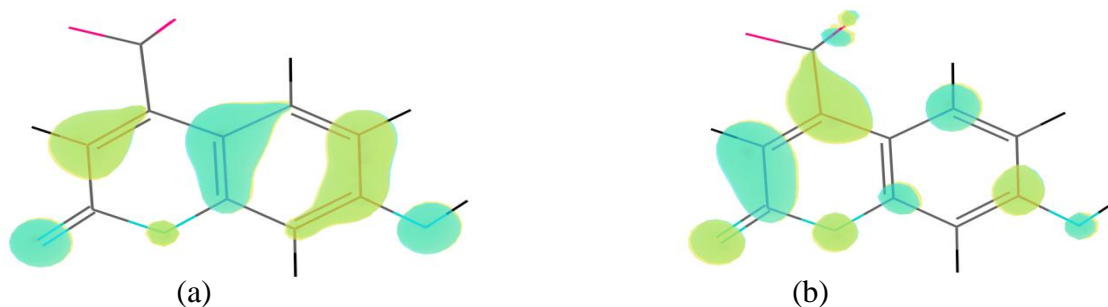


Fig. 9. Molecular orbital of the LUMO (a) and HOMO (b) for 7H4TFMC by B3LYP/ 6-311G** level

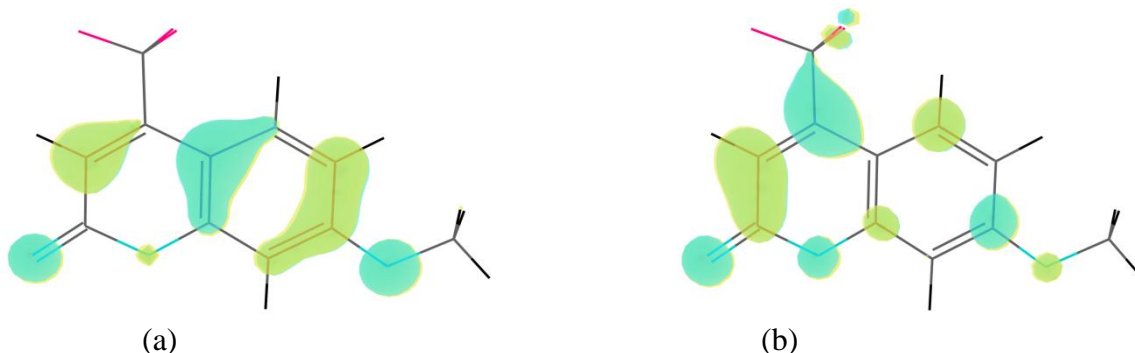


Fig. 10. Molecular orbital of the LUMO (a) and HOMO (b) for 7M4TFMC by B3LYP/ 6-311G** level

3.4 Vibrational Spectral Analysis of Coumarin Derivatives

Absorption of radiation in the Infrared (IR) region results in the excitation of bond deformation, either stretching or bending. Various stretching and bending vibrations occurs at certain quantized frequency. When IR light of that frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased. Vibrational frequencies were computed on optimized structure to ensure local minima of the compounds [24,25] by DFT method and they were also recorded by FTIR. For visual comparison, the observed and simulated IR spectra are presented in Figs.11-15. The vibrational frequency (IR intensity and IR spectra) are powerful structural techniques for investigate the biomolecule. The IR intensity plays an important role in the biological activity.

C-H vibrations

The heteroaromatic structure shows the presence of the C-H stretching vibrations in the region 3100–3000 cm^{-1} which is the characteristic region for the identification of the C-H stretching vibrations [24-31] and multiple weak bands recorded in this region. The C-H vibrations of the coumarin derivatives are observed at different vibrational frequency. The DFT computations predict these modes for B3LYP/6-311G** level of theory. The results showed that the theoretical data were in good agreement with the experimental results. The qualitative interpretation of intensities must rely upon the understanding of some basic aspects of intramolecular charge distribution and on their effects on infrared intensities.

The computed C-H stretching vibration values of coumarin compounds at C-H bond are 3222, 3217, 3247, 3227, 3238 and cm^{-1} for 57DH4MC, 67DH4TFMC, 7DEA4MC, 7DEAC, 7H4TFMC and respectively.

We determine via the DFT study that the stretching vibration of C-H bond of these five coumarin derivatives comes out of this range (3100 - 3000 cm^{-1}). It means there are no weak bands so this bond cannot overlap with one another. The theoretical IR intensity is found to be lower than the experimentally observed IR spectra between the region 3100-3000 cm^{-1} for 57DH4MC. For 67DH4TFMC the FTIR peaks are observed at 3075 and 3020 cm^{-1} which is in good agreement with the values given in literature and the calculated wavenumber for the vibrations is 3140 and 3080 cm^{-1} by B3LYP/6-311G** method are assigned to C-H stretching vibrations which are compared with the experimental results in Fig.12(a, b). The C-H stretching vibrations calculated by B3LYP/6-311G** method for 7DEAc and 7DEA4MC are 3150; 3099 cm^{-1} and 3140; 3080 cm^{-1} respectively (Figs. 13, 14). The C-H stretching vibrations for 7H4TFMC are weak when calculated by B3LYP/6-311G** method but we get clear IR bands in FTIR spectra as shown in Fig. 15(a,b).

C-H in-plane vibrations

The bands corresponding to the C-H in-plane bending vibrations are observed in the in the range 1500-1100 cm^{-1} [27,29,32,33]. The respective predicted bands are: 1428, 1403, 1397 and 1275 cm^{-1} when calculated by DFT method for B3LYP/6-311G** level and 1420, 1400, 1300 and 1270 cm^{-1} when measured experimentally for 57DH4MC (Fig. 11 a, b). The theoretical and experimental results are correlates well. Similarly the theoretical C-H in-plane bending vibrations are assigned at 1450, 1290, 1226, 1199 and 1150 cm^{-1} ; 1505 and 1462 cm^{-1} ; 1445, 1495, 1300 and 1160 cm^{-1} and 1355, 1309, 1250 and 1200 cm^{-1} for 67DH4TFMC, 7DEA4MC, 7DEAC and 7H4TFMC respectively. The experimental C-H in-plane vibrations are observed at: 1580, 1440, 1390, 1280 and 1170 cm^{-1} ; 1425, 1380, 1220 and 1550 cm^{-1} ; 1500, 1425, 1400, 1365, 1290 and 1190 cm^{-1} and 1515, 1400, 1310, 1250 cm^{-1} for 67DH4TFMC, 7DEA4MC, 7DEAC and 7H4TFMC respectively (Figs. 12 -15).

C-H out-of-plane vibrations

The C-H out-of-plane bending vibrations are predicted in the region 1000-750 cm^{-1} [28,34]. The computed wavenumber by B3LYP/6-311G** method for this mode of vibration is 1025, 890 and 840 cm^{-1} for 57DH4MC; 920, 750 and 690 cm^{-1} for 67DH4TFMC; 1090, 800 and 870 cm^{-1} (both weak bands) for 7DEA4MC; 990 and 850 cm^{-1} (weak) for 7DEAC and 895, 860 and 800 cm^{-1} (weak bands) for 7H4TFMC respectively. The band recorded experimentally at 850 and 800 cm^{-1} for 57DH4MC; 910, 880, 830, 765 cm^{-1} for 67DH4TFMC; 1035, 925, 875, 820 cm^{-1} for 7DEA4MC and 860 cm^{-1} (weak band) for 7H4TFMC respectively are assigned to C-H out-of-plane bending vibrations. The computed and FTIR spectra are shown in Figs. 11-15.

C=O vibrations

Coumarins have two characteristics strong absorption bands arising from C=O and C-O stretching vibrations. This vibration is particularly clear and is sensitive to the infrared environment [28,35]. The intense C=O stretching vibrations occurs at higher frequencies than that normal ketones. The frequency of C=O stretching depends on various factors. The α , β and γ , δ -unsaturated, δ lactones frequently display two carbonyl absorption bands in 1775-1740 cm^{-1} and 1740-1715 cm^{-1} regions, even though only one carbonyl group is present mainly due to Fermi resonance [28,36]. The C=O stretching vibrations are 1885, 1825, 1841, 1835 and 1846 cm^{-1} for 57DH4MC, 67DH4TFMC, 7DEA4MC, 7DEAC and 7H4TFMC respectively as computed by B3LYP/6-311G** level [37,38]. These results show a deviation of about 100-150 cm^{-1} which may be due to the presence of strong intermolecular hydrogen bonding. The experimental C=O stretching vibrations are observed at 1700, 1750, 1700, 1680 and 1765 cm^{-1} for 57DH4MC, 67DH4TFMC, 7DEA4MC, 7DEAC and 7H4TFMC respectively. The C=O in-plane and out-of-plane bending vibrations computed by B3LYP/6-311G** method shows good agreement with recorded spectral data. The simultaneous IR activation of the ring mode and carbonyl mode clearly explains the charge transfer interaction between the electron-donating group and the acceptor group through the π -conjugated system. The π -electron cloud movement from the donor to the acceptor can make the molecule highly polarized through the single/ double path, when it changes from the ground state into the first excited state. It is inferred that this mechanism plays an important role in the biological activity of coumarin compound.

C-C stretching vibrations

The ring C-C stretching vibrations have given rise to characteristic bands covering the spectral range from 1625-1280 cm^{-1} [26-28] for the five bands in this region. According to Scorates [39], the presence of conjugate substituent such as C-C causes a heavy doublet formation around the region 1625-1575 cm^{-1} . The six ring carbon atoms undergo coupled vibrations which are known as skeleton vibrations to give a maximum of four bands in the region 1660-1420 cm^{-1} . The actual positions of these bands are determined not by the nature of the substituents but rather by the form of the substitution around the aromatic ring. The theoretically computed

wave number by B3LYP/6-311G** level are 1697, 1675, 1428, 1403, 1397 cm^{-1} are assigned to C-C stretching vibrations for the molecule 57DH4MC which present consistent agreement with FTIR observation at 1675, 1600, 1575, 1500, 1400 and 1300 cm^{-1} (Fig. 11). For the molecule 67DH4TFMC the computed and experimental wave number assigned to this mode of vibrations are 1675, 1562, 1450, 1358, 1290 cm^{-1} and 1620, 1580, 1440, 1390 cm^{-1} . The theoretical wave number at 1676, 1666, 1505 cm^{-1} (weak); 1676, 1665, 1445, 1300 cm^{-1} ; 1684, 1681, 1600, 1355 cm^{-1} are assigned to C-C stretching vibrations for 7DEA4MC, 7DEAC and 7H4TFMC respectively. The FTIR bands observed are in good agreement to the theoretical results. The C-C in-plane and out-of-plane bending vibrations are well within the region and are good agreement with the experimental values as shown in the Figs. 11-15.

CH₃ stretching vibrations

Methyl group are generally referred to as electron donating substituents in the aromatic ring system. The asymmetric and symmetric stretching modes of CH₃ group normally appear in the region 3000-2850 cm^{-1} [39-41]. The out-of-plane stretching mode of CH₃ group is expected around 2980 cm^{-1} and symmetric one is expected around 2870 cm^{-1} . The methyl group hydrogen atoms in coumarin derivatives are subjected to the electronic effect of hyperconjugation leading to the decrease of infrared intensities and blue shifting of stretching wave numbers. The computed CH₃ vibration modes by B3LYP/6-311G** level are 2959 and 2975 cm^{-1} for 7DEA4MC and 7DEAC respectively, which is in agreement of the experimental IR spectra shown in Figs.13 and 14. The asymmetric and symmetric bending vibrations of CH₃ group are expected in the region 1465-1410 cm^{-1} and 1390-1370 cm^{-1} [39,41,42]. The computed and FTIR bands are in good agreement with the literature data mentioned above. The rocking vibrations of the -CH₃ group normally appear in the region 1070-1010 cm^{-1} [26,39]. The theoretical calculated values by B3LYP method show agreement with literature as well as the experimental observations for 7DEA4MC and 7DEAC respectively.

O-H vibrations

The hydroxyl stretching and bending vibrations can be identified by the strength of the band, which are dependent on the extent of hydrogen bonding [26,40]. The non-hydrogen bonded or free hydroxyl group absorbs strongly in the region 3700-3584 cm^{-1} while the existence of intermolecular hydrogen bond formation can lower the O-H stretching wavenumber to the region 3550-3200 cm^{-1} . The computed wavenumber by B3LYP/6-311G level at 3917 cm^{-1} for 57DH4MC is assigned to the O-H vibration, while the experimentally observed IR spectrum shows a peak at around 3400 cm^{-1} are assigned to O-H stretching vibration, which reveals the presence of intermolecular hydrogen bonding network. For 67DH4TFMC the IR bands are calculated at 3847 and 3772 cm^{-1} by B3LYP/6-311G level are assigned to the O-H stretching vibrations. While for 7H4TFMC the calculated IR band at 3819 cm^{-1} is assigned to O-H stretching vibration, while the bands observed between 3500-3400 cm^{-1} are assigned to these modes. This again clearly shows the presence of intermolecular hydrogen bonding. The appearance of the red shift in the O-H stretching vibration is due to the formation of O-H...O hydrogen bond. The lone pairs of oxygen (electron donor) with the σ^* (O-H) leads to increase the electron density in this orbitals followed by weakening the O-H bond is evident from lowering the O-H stretching wavenumber [28, 43].

The O-H in-plane and out-of-plane bending vibrations are also observed. Normally O-H in-plane bending vibration is found with C-H in-plane and C-C stretching vibrations. The position of the band is dependent on the strength of the hydrogen bond, stronger the hydrogen bond, the higher the wavenumber. The presence of hydrogen bonding, the characteristics band due to out-of-plane bending is observed at 450-350 cm^{-1} [39,41]. These bands are observed in the experimental spectra of all the three hydroxyl derivatives of the coumarins.

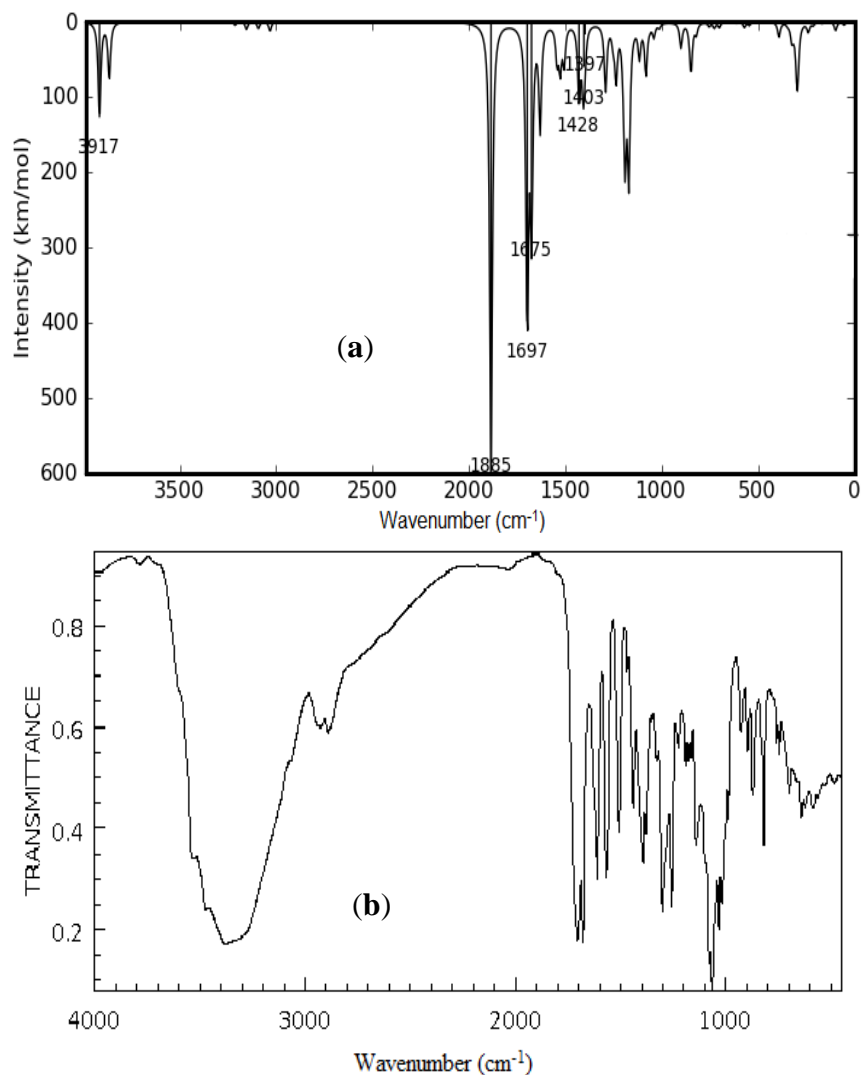
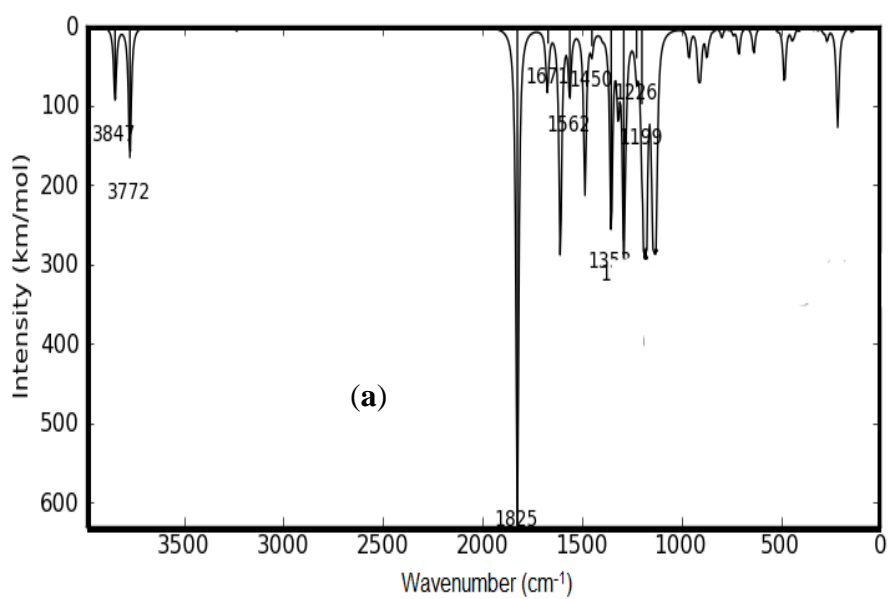


Fig.11. Experimental FT Infrared spectrum (a) and Computed Infrared spectrum (b) of 57DH4MC by B3LYP/6-311G** level.



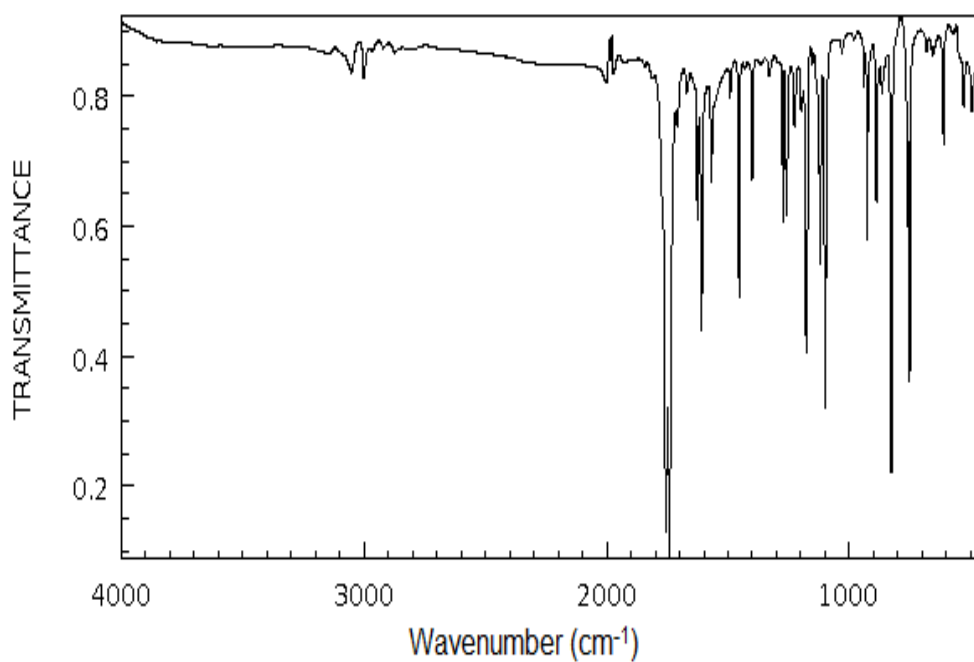
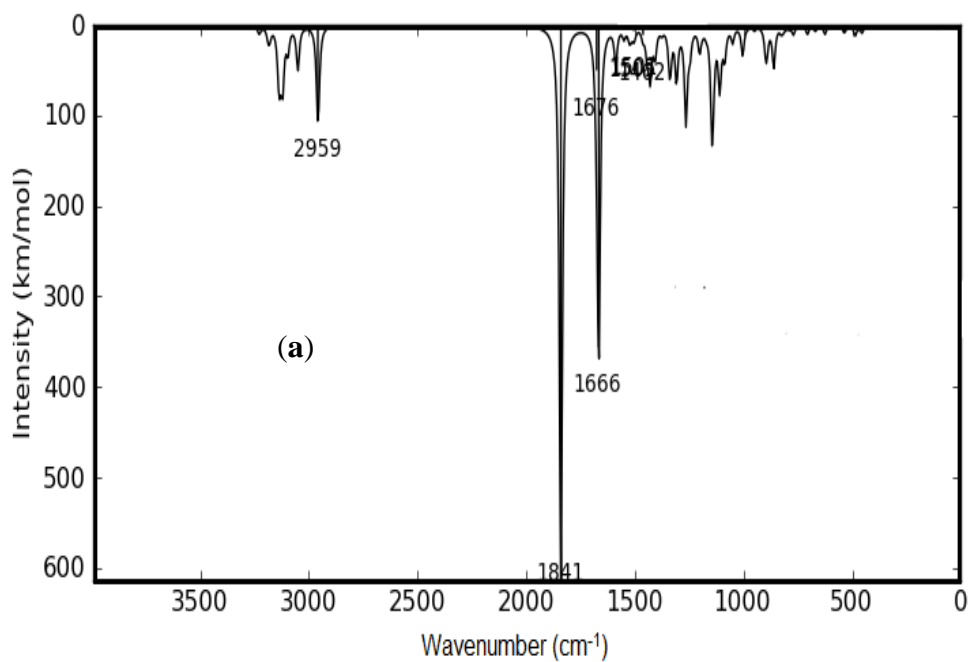


Fig.12. Experimental FT Infrared spectrum (a) and Computed Infrared spectrum (b) of 67DH4TFMC by B3LYP/ 6-311G** level



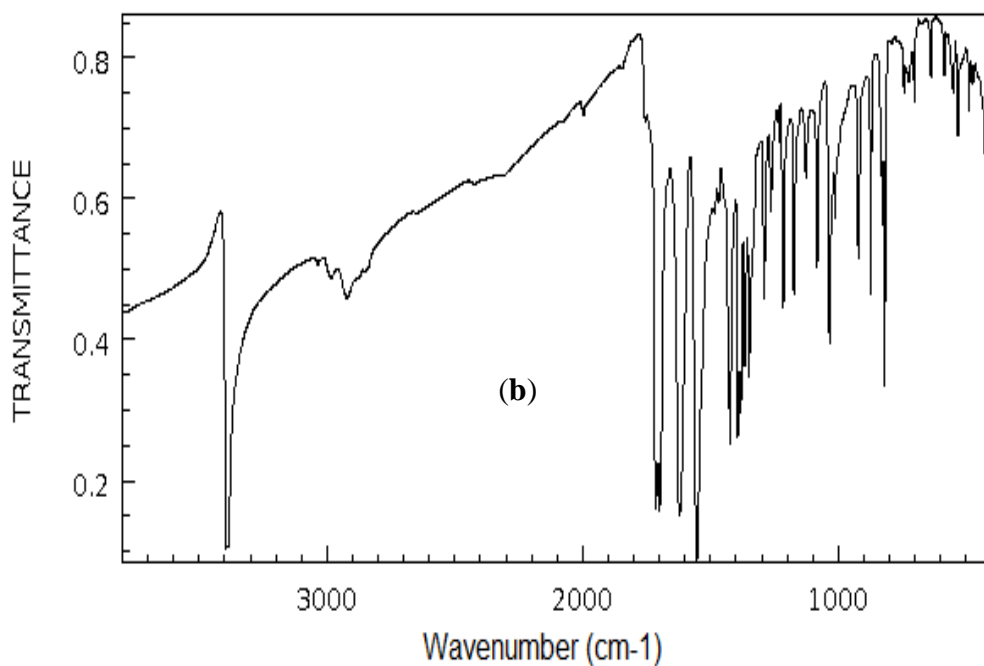
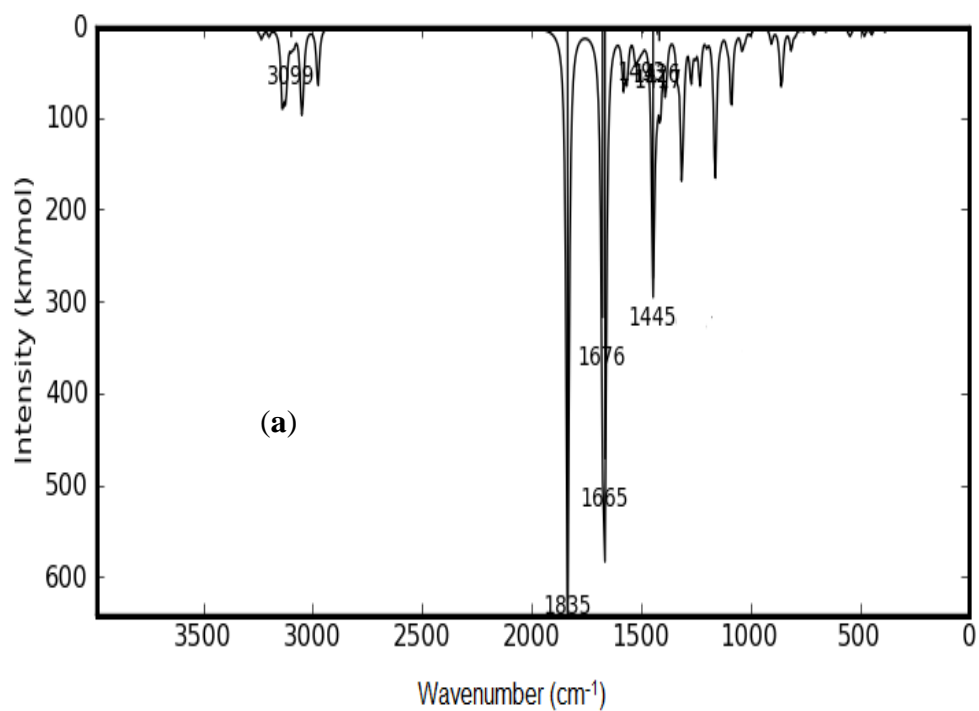


Fig. 13. Experimental FT Infrared spectrum (a) and Computed Infrared spectrum (b) of 7DEA4MC by B3LYP/6-311G** level



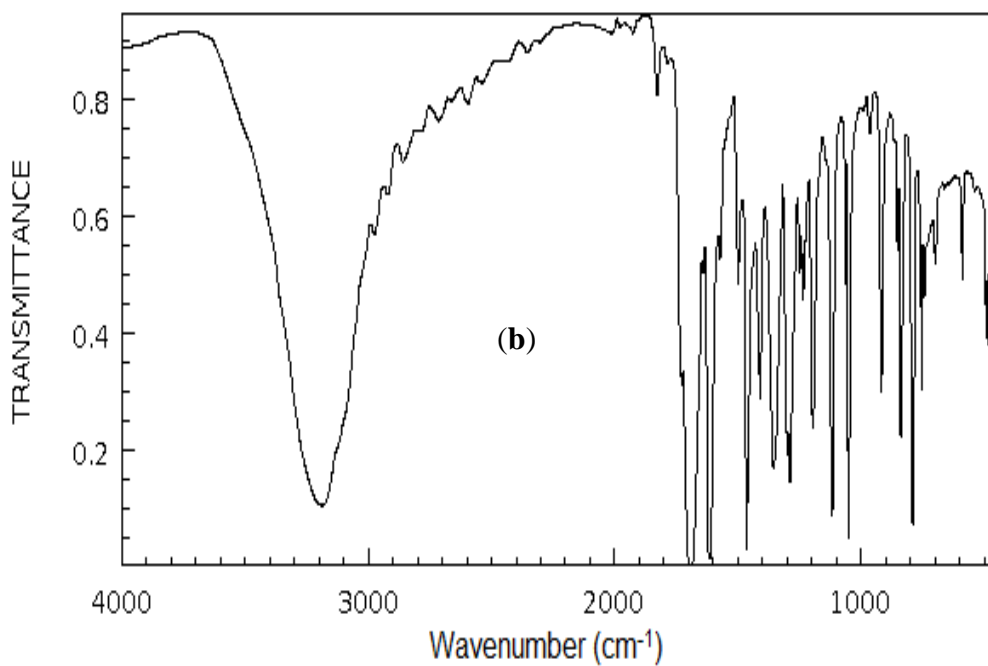
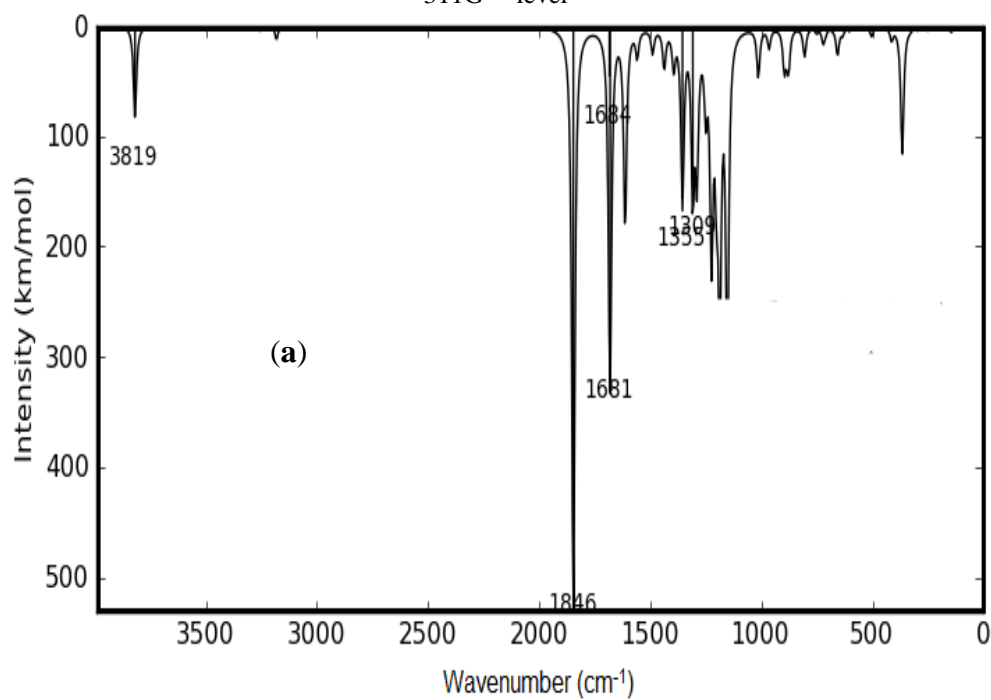


Fig.14. Experimental FT Infrared spectrum (a) and Computed Infrared spectrum (b) of 7DEAC by B3LYP/ 6-311G** level



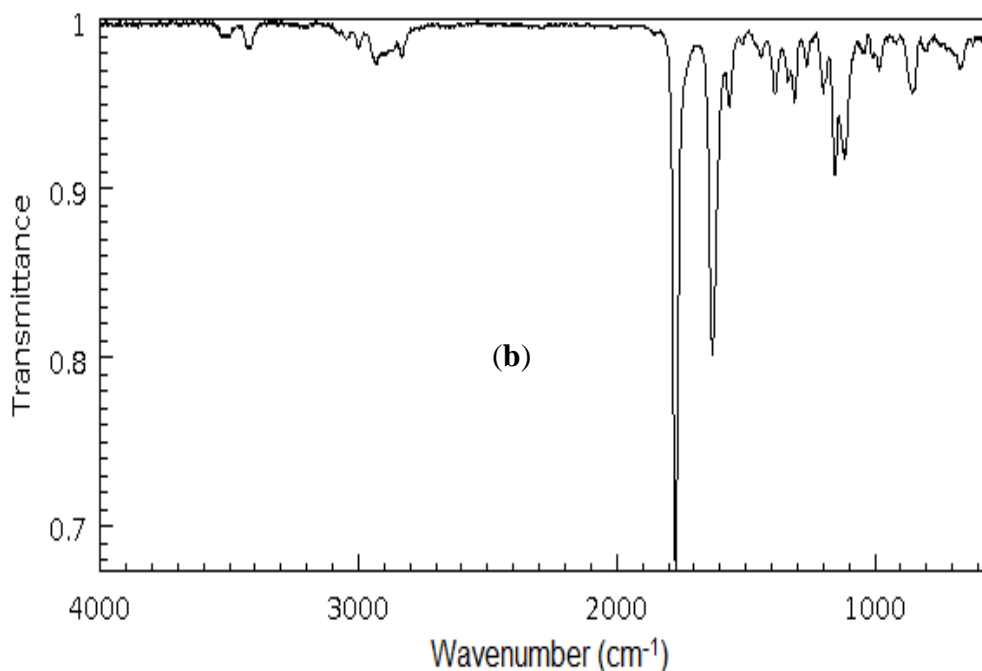


Fig.15. Experimental FT Infrared spectrum (a) and Computed Infrared spectrum (b) of 7H4TFMC by B3LYP/6-311G** level

IV. Conclusions

The coumarin derivatives have photochemical, photophysical, and pharmaceutical properties. Because of these properties, the DFT study of coumarin derivatives was performed by using B3LYP/6-311G** level of theory. Density functional theory (DFT) methods are often used for determining the molecular electronic structure, even though many of the most functions use parameters derived from empirical data, or from more complex calculations, such as NBO analysis, Vibrational frequency. Bond length of coumarin derivatives at C4-C13 (C4-H13 for 7DEAC) was calculated that bond length is partly single bonded. Bond length for C2=O11 bond is partly single bonded and O1-C9 bond is double bond and C6-C7 bond is partly double bonded. HOMO-LUMO energy gap were calculated and it was found that 57DH4MC have high HOMO-LUMO energy gap. It means that this coumarin derivative is more stable than others. The UV/VIS absorption maxima shift was interpreted in terms of electron donor/acceptor strength of coumarins. The intramolecular charge transfer occurred due to a “push–pull” effect which leads to a predominance of resonance states in benzene rings of these coumarins. Increasing the “push-pull” effect reduced coumarin band gaps and lead to a spectral red shift in UV/VIS absorption and this was supported by quantum chemical calculation. This structure-property relationship studies on coumarins is useful in understanding their electronic operational mechanism so that more efficient coumarin dye for laser and dye-sensitized solar cells (DSSC) application can be designed. The IR spectra of coumarin derivatives was calculated by DFT at B3LYP/6-311G** level. The difference between observed and computed wave number values of most of IR vibrations was small. So the assignment made at DFT level with only reasonable deviation from experimental values seemed to be correct.

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