Analysis of solvent induced Spectral Shifts in 3-Carbethoxy Coumarin using Solvatochromic Techniques

RAVIKANTHA M. N
Assistant Professor of Physics,
HPPC Government First Grade College,
Challakere-577501. Chitradurga-Dist.

ABSTRACT

In the present paper, the role of various solvatochromic parameters on the solvent induced Spectral Shifts in 3-Carbethoxy Coumarin (3CECO) is reported. The solvatochromism of 3CECO is investigated in solvents with varying polarities using Lippert's bulk solvent polarity parameter and Reichardt's microscopic solvent polarity scale. A double linear correlation approach is employed to rule out the interference of specific solvent effects. To get deeper insight into the specific and non-specific solute-solvent interactions, we also use multiparametric regression techniques, including Kamlet-Taft and Catalan models. The ground-state dipole moment of 3CECO is computed using DFT (Density Functional Theory), while the excited-state dipole moments are derived from solvatochromic shifts using Lippert-Mataga, Bakhshiev, and Reichardt methods.

Keywords: ***Coumarins, solvatochromism, dipole moments, TD-DFT, Stoke's shifts***

1. INTRODUCTION

Solvatochromism is a powerful technique for investigating the electronic properties and interactions between solute and solvent, especially for systems where the solvent environment influences the electronic states of the solute. In non-polar solvents, non-specific interactions, such as dielectric effects and dispersion forces dominate. However, specific interactions like hydrogen bonding become crucial in polar and protic solvents. The balance between these interactions determines the overall shift in the absorption or emission spectra. By combining approaches such as the Lippert-Mataga equation, Reichardt's polarity scale, and Kamlet-Taft parameters, one can separate the contributions of various solute-solvent interactions and gain insights into both the electronic structure and potential applications of the studied molecules.

The excited-state properties of the molecules in solvent media are quite sensitive towards intermolecular solute–solvent interactions and in turn affect the energy of the electronic states, which depends on the nature (i.e., on charge distribution or the dipole moment) of respective states. A difference in charge distribution or the dipole moment for ground and excited states can give rise to spectral shift. Thus, the dipole moment is a crucial molecular parameter, offering insights into the change in densities of electronic charge distribution when a molecule is excited. A prior knowledge of the dipole moments in the excited state is often useful in the design of non-linear optical materials[1].

The solvatochromic analysis allows for the estimation of dipole moments in both the ground and excited states. The shift in absorption or emission maxima in response to solvent polarity provides insights into how the electronic distribution within the molecule changes upon excitation. This change in dipole moment is crucial for understanding molecular reactivity and interactions in different environments. To determine the dipole moment in excited state by the solvatochromic method, several approaches have been used including those developed by Lippert[2], Bakhshiev[3], Kawski–Chamma–Viallet [4] and Suppan[5]. Other electro optic methods such as electronic polarization of fluorescence, electric dichroism, microwave conductivity and Stark splitting are generally considered to be very accurate but their use is limited because they are equipment sensitive and hence these methods have been confined to relatively simple molecules. However, the experimental determination of dipole moment based on the analysis of the solvatochromism of absorption and fluorescence maxima is quite popular. Many workers have reported the ground state and excited state dipole moment using different solvatochromic methods[6–10].

Coumarins (2H-1-benzopyran-2-ones) are important oxygen containing fused heterocycles used in drugs and dyes[11]. Coumarin dyes are widely used in dye lasers to achieve tunable blue green light, and are also employed in other important applications of industrial and biological interest. 7-hydroxycoumarins have been extensively investigated for electronic and photonic applications such as charge-transfer complexes, additives to cosmetics, laser dyes, optical brighteners, fluorescence whiteners in detergent products, and solar energy collectors[12]. Certain hydroxycoumarin derivatives show marked biological activity, such as enzyme inhibition, hypotoxicity, carcinogenicity, hepatoprotective, anticoagulant, anti-inflammatory, antiallergic, antiviral, anticarcinogenic and anticoagulant activities[13]. coumarins Other uses of coumarins include their applications in food constituents, antioxidants, stabilizers and immunomodulatory substances, indicators of biophysical processes, as fluorescent markers for use in analyses, in stains, and in clinical use[14].

The present work deals with the absorption and fluorescence characteristics of 3CECO in different solvents. The Organic fluorophore used in the present study is a coumarin derivative and has a wider application as π conjugated luminophores, as fluorescent sensor, for biological imaging and for other optoelectronic application due to its optical properties and structure tenability. Despite the various contributions made to the subject, streamlined analysis has not been carried out on the effect of solute-solvent interactions, particularly specific interactions. This information is highly desirable for the optical characterization of the molecule and could be useful in providing a fluorescent probe with unique features for possible analytical applications. The wide range of application of this molecule and significance of solvatochromism and dipole moments motivated us to take up this work. The main objective of this contribution is to discuss the effect of pure solvents with varying polarity, as well as binary solvent mixtures on the steady-state spectral data of 3CECO, to get quantitative information regarding their mechanisms of action at the molecular level. The approach was to elucidate the experimental spectral data based on Lippert's macroscopic (Δf) and Reichardt's microscopic solvent polarity parameters (E_T^N). The relative contributions from non-specific and specific interactions to the observed spectral properties in the investigated molecules were revealed by the solvatochromic comparison methods proposed by Kamlet-Taft and Catalan. Additionally, to gain a deeper insight into the optical and electronic properties of these molecules, the difference in the excited and ground state dipole moments were estimated using solvatochromic models due to Lippert-Mataga, Bakhshiev, and Reichardt.

2 MATERIALS AND METHODS

2.1 Materials

The chemical structure of the experimental coumarin derivative, ethyl-2-oxo-2H-chromene-3-carboxylate or 3-carboethoxy coumarin (3CECO) is given in Figure 1. All the solvents used in the present investigation (Table 1) were spectroscopic (HPLC) grade, obtained from different commercial sources, and used without further purification. The solvents were carefully selected to include a wide range of solvent polarity while also considering their capacity to interact (non-specific and /or specific interactions) with the investigated molecule. They are listed in the Table according to the increase in solvent polarity (E_T^N) parameter.

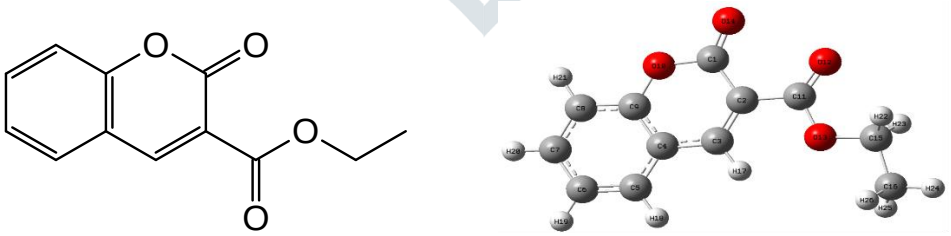

Figure 1: (a) The Chemical structure and (b) Optimised Geometrical structure of 3CECO molecule [DFT-B3LYP/631g+(d,p)].

2.2 Experimental methods

The UV-Vis absorption spectra were recorded in the range 200–800 nm with a data resolution of 0.2 nm using UV-Vis Spectrophotometer (Lab India, Model: UV-3092. Fluorescence spectra were recorded at 5 nm slit width for excitation and emission of the incident excitation beam using Fluorescence Spectrometer (Shimadzu, Model: RF-6000) with a data resolution of 1 nm. The excitation wavelength is fixed at 330 nm.

2.3 Computational Methods

The computational (DFT and TD-DFT) studies were done using Gaussian 09W: Rev C.01 computational package[15] and all the molecular simulations of the output were rendered by Gauss View 6.0.16[16]. The optimization of ground state geometry of the proposed molecule in vacuum (gas phase) and in dissolved solvents was performed using the integral equation formalism polarizable continuum model (IEF-PCM)[17] coupled with DFT-B3LYP exchange-correlation functionals and 6-31+G(d,p) basis set. The excited state calculations were performed employing TD-DFT with the same level of theory on optimized ground-state geometries.

2.4 Theoretical Models of Solvatochromism

The effect of solvent polarity on the solvatochromic response of the proposed molecule can be correlated by single parameter solvent polarity scales proposed by Lippert-Mataga and Reichardt and by multiparametric solvent polarity scales proposed by Kamlet-Taft and Catalan models.

According to Lippert[2] and Mataga[18] model, the variation in spectral parameters (ν_a, ν_f or $\Delta\nu$) of a molecule with change in solvent polarity is a function of the Lippert's bulk solvent polarity parameter, F_{LM} and is expressed in terms of refractive index (n) and dielectric constant (ε) of the solvent as follows:

$$F_{LM} = \left[\left(\frac{\varepsilon-1}{2\varepsilon+1}\right) - \left(\frac{n^2-1}{2n^2-1}\right)\right] \quad \ldots (1)$$

This equation assumes that the shifts are driven primarily by non-specific solvent effects, i.e., dielectric interactions between the solute and the bulk solvent[19].

Reichardt's E_T^N parameter is a microscopic solvent polarity scale, which provides a single measure for both polar and hydrogen-bonding effects. It accounts for both specific (e.g., hydrogen bonding) and non-specific (dipole-dipole) solvent-solute interactions. The theoretical basis for the correlation of the spectral band shift with E_T^N was proposed by Reichardt[20] and developed by Ravi et al[1]. Many literature reports suggest that E_T^N parameter provides better correlations than the traditionally used bulk solvent polarity functions.

Although solvent polarity scales may serve as good approximations of solvent polarity, in many cases, a good correlation cannot be obtained from single solvent parameter[21]. A more detailed understanding of solvent-solute interactions by breaking down solvent effects into specific components can be obtained by using multiparametric models of Kamlet et. al.[22] and Catalan[23]. The Kamlet-Taft method uses three independent empirical solvent descriptors π^*, and α, β related to a solvent-dependent spectroscopic parameter (y) of interest as

$$y = y^o + a_\alpha\alpha + b_\beta\beta + c_\pi\pi^* \quad \ldots (2)$$

Where y^o is the respective spectroscopic property in gas phase and the coefficients a_α and b_β are measure of hydrogen-bond donor (HBD) strength (α) and hydrogen-bond acceptor (HBA) strength of the solvent respectively, while, c_π is a measure of non-specific dielectric interactions (π*).

The Kamlet's approach includes dipolarity and polarizability of solvent in single parameter π^* and thus, it is difficult to identify their individual contributions[24]. Catalan[23], introduced generalized treatment of solvent effect based on four empirical scales namely; HBD acidity (SA), HBA basicity (SB), polarizability (SP), and dipolarity (SdP) of solvent medium. According to Catalan model,

$$y = y^0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \quad \ldots (3)$$

where y and y^o have their usual meanings as discussed earlier, the independent constants a_{SA}, b_{SB}, c_{SP} and d_{SdP} are respectively measure of the relative contributions of acidity (SA), basicity (SB), polarizability (SP) and dipolarity (SdP) of the solvent medium.

2.5 Estimation of dipole moments

The experimental determination of the dipole moments μ_g and μ_e in the ground and excited state of an organic molecule can be done by correlating the solvent-induced Stokes shifts with the solvent polarity functions[25]. Most of the solvatochromic theories yield similar expressions for the solvent induced spectral shifts. However, the solvent polarity parameters F(ε, n) used in these theories can vary significantly depending on the assumptions and simplifications used in the model. The following solvatochromic techniques are used in the present discussion:

The Lippert-Mataga model takes into account only general solvent effects are present in the solvent medium and ignores the polarizability of the solute molecule (α = 0) and chemical interactions. The Lippert-Mataga equation is

$$\bar{\nu}_a - \bar{\nu}_f = m_{LM} F_{LM}(\varepsilon, n) + constant \quad ...(4)$$

Bakhshiev's model[26] takes into account the solute polarizability (polarizability factor, $2\alpha/a^3 = 1$) besides specific solute-solvent interactions[27]. Bakhshiev's equation reads as

$$\left(\bar{\nu}_a - \bar{\nu}_f\right) = m_B F_B(\varepsilon, n) + constant \quad ... (5)$$

The corresponding solvent polarity functions are given by

$$F_{LM}(\varepsilon, n) = \left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right) \text{ and } \quad F_B(\varepsilon, n) = \left(\frac{2n^2+1}{n^2+2}\right)\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \quad ... (6)$$

Where, the parameters, $m_{LM} = m_B = \frac{2(\mu_e - \mu_g)^2}{hca_o^3}$ are obtained from the slopes by plotting spectral shifts against respective solvent polarity functions using Eqs.(4-5). Here, a_o represents the Onsager cavity radius of the molecule and can be found by knowing the volume of the molecule according to relation, $a_o = \left(\frac{3V}{4\pi}\right)^{1/3}$ given by Suppan's equation[28].

The change in dipole moment of the molecule can be estimated using the relation

$$\Delta\mu_{LM} = \left(\mu_e - \mu_g\right) = \sqrt{\frac{hca_o^3}{2} m_{LM}} \quad and \quad \Delta\mu_B = \sqrt{\frac{hca_o^3}{2} m_B} \quad ...(7)$$

For the correlation between spectral shift and microscopic solvent polarity parameter (E_T^N), Reichardt[20] proposed an equation for the spectral shift given by

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2 \left(\frac{a_B}{a_o}\right)^3\right] E_T^N + constant \quad ...(8)$$

Where $\Delta\mu_B = 9D$ and $a_B = 6.2$ Å are dipole moment changes on excitation and Onsager cavity radius respectively of betaine dye molecule. $\Delta\mu$ and a_o are corresponding quantities of the change in dipole moment of the molecule. As explained by Ravi et al. [[1], the problem associated with the error in estimation of Onsager radius 'a' has been minimised since a ratio of two Onsager radii (a_B/a) is involved.

The excited state dipole moment can be evaluated from the slope (m) of linear plot of E_T^N against Stokes shift (Eq. (7)) and is given by the equation

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{11307.6 \times \left(\frac{6.2}{a}\right)^3}} \quad ...(9)$$

For a more comprehensive description, the Bilot-Kawski model considers the polarizability of the solute and solvent, which impacts the dipole moment calculations. This model refines the solvatochromic analysis by factoring in the polarizability of both the solvent and solute, allowing a more nuanced interpretation of the shifts observed in various solvent environments. For a polarizable dipole, Bilot and Kawski[29] obtained polarizability-dependent polarity function (F_{BK}) which takes the form of Eq. (10) when a spherical Onsager cavity of radius (a_0) is assumed.

$$f_{BK}(\varepsilon, n) = \frac{\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}}{\left(1 - \frac{2\alpha}{a_o^3}\frac{\varepsilon-1}{2\varepsilon+1}\right)\left(1 - \frac{2\alpha}{a_o^3}\frac{n^2-1}{2n^2+1}\right)^2} \quad ... (10)$$

Here, α is the polarizability of the solute molecule.

3. RESULTS AND DISCUSSION

3.1 Influence of solvents on absorption and emission spectra

The steady-state UV-Vis absorption spectra and fluorescence emission of 3-carboethoxy coumarin (3CECO) were recorded at room temperature in neat solvents of different polarities. The data of absorbance in (cm^{-1}), emission in (cm^{-1}), stokes shift in (cm^{-1}) in different solvents taken in Table 1 and the absorption and emission spectra are shown in Figure 2.

Table 1: Solvent-dependent steady-state spectral data of 3-carboethoxy coumarin

No.	Solvent	E_T^N	λ_a	λ_f	ν_a	ν_f	ν_a-ν_f	ν_a+ν_f
1	Cyclohexane	0.0060	315.8	401	31666	24938	6728	56603
2	Toluene	0.0990	316.4	404	31606	24752	6853	56358
3	Benzene	0.1110	317.4	408	31506	24510	6996	56016
4	Tetrahydrofuran	0.2070	318.8	412	31368	24272	7096	55639
5	NN-dimethyl formamide	0.3860	319.8	418	31270	23923	7346	55193
6	Acetonitrile	0.4600	321.0	424	31153	23585	7568	54738
7	2-Propanol	0.5460	324.6	430	30902	23256	7647	54158

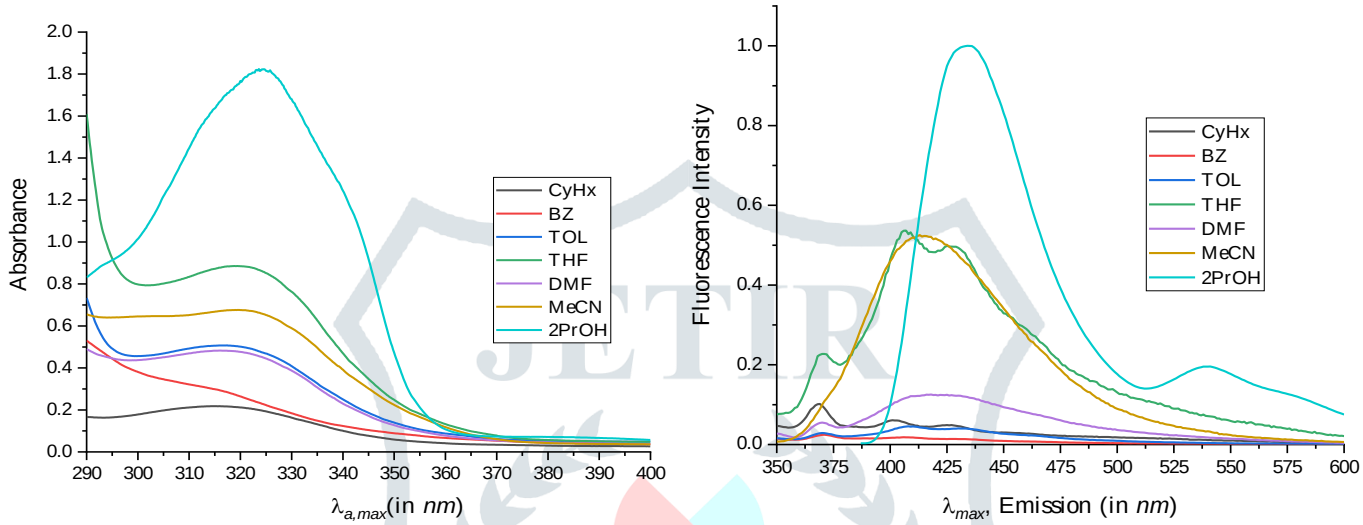

Figure 2 (a) Absorption spectra and (b) Emission spectra of 3CECO molecule in different solvents.

The long wavelength absorption bands of 3CECO is localized in the range of 315-325 nm for the absorption spectra of 3CECO in the used solvents. The bands are found to be broad and structureless. With the increase of the solvent polarity, the absorption maximum slightly shifted to the red end indicating a bathochromic shift (< 10 nm). The long wavelength band can be attributed to π–π* transitions due to intramolecular charge transfer (ICT). The solvent polarity directly influenced the excited state of 3CECO. The fluorescence maxima changed its position from 401 to 430 nm as we move from cyclohexane to 2-Propanol. This significant fluorescence spectral shift suggested that the proposed molecules are more polarized in the excited state over the ground state, and therefore, the expected value of μ_g would be less than μ_e. The positive solvatochromism and higher value of dipole moment in the excited state indicates the greater intermolecular (π–π*) interaction in the excited state of the polar solvents[7] and cause an enhanced stabilization of the excited state in comparison to that of the ground state[30] as shown in Figure 3.

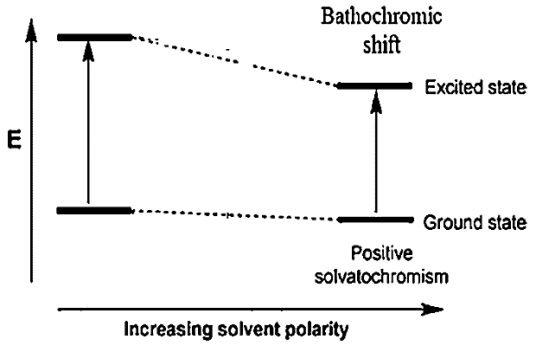

Figure 3 Stabilization of the excited state in comparison to that of the ground state of 3CECO.

3.2 Analysis of Solvatochromism

The traditional approach to understand the solvatochromic behaviour is to correlate the spectroscopic properties with solvent polarity parameters. Many solvent polarity scales are available to explain the solvent-dependent chemical

processes. In this work, the solvatochromism of proposed molecules in neat and binary solvent mixtures was analyzed using the solvatochromic models proposed by Lippert[18,19], Reichardt[20], Kamlet-Taft[22], and Catalan[23].

3.2.1 Correlation of solvatochromic shifts with the solvent parameters.

In order to understand the solvatochromic behaviour of the studied coumarin derivative, the electronic spectroscopic properties were studied as a function of solvent polarity. First, the absorption maximum of the title molecules was plotted as a function of the orientation polarizability, Δf (ε, n) also known as Lippert's bulk solvent polarity parameter, $\Delta f = F_{LM} = \left[\left(\frac{\varepsilon-1}{2\varepsilon+1}\right) - \left(\frac{n^2-1}{2n^2-1}\right)\right]$. Figure 4a displays the correlation between the Δf and spectral Characteristics (ν_a, ν_f, and ν_a-ν_f) of 3CECO in solvents of different polarity. The regression coefficients (r) equal to 0.875, 0.901 and 0.901 are obtained for absorption, emission and Stoke's shift respectively. These poor correlations indicate that Lippert's bulk solvent polarity parameter is not the sole parameter governing the solvatochromic shift of 3CECO. Furthermore, the positive slope obtained for the Stoke's shift suggest that the energy required for solvation is negative and specific interactions, such as dipole–dipole and hydrogen bonding have an important influence on solvatochromism of investigated molecule[31]. In order to have a better understanding of the solvatochromic behaviour of the proposed molecule, an attempt has been made to explain spectroscopic properties with solvent polarity parameter, E_T^N. In the Figure 4b, the plot of Spectral Characteristics (ν_a, ν_f, and ν_a-ν_f) of 3CECO as function of Reichardt's microscopic solvent polarity parameter (E_T^N) was presented. In this case, The least square correlation coefficients (r) equal to 0.973, 0.990 and 0.991 are obtained for absorption, emission and Stoke's shift respectively. These values suggest that the increasing solvent polarity stabilizes the molecule through dipole–dipole and dipole induced dipole forces which are assumed to be the predominant interactions[32].

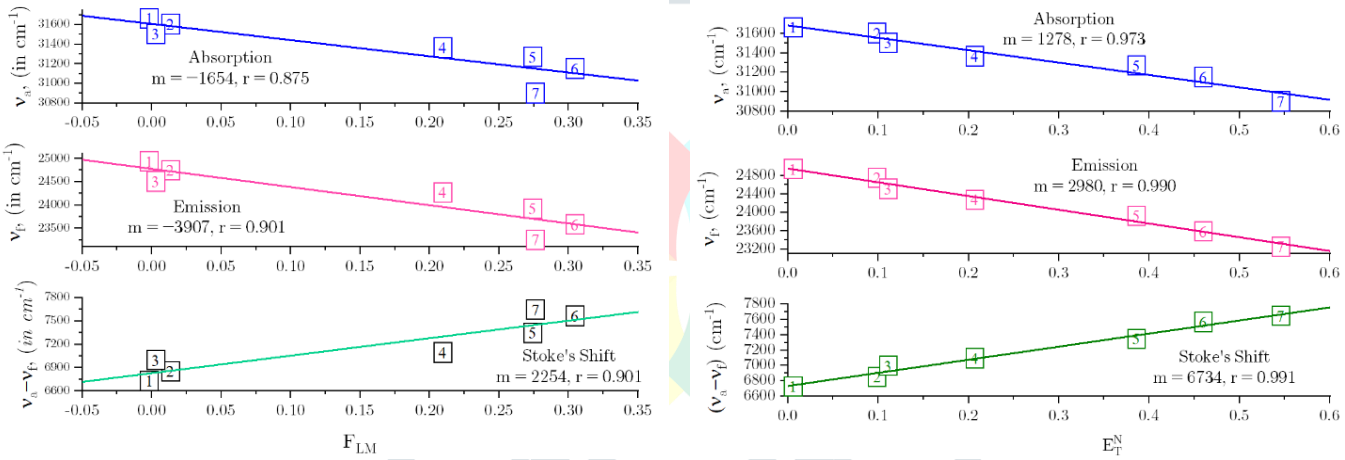

Figure 4 Plot of Spectral Characteristics (ν_a, ν_f, and ν_a–ν_f) of 3CECO as function of (a) Lippert's bulk solvent polarity parameter and (b) Reichardt's microscopic solvent polarity parameter.

3.3.2 Correlation with multiparameter solvent polarity scales

In order to get information about individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of solvents on the spectral properties of investigated coumarin derivative, the experimental spectral data of the investigated molecule was analysed by using the regression equations for Kamlet-Taft and Catalan models discussed in section 2, and the respective experimental data assembled in Table 2. In addition, to facilitate the interpretation of the nature of the solute-solvent interactions, the relative contributions of non-specific and specific interactions on spectral characteristics of proposed molecule are also presented.

Table 2 The regression coefficients of Kamlet-Taft (α, β and π*) parameters / Catalan (SA, SB, SP and SdP) parameters and their relative contributions to solute-solvent interactions in the present spectroscopic analysis of 3CECO

Spectral Characteristics	K-T Parameters#			Intercept	Regression Coefficient
	α	β	π*		
ν_{abs}	–622 (53%)	–201 (17%)	–348 (30%)	$\nu_{o,\ abs}$ = 31705	0.967
ν_{emi}	–1468 (52%)	–272 (10%)	–1075 (38%)	$\nu_{o,\ emi}$ = 25068	0.951
$\Delta\nu$	848 (52%)	71 (4%)	726 (44%)	$\Delta\nu_o$= 6638	0.936
	Catalan Parameters#				
	SA	SB	SP	SdP	
ν_{abs}	–1400 (64%)	17 (1%)	374 (17%)	–413 (19%)	$\nu_{o,\ abs}$ = 31384	0.989
ν_{emi}	–3128 (57%)	373 (7%)	724 (13%)	–1229 (23%)	$\nu_{o,\ emi}$ = 24371	0.990
$\Delta\nu$	1731 (53%)	–355 (11%)	–356 (11%)	815 (25%)	$\Delta\nu_o$= 7017	0.990

#Values in the parenthesis denote the relative contribution from the respective solvent parameter to solute-solvent interaction.

A closer examination of these parameters reveal the following features for solvatochromism of 3CECO: The regression parameters afford a good correlation ($0.93 \leq r \leq 0.99$) of the experimental data for investigated solvents in 3CECO and confirm that these equations can be employed to further investigations. For interaction of 3CECO with solvents, both the nonspecific dipolar interactions (π*=30% and SP+SdP =36%) and the hydrogen bond donor acidity (α =53% and SA = 64%) are decisive factors for the position of the absorption spectrum. The results also suggest that the only C=O is involved in specific interactions. The position of emission spectrum of 3CECO due to interaction with different solvents was also influenced by both the nonspecific dipolar interactions (π*=38% and SP+SdP=36%) and the hydrogen-bond donor (HBD) strength (α =52% and SA = 67%). The observed Stoke's shifts due to solute-solvent interactions are characterized by the relative contributions from nonspecific dielectric interactions (π*=44% and SP+SdP = 36%) and hydrogen-bonding interactions (α = 52% and SA = 53%). The relative contributions from solvent parameters indicate that, the specific interactions between tested molecules and alcoholic solvents are present either in its ground and excited states. The role of HBA (β) is insignificant in both absorption and emission process. The negative signs of the regression coefficients predicted by used models indicate that both specific and non-specific interactions may stabilize the excited state more than the ground state, resulting in bathochromic shift[33]. This behavior can be justified by considering the value of the electric dipole moment of 3CECO ($\mu_e > \mu_g$).

3.3.2 Estimation of ground and excited-state dipole moments

Among the several different optical methods available for determining dipole moments of molecules in the ground and excited states, one of the prominent methods is the method of spectral shifts[25] which is based on the estimation of Stokes shift ($\Delta\bar{\nu}$) of the fluorescence spectrum with respect to corresponding absorption spectrum as a function of solvent polarity.

Ground and excited state dipole moment was also estimated from quantum chemical calculations using DFT-B3LYP / 6311g+(d,p) level of theory and the optimized structures in these states are presented in Figure 5. The figure shows that the dipole moments are almost parallel to each other.

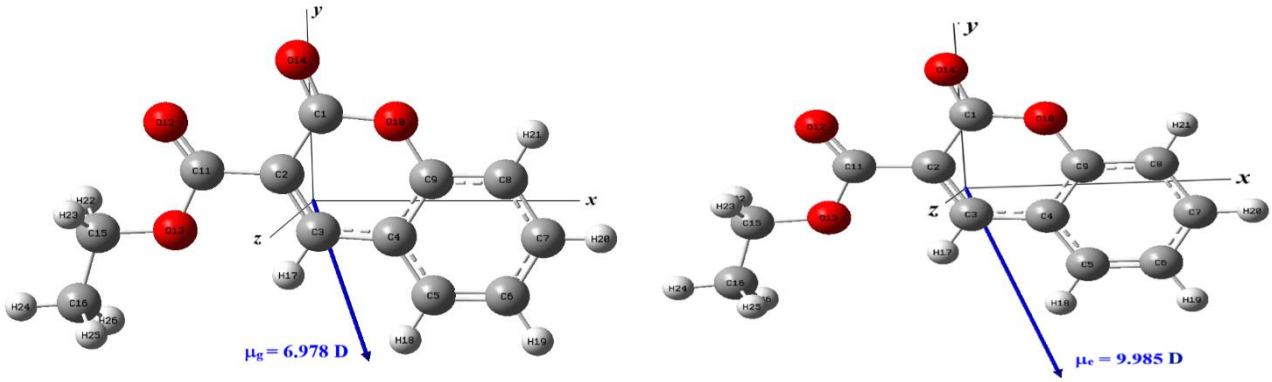

Figure 5 Optimized Geometry and dipole moment vectors of 3CECO in (a) ground state and (b) excited state.

In order to determine the excited-state dipole moment values, the Stokes shifts $(\bar{\nu}_a - \bar{\nu}_f)$ were plotted against the solvent polarity functions (F_{LM}, F_B, and E_T^N), according to equations discussed in section 2 and are displayed in Figure 6. The results of the statistical treatment of solvatochromic correlations are summarized in Table 3**.** Good linearity with acceptable correlation coefficients was obtained for selected number of data points in all cases of study.

Table 3 Calculated excited state dipole moments from different solvatochromic models.

Solvatochromic Model	**DFT/TD-DFT : μ_g = 6.978 D, μ_e = 9.985 D, a = 4.058 Å**		
	Slope (m)	Δμ (D)	μ_e (D)
Lippert-Mataga	2254	3.870	10.848
Bakhshiev	783	2.281	9.259
Reichardt E_T^N Parameter	1704	3.365	10.343

The dipole moments, and Onsager cavity radius were determined from quantum mechanical computations using DFT/TDDFT -B3LYP / 6311g+(d,p) level of theory.

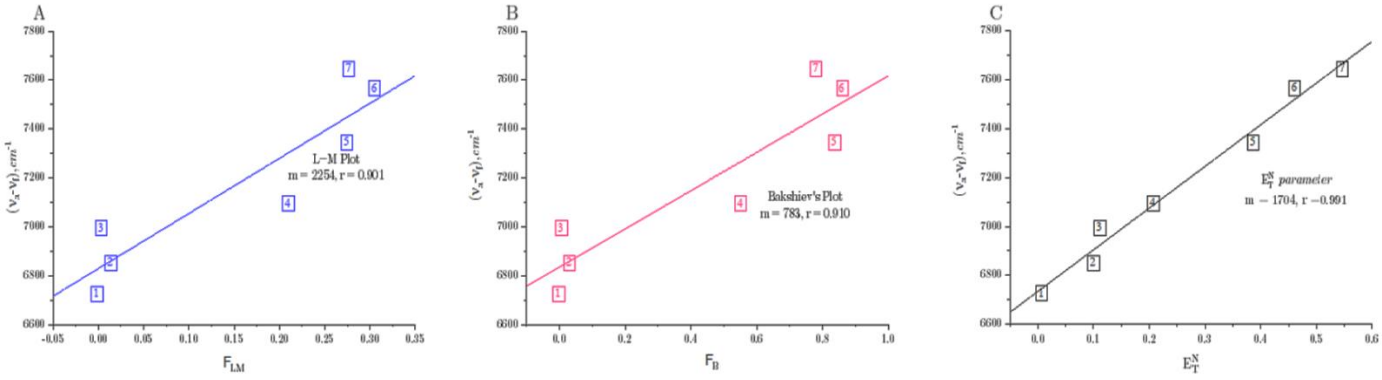

Figure 6 Stokes shifts $(\bar{\nu}_a - \bar{\nu}_f)$ plotted against the solvent polarity functions (F_{LM}, F_B, and E_T^N).

The estimated dipole moments and change in dipole moments are given in Table 3. As seen from the table, the excited state dipole moment of 3CECO is higher than the ground state in all the methods used, it may be concluded that excited state is more polar than the ground state, likely due to the strong resonance electron-donating effects of the C=O and C–O bonds in the excited state.

5.4 Effect of polarizability of the solute on dipole moment

In order to account for the influence of the solute polarizability (α) on the change in dipole moment, the analysis of Δμ as function of $2\alpha/a^3$ parameters ($0 \leq 2\alpha/a^3 \geq 1$) according to Bilot-Kawski approach. The estimated values of Δμ and μ_e are given in the Table 4. The Δμ for extreme values of $2\alpha/a^3$ is found to differ by about 15%, which confirms that solute polarizability affects the ground and excited state dipole moments.

Table 4 Values of F_{BK}, $\Delta\mu$ (D) and μ_e (D) for 3CEC as a function of $2\alpha/a^3$ parameter.

	F(BK), ($0 \leq 2\alpha/a^3 \geq 1$), ($\mu_g$ = 6.978 D, a = 4.058 Å)					
$2\alpha/a^3$ =	**0.0**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
CyHx	-	-	-	-	-	-
	0.0016	0.0019	0.0021	0.0024	0.0028	0.0033
BZ	0.0137	0.0158	0.0183	0.0214	0.0253	0.0301
TOL	0.0029	0.0033	0.0039	0.0045	0.0053	0.0063
THF	0.2096	0.2473	0.2952	0.3569	0.4385	0.5491
DMF	0.2744	0.3301	0.4031	0.5013	0.6378	0.8356
MeCN	0.3046	0.3617	0.4356	0.5337	0.6678	0.8593
2PrOH	0.2762	0.3285	0.3961	0.4854	0.6069	0.7787
Slope (m)	2254	1891	1563	1271	1011	783
$\Delta\mu$ (D)	3.870	3.544	3.222	2.906	2.592	2.281
μ_e (D)	10.848	10.522	10.200	9.884	9.570	9.259

4. CONCLUSION

In the present work, it was found that both the absorption and emission maxima suffered a red shift indicating that the 3CECO molecule is more stabilized in the excited state than ground state. This is attributed to π–π* transitions due to intramolecular charge transfer (ICT). The solvatochromic data has been analyzed using Lippert-Mataga and Reichardt's E_T^N solvent polarity scales. The plots show that both general interactions (dipole–dipole) and specific interactions, such as hydrogen bonding have an important influence on solvatochromism of investigated molecule. The Kamlet-Taft and Catalan models provided deeper insight into observed solvatochromism in 3CECO. The relative contributions from K-T and Catalan parameters indicate that, nonspecific dielectric interactions (π*≈45%) and HBD interactions (α≈50%) are present in both ground and excited states. However, HBA strength (β) is insignificant in solvatochromic shifts of 3CECO. The transition dipole moment (Δμ) and excited state dipole moments estimated using different solvatochromic models are in good agreement with each other.

REFERENCES

[1] M. Ravi, T. Soujanya, A. Samanta, T.P. Radhakrishnan, J. Chem. Soc. Faraday Trans. 91 (1995) 2739–2742.

[2] E. Lippert, Zeitschrift Für Elektrochemie, Berichte Der Bunsengesellschaft Für Phys. Chemie 61 (1957) 962–975.

[3] N.G. Bakhshiev, Opt Spektrosk 13 (1962) 192–201.

[4] A. Chamma, P. Viallet, CR Acad Sci Paris Ser C 270 (1970) 1901–1904.

[5] P. Suppan, Chem. Phys. Lett. 94 (1983) 272–275.

[6] S. Joshi, S. Kumari, A. Sarmah, R. Sakhuja, D.D. Pant, J. Mol. Liq. 222 (2016) 253–262.

[7] U.P. Raghavendra, M. Basanagouda, A.H. Sidrai, J. Thipperudrappa, J. Mol. Liq. 222 (2016) 601–608.

[8] J. Basavaraja, S.R. Inamdar, H.M. Suresh Kumar, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 137 (2015) 527–534.

[9] K.H. Nagachandra, J.R. Mannekutla, S.M. Amarayya, S.R. Inamdar, Eur. J. Chem. 3 (2012).

[10] D. Nagaraja, N.R. Patil, R.A. Kusanur, H.D. Patil, R.M. Melavanki, Int. J. Sci. Res. Publ. 2 (2012).

[11] S. Rajasekaran, G.K. Rao, S.P.N. Pai, A. Ranjan, Int. J. Chem Tech Res. 3 (2011) 555–559.

[12] A. Fischer, C. Cremer, E.H.K. Stelzer, Appl. Opt. 34 (1995) 1989–2003.

[13] R.. O'Kennedy, R.D.. Thornes, (1997) 348.

[14] D. Lafitte, V. Lamour, P.O. Tsvetkov, A.A. Makarov, M. Klich, P. Deprez, D. Moras, C. Briand, R. Gilli,

Biochemistry 41 (2002) 7217–7223.

[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Had, D.J. Fox, Gaussian 09, Rev.C.01; Gaussian, Inc. Wallingford CT, 2010. (2010).

[16] R.D. Dennington II, A. Keith,Todd, M.M. John, (2016) Semichem Inc., Shawnee Mission KS.

[17] J. Tomasi, B. Mennucci, E. Cancès, in: J. Mol. Struct. THEOCHEM, 1999.

[18] N. Mataga, Y. Kaifu, M. Koizumi, Bull. Chem. Soc. Jpn. 29 (1956) 465–470.

[19] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer, 2006.

[20] C. Reichardt, Chem. Rev. 94 (1994) 2319–2358.

[21] C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, 4th ed., Wiley-VCH, 2011.

[22] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. 48 (1983).

[23] J. Catalán, J. Phys. Chem. B 113 (2009) 5951–5960.

[24] U.P. Raghavendra, M. Basanagouda, R.M. Melavanki, R.H. Fattepur, J. Thipperudrappa, J. Mol. Liq. 202 (2015) 9–16.

[25] A. Kawski, Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci. 57a (2002) 255–262.

[26] N.G. Bakhshiev, Opt. i Spektrosk. 16 (1964) 821–832.

[27] M. Józefowicz, P. Milart, J.R. Heldt, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 74 (2009) 959–963.

[28] P. Suppan, Chem. Phys. Lett. 94 (1983) 272–275.

[29] A. Kawski, B. Kukliński, P. Bojarski, H. Diehl, Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci. 55 (2000) 817–822.

[30] C. García, R. Oyola, L. Piñero, D. Hernández, R. Arce, J. Phys. Chem. B 112 (2008).

[31] A. Alimmari, B. Božić, D. Mijin, A. Marinković, N. Valentić, G. Uščumlić, Arab. J. Chem. 8 (2015) 269–278.

[32] S.P. Olivares, S. Risso, M.I. Gutiérrez, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 71 (2008) 336–339.

[33] M.I. Sancho, M.C. Almandoz, S.E. Blanco, E.A. Castro, Int. J. Mol. Sci. 12 (2011).