Studies of Substituent and Solvent effect on Spectroscopic Properties of 6-OH-4-CH₃, 7-OH-4-CH₃ and 7-OH-4-CF₃ Coumarin

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Abstract

This paper reports the solvent effects on the electronic absorption and fluorescence emission spectra of 6-OH-4-CH₃, 7-OH-4-CH₃ and 7-OH-4-CF₃ Coumarin derivatives having -OH, -CH₃ and -CF₃ substituent at different positions in various solvents (Polar and Non-Polar). The first excited singlet state dipole moment and ground state dipole moment were calculated using Bakhshiev, Kawski-Chamma-Viallet and Reichardt-Dimroth equations and were compared for all the Coumarin studied. In all cases the dipole moments were found to be higher in the excited singlet state then in the ground state indicating a substantial redistribution of π-electron density in the excited state. The angle between the excited singlet state and ground state dipole moment is also calculated. The red shift of the absorption and fluorescence emission bands, observed for all the Coumarin studied upon increasing the solvent polarity indicating that the electronic transitions were π→π* nature.

Keywords: Coumarin, Solvent effects, Absorption spectra, Emission spectra, Excited Singlet state dipole moment, Ground state dipole moment, Solvatochromism.

1. INTRODUCTION

Coumarin Dyes are widely used to generate lasers in the blue green region of the spectrum [1]. Coumarins known for their pleasant odor are used in perfumery, foods and beverages manufacture [2]. Also Coumarin derivatives can be used as intermediates in the manufacture of agrochemicals and pharmaceuticals with strong
anti-bacterium, anti-cancer, anti-HIV activities etc. [3-8]. Moreover Coumarins are known to be strongly fluorescent with absorption and emission phenomenon and can be used as photo luminescent materials [9,10]. The fluorescence of Coumarin molecule is strongly dependent on the local environment such as polarity, hydrogen bonding ability and pH etc apart from the different substituent on Coumarin moiety.

The optical properties and solvatochromic behavior of the Coumarin depend on the nature of electron donor / acceptor substituents, charge transfer (CT) mechanism and solute-solvent interactions [11].

The process by which solvent molecules surround and interact with solute molecule is called as solvation. Solvation plays a crucial role in various processes taking place in the liquid phase and thus studying the solvation process is important for understanding the solvent effect on chemical reactions [12], many biological processes including transportation, signaling, metabolism are also controlled by solvation [13,14]. Solvent parameter such as dielectric constant and refractive index are involved in representing various solvent properties. Polarity is an important solvent property for explaining solvent effect of many chemical processes. Solvent molecules are considered to be as dielectric continuum and create the reaction filed through the dipolar interaction with the solute molecule. The reaction field is proportional to the magnitude of the dipole moment and polarizability of the solvent.

The concept of reaction field theory is useful in relating solvent effect with the change of electronic transition energy and frequency shift. The electronic emission spectra as well as the absorption spectra of many chromophore containing organic molecules are commonly modified by the solvents. Spectral changes due to solvent properties may arise from either the physical inter-molecular solute-solvent interactions such as dipolar interaction or the chemical processes such as electron (or proton) transfer, complexation, isomerization etc. The solvent effects on the stokes shift of Coumarin molecules were found to be correlated with this model.

Coumarin moiety as such is non-fluorescent, However, Coumarins having substituents at different places show fluorescence. In general electron donating substituents tend to enhance emission intensity while electron accepting or with drawing substituent tends to diminish it. Also the shift in position of the electronic bands of aromatic compounds due to substitution of the exocyclic group depends on the nature of the substituent group and its electronic interaction with the parent molecule. Substituent leads to a redistribution of charge in the ground as well as the excited state [15]. Some times more efficient conjugation takes place due to intra molecular charge transfer in the excited state. The substituent group provides additional levels for absorption and fluorescence to take place. The spectral characteristics of these Coumarin dyes are strongly altered by the nature of substituent, position of substituent on Coumarin ring and its surrounding.
As the substitution changes the excited state dipole moment of substituted Coumarin molecule as well as location of absorption and fluorescence band which improves solubility in organic solvents and modulate their resistance to chemical and photochemical protonation in certain environment. Present paper reports the effect of solvent and substituent in 6-OH-4-CH₃, 7-OH-4-CH₃, and 7-OH-4-CF₃ Coumarin having almost identical structure with substituent –OH, -CF₃ and –CH₃ at different position.

It is a known fact that dipole movement of a molecule is different in ground and excited state, because of change in electron density. A prior knowledge of dipole moment of electronically excited state is often useful in design of non-linear optical materials and elucidation of many Photochemical transformation. The experimental data on dipole moment are useful in parameterization of quantum chemical methods. Dipole moments are also useful in understanding the nature of the emitting state and also in the evaluation of the dielectric friction contribution to the rotational reorientation of polar solutes in solvents. The Stoke’s shift and yield of fluorescence and the potential for lasing are influenced by the maintenance of a large excited state dipole moment. Dye substitution pattern and dye media both play important role in dipole stabilization.

The influence of solvents on fluorescence spectra may have several origin ranging from perturbation due to the solvent refractive index and dielectric constant to hydrogen bonding or even complexation between the fluorophore and the solvent. These factors can change the energy difference between the ground (S₀) and first excited state (S₁) and can shift the emission spectra. Hydrogen bonding and solvent polarity are the key factors in controlling pathways of energy dissipation following electronic excitation. Solvent moderated shifts of the energy level may enhance or inhibit radiation less transition to the ground state via the proximity effect as discussed by lim [16]. Different methods in literature are available for the estimation of excited state dipole moment such as externally cause spectral shift (electrochromism) or internally caused spectral shift (solvatochromism).

Methods such as electric fluorescence polarization [17], electric dichroism [18], microwave conductivity [19] and stark splitting [20] are generally considered as more accurate method but because of equipment and restriction on the molecules to be chosen for the study, these methods are not used widely. However the solvatochromic method is based on the shift of the UV-VIS absorption and fluorescence maxima in different solvents of varying polarity. A radiative transition (absorption or emission) connects a relaxed initial state to a Franck-Condon (FC) final state. When the molecule is surrounded by a liquid solvent each state is stabilized (or destabilized) by an energy Eₛ which is salvation energy. The difference in the salvation energy of the initial and final states in various solvents is observed as solvatochromic shifts. Because of change in excited state of molecule is different from the ground state the change of dipole moment is greater in excited state than in ground state. The change in dipole moment of the 6-OH-4-CH₃, 7-OH-4-CH₃ and 7-OH-4-CF₃ Coumarin in
exited state with respect to ground state is determined by using following solvatochromic methods.

**METHOD I**

It has been suggested that Bakshiev [21] and Kawski-Chamma-Viallets [22] Eqs. I and II gives the best results which are

\[ \nu_a - \nu_f = m_1 F_1 (\epsilon, n) + \text{const.} \]  
(1)

\[ \frac{(\nu_a + \nu_f)}{2} = m_2 F_2 (\epsilon, n) + \text{const.} \]  
(2)

Where \( \nu_a \) is an absorption maximum and \( \nu_f \) is an fluorescence maximum, wave number given in cm\(^{-1}\).

The expressions for \( F_1 (\epsilon, n) \) (Bakshiev’s polarity function) and \( F_2 (\epsilon, n) \) (Kawski-chamma-Viallet polarity function) are given as:

\[ F_1 (\epsilon, n) = (2n^2 + 1/n^2 + 2) * ((\epsilon - 1/ \epsilon - 2) - (n^2 - 1/n^2 + 2)) \]  
(3)

\[ F_2 (\epsilon, n) = [(2n^2 + 1/2(n^2 + 2)) * ((\epsilon - 1/ \epsilon - 2) - (n^2 - 1/n^2 + 2) + (3(n^4-1)/2(n^2 + 2)^2)] \]  
(4)

In equations (3) and (4), \( n \) is refractive index and \( \epsilon \) is the dielectric constant of the solvents.

From equations (1) and (2), expression for slopes \( m_1 \) and \( m_2 \) are given as:

\[ m_1 = 2(\mu^* - \mu)^2 / hca^3 \]  
(5)

\[ m_2 = 2(\mu^{*2} - \mu^2) / hca^3 \]  
(6)

Where \( \mu \) is ground state and \( \mu^* \) is excited state dipole moment of the solute molecule; \( h \) is the Planck’s constant, \( c \) is the velocity of light in vacuum, and \( a \) is the Onsagar cavity radius of the solute molecule. The values of the solute cavity radii \( a \) were calculated using the method of partial volume addition as suggested by Edward [23].

The ground and excited state dipole moments are estimated by means of the following equations. Assuming that the symmetry of the investigated solute molecule remains unchanged upon electronic transition, the angle between the ground and excited state dipole moments is small, and the cavity radius \( a \) is same in both ground and excited state, based on equations (5) and (6):

\[ \mu = |m_2 - m_1| / 2 [hca^3 / 2m_1]^{1/2} \]  
(7)

\[ \mu^* = |m_2 + m_1| / 2 [hca^3 / 2m_1]^{1/2} \]  
(8)
The slopes $m_1$ and $m_2$ can be determined by plotting the $(\nu_a - \nu_f)$ Stokes shift and $(\nu_a + \nu_f)/2$ against the bulk solvent polarity functions $F_1(\varepsilon, n)$ and $F_2(\varepsilon, n)$ respectively, for different solvents.

**METHOD II**

The value of excited state dipole moment was also calculated using Richardt-Dimroth equation, as suggested by J.J.Aaron et.al.[24]. The excited state dipole moment of several substituted coumarins was calculated by means of microscopic solvent polarity parameter, $E^{N}_T$ (Method II). Correlation of solvatochromic Stokes shift was superior to the one obtained by using bulk solvent polarity functions. Also the error in estimation of Onsagar cavity radius $a$ has been minimized since a ratio of two Onsagar radii is involved.

The excited state dipole moment is determined by:

$$\nu_a - \nu_f = 11307.6(\frac{\Delta \mu}{\delta \mu_B})^2 * (a_B/a)^2 \ E^{N}_T + \text{const.} \quad (9)$$

Where $E^{N}_T$ is the solvent polarity parameter proposed by Reichardt [25] which is based on the absorption wavenumber of a standard betaine dye in the solvent. Its value for different solvents is given in Table II. $\Delta \mu_B$ ($= 9D$) and $a_B$ ($= 6.2\text{Å}$) are the dipole moment changes on excitation and Onsagar cavity radius respectively of betaine dye, whereas $\delta \mu$ and $a$ are corresponding quantities for the molecules of interest. The change in dipole moment $\delta \mu$ is evaluated using the plot of $(\nu_a - \nu_f)$ Stokes shift verses $E^{N}_T$, then value of excited state dipole moment is estimated by using the value of ground state dipole moment calculated from Method I.

2. **Experimental**

The Experimental data of the values for $U_a$ and $U_f$ in different solvents for 6-OH-4-CH$_3$ 7-OH-4-CH$_3$ and 7-OH-4-CF$_3$ Coumarin were taken as it is from Ref. M.M. Hussain et al. [26] and N. Pandey et al. [1] and Ph.d.thesis of R. Giri submitted to Delhi University. The molecular structures of 6-OH-4-CH$_3$ 7-OH-4-CH$_3$ and 7-OH-4-CF$_3$ Coumarin are given in Fig. 1.
3. RESULT AND DISCUSSION

We have divided our study into two parts (A) SOLVENT EFFECT (B) SUBSTITUENT EFFECT

A) SOLVENT EFFECT: The observed values of $\nu_a$ and $\nu_f$ in various polar and nonpolar solvents are listed in Table 1-3. The calculated value of the solvent parameter $F_1 (\varepsilon,n)$, $F_2 (\varepsilon,n)$ and $E_{TN}$ are also given in Table 1-3.

Table 1: Observed Values of $\nu_a$ (cm$^{-1}$) and $\nu_f$ (cm$^{-1}$) for 6-OH-4-CH$_3$ coumarin studied in different solvents along with the calculated values of solvent parameters $F_1 (\varepsilon,n)$, $F_2 (\varepsilon,n)$ & $E_{TN}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-OH-4-CH$_3$ Coumarin</td>
<td>$\nu_a$</td>
<td>292.2</td>
<td>296.7</td>
<td>292.4</td>
<td>289.5</td>
<td>295.0</td>
<td>289.0</td>
<td>289.8</td>
<td>291.5</td>
<td>294.1</td>
<td>294.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_f$</td>
<td>234.7</td>
<td>238.1</td>
<td>234.7</td>
<td>238.1</td>
<td>235.1</td>
<td>227.3</td>
<td>235.3</td>
<td>228.8</td>
<td>240.4</td>
<td>240.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_1 (\varepsilon,n)$</td>
<td>0.790</td>
<td>0.590</td>
<td>0.489</td>
<td>0.866</td>
<td>0.373</td>
<td>0.370</td>
<td>0.841</td>
<td>0.545</td>
<td>0.838</td>
<td>0.003</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>$F_2 (\varepsilon,n)$</td>
<td>0.639</td>
<td>0.582</td>
<td>0.497</td>
<td>0.656</td>
<td>0.426</td>
<td>0.487</td>
<td>0.744</td>
<td>0.549</td>
<td>0.711</td>
<td>0.339</td>
<td>0.351</td>
</tr>
<tr>
<td></td>
<td>$E_{TN}$</td>
<td>0.355</td>
<td>0.309</td>
<td>0.228</td>
<td>0.472</td>
<td>0.117</td>
<td>0.259</td>
<td>0.444</td>
<td>0.207</td>
<td>0.400</td>
<td>0.111</td>
<td>0.009</td>
</tr>
</tbody>
</table>

A= Acetone, B= Dichloromethane, C= Ethyl Acetate, D= Acetonitrile, E= Diethyl ether, F= Chloroform, G=DMSO, H= THF, I= DMF, J= Benzene, K= Toluene
Table 2: Observed Values of $\nu_a$ (cm$^{-1}$) and $\nu_f$ (cm$^{-1}$) for 7-OH-4-CH$_3$ coumarin studied in different solvents along with the calculated values of solvent parameters $F_1$ ($\varepsilon,n$), $F_2$ ($\varepsilon,n$) & $E_{TN}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>X10$^2$ (cm$^{-1}$)</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-OH-4-CH$_3$</td>
<td>$\nu_a$</td>
<td>309.6, 311.5, 310.5, 308.6, 308.6, 307.7, 307.7, 305.8, 311.5</td>
<td>A, B, C, D, E, F, G, H, I</td>
</tr>
<tr>
<td></td>
<td>$\nu_f$</td>
<td>259.7, 259.7, 221.7, 258.4, 260.4, 257.7, 221.23, 263.1, 259.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_1$ ($\varepsilon,n$)</td>
<td>0.850, 0.003, 0.910, 0.810, 0.780, 0.750, 0.894, 0.043, 0.590</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_2$ ($\varepsilon,n$)</td>
<td>0.650, 0.339, 0.680, 0.650, 0.510, 0.646, 0.810, 0.290, 0.582</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{TN}$</td>
<td>0.720, 0.111, 1.000, 0.650, 0.617, 0.586, 0.775, 0.164, 0.309</td>
<td></td>
</tr>
</tbody>
</table>

A= Methanol, B=Benzene, C=Water, D= Ethanol, E=N-propanol, F=n-butanol, G=formamide, H= Dioxane, I= DCM.

Table 3: Observed Values of $\nu_a$ (cm$^{-1}$) and $\nu_f$ (cm$^{-1}$) for 7-OH-4-CF$_3$ coumarin studied in different solvents along with the calculated values of solvent parameters $F_1$ ($\varepsilon,n$), $F_2$ ($\varepsilon,n$) & $E_{TN}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>X10$^2$ (cm$^{-1}$)</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-OH-4-CF$_3$</td>
<td>$\nu_a$</td>
<td>283.8, 280.0, 277.1, 278.6, 281.2, 272.3, 269.4, 267.7</td>
<td>A, B, C, D, E, F, G, H</td>
</tr>
<tr>
<td></td>
<td>$\nu_f$</td>
<td>213.4, 214.0, 214.4, 218.7, 211.8, 200.6, 194.5, 196.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_1$ ($\varepsilon,n$)</td>
<td>0.370, 0.413, 0.430, 0.595, 0.492, 0.557, 0.841, 0.895</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_2$ ($\varepsilon,n$)</td>
<td>0.490, 0.471, 0.550, 0.584, 0.499, 0.652, 0.744, 0.750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_{TN}$</td>
<td>0.259, 0.241, 0.228, 0.309, 0.228, 0.762, 0.444, 0.775</td>
<td></td>
</tr>
</tbody>
</table>

A= Chloroform, B= n-butyl Acetate, C= Ethyl Benzoate, D= dichloromethane, E=Ethyl Acetate, F=Methanol, G=DMSO, H=Formamide

The polarity of a molecule depends on electron density. With supply of additional energy there will be transition of electron from $\pi$ orbital (ground state) to $\pi^*$ orbital at higher level. Due to the movement of electron from ground state orbital to higher orbital there will be increase of dipole moment with reference to ground state dipole moment indicating $\pi \rightarrow \pi^*$ transition. It is observed from Table 1-3 that with increase in the polarity of the solvent the fluorescence and absorption band maxima undergo bathochromic shifts indicating $\pi \rightarrow \pi^*$ transitions. Using the values of $\nu_a$ and $\nu_f$ and eqs. 1,2,3,4,5,6,7,8, and 9 (Method I to Method II) obtained from theoretical consideration the excited and ground state dipole moments are calculated.
The slopes $m_1$, $m_2$ and $m_3$ are obtained by plotting the stokes shift $(\nu_a - \nu_f)$ verses $F_1 (\varepsilon,n)$ and $E_T^N$ also $\frac{1}{2} (\nu_a + \nu_f)$ verses $F_2 (\varepsilon,n)$. Plots drawn were shown in Fig. 3a,b,c Fig. 4a,b,c, and Fig. 5 a,b,c. The plots were drawn using least square fit method. Although some points deviates from linearity which could occur due to many different reasons such as excimer formation, intermolecular hydrogen bonding, the difference between the effective and bulk solvent polarity values or some other specific solute-solvent interactions.

**Figure 2:** Shifting of energy levels due to electron donating and electron withdrawing substituent

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**Fig. 3a** Graph between $(\nu_a - \nu_f) \times 10^{-2}$ V/S $F_1 (\varepsilon,n)$ for 6-OH-4-CH$_3$ Coumarin

\[ y = -15.697x + 272.55 \]  
\[ R^2 = 0.5363 \]
Fig. 3c Graph between $(\nu_a - \nu_f)$ V/S $E_T^N$ for 6-OH-4-CH$_3$ Coumarin

Fig. 3b Graph between $\frac{1}{2} (\nu_a + \nu_f)$ V/S $F_2 (\varepsilon, n)$ for 6-OH-4-CH$_3$ Coumarin
**Fig. 4b** Graph between $\frac{1}{2} (\nu_a + \nu_r)$ V/S $F_2(\varepsilon,n)$ for 7-OH-4-CH$_3$ Coumarin

\[ y = -61.317x + 278.36 \]
\[ R^2 = 0.8673 \]

**Fig. 4a** Graph between $(\nu_a - \nu_r)$ V/S $F_1(\varepsilon,n)$ for 7-OH-4-CH$_3$ Coumarin

\[ y = -61.317x + 278.36 \]
\[ R^2 = 0.8673 \]
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**Fig. 4c** Graph between \((\nu_a - \nu_f)\) V/S \(E_{TN}\) for 7-OH-4-CH$_3$ Coumarin

\[y = -61.317x + 278.36\]
\[R^2 = 0.8673\]

**Fig. 5c** Graph between \((\nu_a - \nu_f)\) V/S \(E_{TN}\) for 7-OH-4-CF$_3$ Coumarin

\[y = -61.317x + 278.36\]
\[R^2 = 0.8673\]
Fig. 5a Graph between (υ_a - υ_f) V/S F_1 (ε,n) for 7-OH-4-CF_3 Coumarin

\[ y = -61.317x + 278.36 \]
\[ R^2 = 0.8673 \]

Fig. 5b Graph between \( \frac{1}{2} (υ_a + υ_f) \times 10^{-2} \) V/S F_2 (ε,n) for 7-OH-4-CF_3 Coumarin

\[ y = -61.317x + 278.36 \]
\[ R^2 = 0.8673 \]
The values of $\mu$ and $\mu^*$ obtained from the plots and the relations are given in table 4.

**Table 4:** Calculated values of $\mu$ and $\mu^*$ along with cavity radius (a) for 6-OH-4-CH$_3$, 7-OH-4-CH$_3$ and 7-OH-4-CF$_3$ coumarin

<table>
<thead>
<tr>
<th>Coumarin</th>
<th>Å</th>
<th>$\mu$(D)</th>
<th>$\mu^$(D)</th>
<th>$\mu$(D)$^\wedge$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-OH-4-CH$_3$</td>
<td>3.28Å</td>
<td>0.61</td>
<td>2.42</td>
<td>2.25</td>
</tr>
<tr>
<td>7-OH-4-CH$_3$</td>
<td>3.28Å</td>
<td>0.52</td>
<td>3.39</td>
<td>2.56</td>
</tr>
<tr>
<td>7-OH-4-CF$_3$</td>
<td>4.18</td>
<td>6.24</td>
<td>5.26</td>
<td></td>
</tr>
</tbody>
</table>

$^\wedge$ Values of excited state dipole moment calculated using Reichardt – Dimroth equation[25]

It can be seen from table 4 that the value of $\mu^* > \mu$ in all the cases i.e. the dipole moment of the molecule increases on excitation. Although there is no limit on using number of solvent for study, However use of more solvents may also give the same result. All the Coumarin molecules studied exhibit marked red shift in the fluorescence maxima compared to the shift in absorption. It indicates that, in all the Coumarin studied, solvation is large in S$_1$ state compared to ground state, i.e., excited state dipole moment is high compared to ground state dipole moment. A plausible explanation for the increase lies in the ICT process. Charge transfer accompanying excitation to the lowest excited singlet state usually results in the excited molecule having greater dipole moment than the ground state molecule. Although the values of $\mu^*$ obtained from method I and II are different but the trend in values is very much clear. The value of angle $\varphi$ calculated from equ.9 is very small nearly equal to zero, indicating that the ground and excited state dipole moment are almost parallel to each other i.e. there is no change in the orientation of dipole moment in excited state for the Coumarins studied.

**B) SUBSTITUENT EFFECT:** Substituent groups could be of various type. Viz. (1) electron donating groups e.g. --NH$_2$, --N(CH$_3$)$_2$, -NH(C$_2$H$_5$), -SH etc. (2) electron withdrawing groups e.g. -CF$_3$, -CHO, -C ≡ N etc. (3) groups like –CH$_3$ which neither donate nor accept electrons.

The substituent leads to a redistribution of charge in the ground as well as the excited state. Some times more efficient conjugation takes place due to intramolecular charge transfer in the excited state. Substituent can activate or deactivate emitting modes, affecting their emission spectra considerably. The effect was demonstrated in terms of the calculated values of excited state dipole moment.

The effect of –OH, -CH$_3$ and CF$_3$ group on ground state and excited state dipole moment is very much visible from the calculated values of $\mu$ and $\mu^*$ listed in table 4. The value of both $\mu$ and $\mu^*$ for 6-OH-4-CH$_3$ and 7-OH-4-CH$_3$ Coumarin are almost same and there is small effect of replacing -OH group from position 6 to position 7 on the Coumarin ring. However the effect of –CF$_3$ group is prominently displayed. –
CF$_3$ group is electron withdrawing in nature and manifests its influence on the excited state of the molecule. The group as a substituent to an aromatic ring, provides a vacant, electron acceptor orbital $\pi^*$ (fig.2), which is lower in energy as compared to $\pi^*$. The net effect is that the energy gap $\pi \rightarrow \pi^* < \pi \rightarrow \pi^*$. As the transitions now takes place between $\pi$ and $\pi^*$ levels, the observed values of $\nu_a$ and $\nu_f$ for 7-OH-4CH$_3$ and 7-OH-4-CF$_3$ Coumarin indicate that this is really so. Also the values of $\mu$ and $\mu^*$ listed in table 4 manifests the same trend.

4. CONCLUSIONS
The present investigation of solvent and substituent effect of 6-OH-4-CH$_3$, 7-OH-4-CH$_3$ and 7-OH-4-CF$_3$ Coumarin indicates

1. On replacing –OH substituent from position 7 to position 6, has not much effect on the ground state and excited state dipole moment values.
2. For all the Coumarins, the emission as well as absorption maxima shifts to lower energy with increasing solvents polarity.
3. There is an increase in the dipole moment for all the Coumarins studied.
4. Increase in the Excited-singlet-state dipole moment for 7-OH-4-CF$_3$ Coumarin is more than 6-OH-4-CH$_3$, 7-OH-4-CH$_3$ Coumarin.
5. The small angle between $\mu^*$ and $\mu$ indicates that there is no change in the direction for excited state dipole moment from ground state for all the Coumarin studied.
6. The effect of –CF$_3$ group was prominently displayed in the observed values of $\nu_a$ and $\nu_f$ and the calculated values $\mu^*$ and $\mu$.

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