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Solvatochromic Effect on the Photophysical Properties of Two Coumarins

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Abstract The absorption and emission spectra of two coumarins namely 7, 8 benzo-4-azidomethyl coumarin (C_1) and 6-methoxy-4-azidomethyl coumarin (C_2) have been recorded at room temperature in solvents of different polarities. The ground state dipole moments (μ_g) of two coumarins were determined experimentally by Guggenheim method. The exited state (μ_e) dipole moments were estimated from Lippert's, Bakhshievs and Chamma-Viallet's equations by using the variation of Stoke's shift with the solvent dielectric constant and refractive index. The ground and excited state dipole moments were calculated by means of solvatochromic shift method and also the excited state dipole moments are determined in combination with ground state dipole moments. It was observed that dipole moments of excited state were higher than those of the ground state, indicating a substantial redistribution of the π-electron densities in a more polar excited state for two coumarins.

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Introduction

The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of interesting investigation [1–3]. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes in the excited state. This can result in an increase or decrease of dipole moment of the excited state as compared to ground state. The dipole moment of an electronically excited state of a molecule is an important property that provides information on the electronic and geometrical structure of the molecule in the short-lived state. Knowledge of the excited state dipole moment of electronically excited molecules is quite useful in designing nonlinear materials, elucidating the nature of the excited states and in determining the course of a photochemical transformation. The excited-state dipole moments of fluorescent dye molecules such as those studied here also determine the tunability range of the emission energy as a function of the polarity of the medium. All the methods available so far for the determination of singlet excited-state dipole moment are based on the spectral shift caused either externally by electrochromism or internally by solvatochromism. The electrooptic 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 considered equipment sensitive and the studies have been restricted to relatively very simple molecules. The solvato-

chromic method is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. Koutek has shown that under suitable conditions, the solvatochromic method yields fairly satisfactory results [4]. The solvent dependence of absorption and fluorescence maxima is used to estimate the excited-state dipole moments of different molecules.

Several workers have made extensive experimental and theoretical studies on ground state (μ_g) and excited-state (μ_e) dipole moments using different techniques in variety of organic fluorescent compounds like coumarins [5], indoles [6], purines [7], exalite dyes [8], curcuminoid dyes [9], fluorescein [10], hemicyanine dyes [11], 4-azido-coumarin dyes, acridinedione dyes,, flavones, PRODAN, BADAN and ACRYLODAN [12], acridines and phenazines [13] and in some laser dyes [14–20] etc.

Coumarins and their derivatives establish a family of dyes which are applicable in different fields of science and technology. They exhibit strong fluorescence in the UV and VISIBLE region which makes them suitable for used as colorants, dye laser media and as nonlinear optical chromospheres. In medicine, coumarin derivatives are used as anticoagulants, as a fluorescent indicators for the physiological pH region and as fluorescent probes to determine the rigidity and fluidity of living cells and its surrounding medium. They also possess distinct biological activity and have been described as potential agents for anticancer. In the present work we report the effects of solvent on absorption and emission spectra, and estimation of ground and excited-state dipole moments of two coumarins namely 7, 8 benzo-4-azidomethyl coumarin (C_1) and 6-methoxy-4-azidomethyl coumarin (C_2) by solvatochromic shift method. However, there are no reports available in literature on the determination of μ_g and μ_e values of these molecules investigated. This prompted us to carry out the present work.

Experimental

Chemicals Used

The solutes of two coumarins namely 7, 8 benzo-4-azidomethyl coumarin (C_1) and 6-methoxy-4-azidomethyl coumarin (C_2) were synthesized in our laboratory using standard methods [21–23]. The molecular structures of these molecules are given in Fig. 1. The solvents used in the present study namely cyclohexane, hexane acetonitrile, dimethylsulfoxide, acetone, ethyl acetate, ethyl alcohol, diethyl ether, 1- hexanol, toluene, benzene, carbon tetrachloride and 1,4 dioxane were obtained from S-D-Fine Chemicals Ltd., India, and they were of spectroscopic grade. The required solutions were prepared at fixed concentration of solutes 1×10^{-4} M in each solvent.

Fig. 1 The molecular structures of C_1 & C_2

7, 8 benzo-4-azidomethyl coumarin (C_1)

6-methoxy-4-azidomethyl coumarin (C_2)
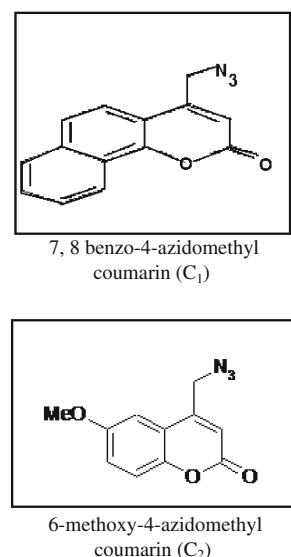
Spectroscopic Measurements

The absorption spectra were recorded using Hitachi 50–20 UV–Vis spectrophotometer. The fluorescence spectra were recorded using HORIBA FLUOROLOG spectrophotometer. Typical absorption and fluorescence spectra of C_1 and C_2 are shown in Figs. 2 and 3. The dielectric constants of the dilute solutions were measured in a suitably fabricated cell of usually small capacitance where the accurate determination of small changes in the capacitance would be possible. The small capacitance can be measured with the help of Forbes Tinsley (FT) 6421 LCR Data Bridge at 10 KHz frequency. The refractive indices of various dilute solutions of the solute for sodium D line were determined by using Abbe's refractometer. All these measurements were carried out at room temperature.

Determination of the Dielectric Constant and Refractive Index

The capacitance of air, the solvent and the solution have been used to measure dielectric constant. By measuring the
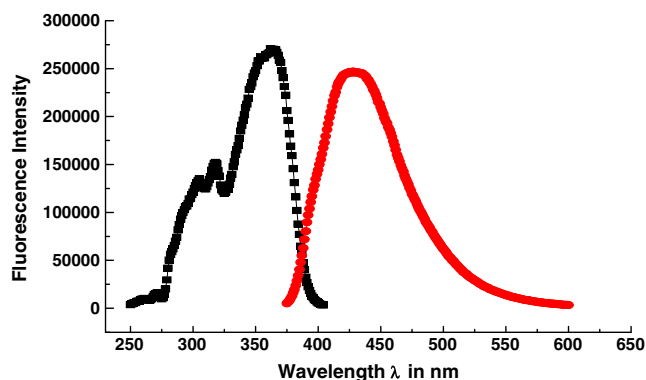

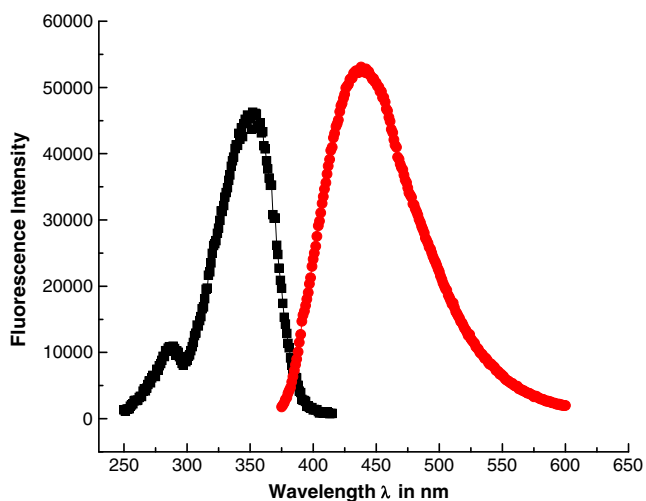**Fig. 2** Typical absorption and fluorescence spectra of C_1

Fig. 3 Typical absorption and fluorescence spectra of C_2

capacitance of different concentrations of the solute in toluene the dielectric constant of the solution (ε_{12}) was calculated using the expression

$$\varepsilon_{12} = \frac{C_A - C_X}{C_B - C_X} \quad (1)$$

where C_A, C_X and C_B, represent the capacitances due to leads, solution, and air respectively. The values of dielectric constants thus determined for C_B and C_A using toluene. The values of refractive indices (n_{12}) of solutions were determined for C_B and C_A using toluene respectively.

Theory

Theoretical Calculations of Ground-State Dipole Moments

The ground-state dipole moments (μ_g) of these two molecules were calculated by quantum chemical calculations. All the computations were carried out using the Gaussian 03 program [24] on a Pentium-4 PC. The basis sets at the levels of theory B3LYP/6–31 g* were used for calculations and corresponding optimized molecular geometries are shown in Fig. 4. The values of ground-state dipole moments obtained from *ab initio* calculations using DFT.

Experimental Calculations of Ground-State Dipole Moments

The ground-state dipole moments (μ_g) of these two dyes were estimated experimentally using Guggenheim's method [25]. According to this the expression for ground-state dipole moment is given by
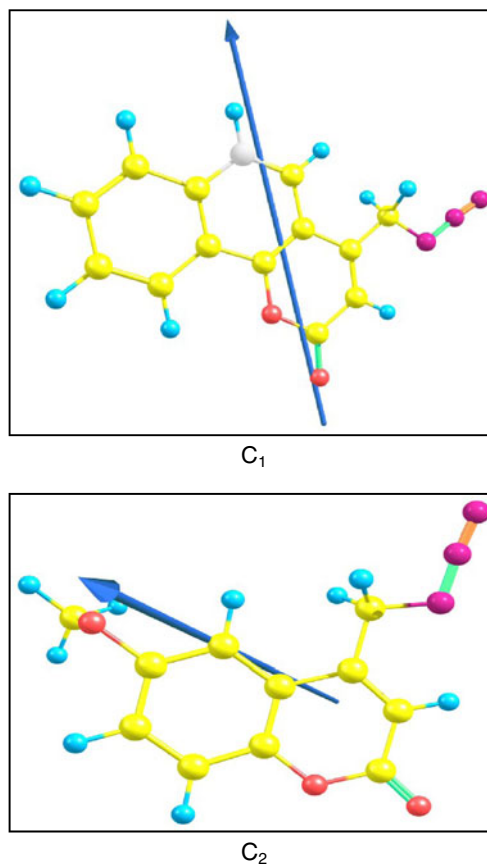

Fig. 4 Ground state optimized molecular geometries of C_1 & C_2. The arrow indicates the direction of dipole moment

$$\mu_g^2 = \left[\frac{27KT}{4\pi N(\varepsilon_1 + 2)\left(n_1^2 + 2\right)} X \frac{\Delta}{C} \right] \quad (2)$$

where

$$\Delta = \left(\varepsilon_{12} - n_{12}^2\right) - \left(\varepsilon_1 - n_1^2\right)$$

where K the Boltzmann constant, T the absolute temperature in Kelvin, N the Avogadro's number, ε_{12} the dielectric constant and n_{12} refractive index of the solution, ε_1 and n_1 are the dielectric constant and refractive index of the pure solvent and C the concentration of the solute in given solvent. The estimated values of the ground-state dipole moments (μ_g) using Eq. 2 for C_1 and C_2 respectively.

Experimental Calculations of Excited State Dipole Moments

The three independent equations used for the estimation of excited state dipole moments of two dyes are as followsLippert's equation [26]

$$\bar{v}_a - \bar{v}_f = m_1 F_1(\varepsilon, n) + \text{Constant} \quad (3)$$

Table 1 Solvatochromic data of C_1 and C_2 along with the calculated values of polarity functions in different solvents

Coumarins	Solvents	λ_a nm	λ_f nm	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$(\bar{\nu}_a - \bar{\nu}_f)$(cm^{-1})	$\frac{1}{2}(\bar{\nu}_a + \bar{\nu}_f)$(cm^{-1})	$F_1(\varepsilon,n)$	$F_2(\varepsilon,n)$	$F_3(\varepsilon,n)$
C_1	Cyclohexane	353.6	425	28280.5	23529.4	4751.0	25904.95	−0.035	−2.13E-3	0.288
	Hexane	352.4	423	28376.8	23640.6	4736.2	26008.70	−0.033	−1.006E-3	0.255
	Acetonitrile	354.4	436	28216.7	22935.7	5281.0	25576.20	0.280	0.79700	0.633
	Dimethylsulfoxide	355.2	437	28153.1	22883.2	5269.9	25518.10	0.259	0.84200	0.744
	Acetone	354.4	436	28216.7	22935.7	5281.0	25576.20	0.274	0.79200	0.641
	Ethyl acetate	353.2	432	28312.5	23148.1	5164.4	25730.30	0.174	0.49300	0.499
	Ethyl alcohol	354.8	433	28184.8	23094.6	5090.2	25639.70	0.281	0.81700	0.654
	Diethyl ether	354.4	432	28216.7	23148.1	5068.6	25682.40	0.132	0.37100	0.425
	1-Hexanol	357.0	436	28011.2	22935.7	5075.5	25473.45	0.227	0.68700	0.627
C_2	Cyclohexane	352.0	441	28409.0	22675.7	5733.3	25542.35	−0.035	−2.13E-3	0.288
	Toluene	352.0	442	28409.0	22624.4	5784.6	25516.70	−0.022	0.02900	0.350
	Benzene	348.0	449	28735.6	22271.7	6464.0	25503.65	−0.032	6.29E-3	0.341
	Ethyl acetate	350.0	485	28571.4	20618.5	7952.9	24594.95	0.174	0.49300	0.499
	Diethyl ether	350.8	463	28506.2	21598.2	6908.0	25052.20	0.17	0.37100	0.425
	Carbon tetrachloride	356.0	449	28089.8	22271.7	5818.1	25180.75	−0.024	0.02300	0.323
	1,4 Dioxane	351.2	461	28473.8	21691.9	6781.9	25082.85	−0.013	0.04400	0.308

Fig. 5 The variation of Stokes shift with F_1 (ε, η) using Lippert's equation for C_1 and C_2
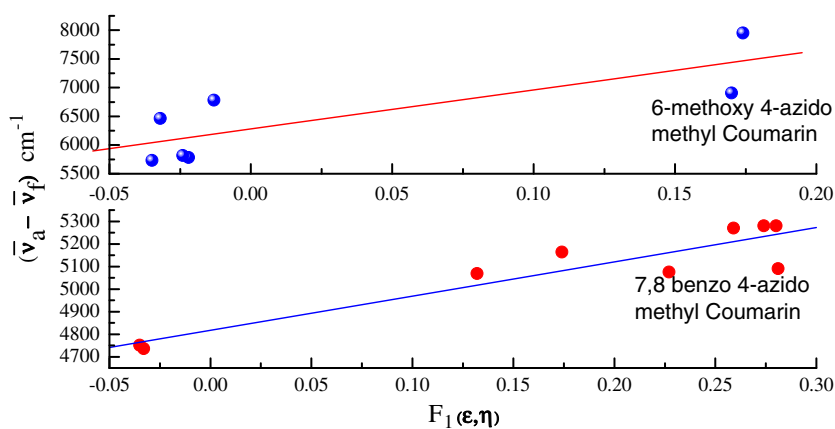
Bakshiev's equation [27]

$$\bar{v}_a - \bar{v}_f = -m_2 F_2(\varepsilon, n) + \text{Constant} \qquad (4)$$

Chamma-Viallet's equation [28]

$$\frac{\bar{v}_a + \bar{v}_f}{2} = m_3 F_3(\varepsilon, n) + \text{Constant} \qquad (5)$$

The expressions for F_1 (ε, n) [Lippert's polarity function], F_2 (ε, n) [Bakshiev's polarity equation] and F_3 (ε, n) [Chamma-Viallet's polarity equation] are given as

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \qquad (6)$$

$$F_2(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \qquad (7)$$

$$F_3(\varepsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \qquad (8)$$

Where $\bar{v}_a$ and $\bar{v}_f$ are absorption and fluorescence maxima wavelength in cm^{-1} respectively. The other

symbols ε and n are dielectric constant and refractive index respectively. From Eqs. 6–8 it follows that $(\bar{v}_a - \bar{v}_f)$ versus F_1 (ε, n), $(\bar{v}_a - \bar{v}_f)$ versus F_2 (ε, n) and $\frac{\bar{v}_a + \bar{v}_f}{2}$ versus F_3 (ε, n) should give linear graphs with slopes m_1, m_2 and m_3 respectively and are given as

$$m_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3} \qquad (9)$$

$$m_2 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca^3} \qquad (10)$$

$$m_3 = \frac{2\left(\mu_e^2 - \mu_g^2\right)}{hca^3} \qquad (11)$$

Where μ_g and μ_e are the ground and excited state dipole moments of the solute molecules. The symbols h and c are Planck's constant and velocity of light in vacuum respectively, 'a' is the Onsager radius of the solute molecule. If the ground state and excited states are parallel, the following expressions are obtained on the basis of

Fig. 6 The variation of Stokes shift with F_2 (ε, η) using Bakshiev's equation for C_1 and C_2
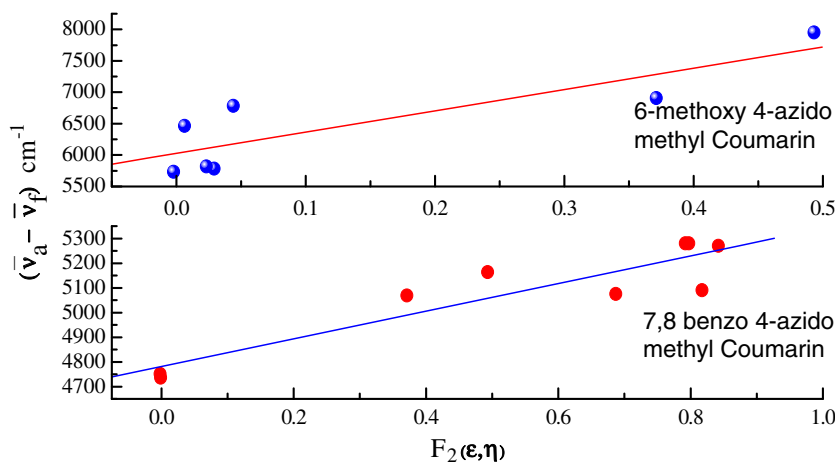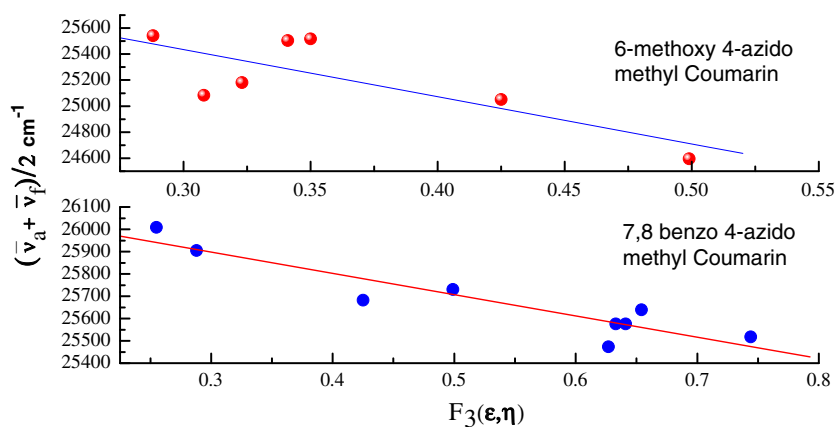
Fig. 7 The variation of arithmetic means of Stokes shift with F_3 (ε, η) using Chamma-Viallet's equation for C_1 and C_2

Eqs. 11–12 [17, 18].

$$\mu_g = \frac{m_3 - m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{\frac{1}{2}} \quad (12)$$

$$\mu_e = \frac{m_3 + m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{\frac{1}{2}} \quad (13)$$

and

$$\mu_e = \left[\frac{m_2 + m_3}{m_3 - m_2} \right] \mu_g \quad \text{for}(m_3 > m_2) \quad \cdots \cdots \quad (14)$$

Results and Discussion

The spectral shifts $(\bar{v}_a - \bar{v}_f)$ and $\frac{1}{2}(\bar{v}_a + \bar{v}_f)$ of two coumarins and solvent polarity function values F_1 (ε, n), F_2 (ε, n) and F_3 (ε, n) for various solvents are presented in Table 1. We have used eight and seven solvents with dielectric constants varying from 2 to 21 for C_1 and C_2 respectively. Figures 5, 6 and 7 show the graph of $(\bar{v}_a - \bar{v}_f)$ versus F_1 (ε, n), $(\bar{v}_a - \bar{v}_f)$ versus F_2 (ε, n) and $\frac{1}{2}(\bar{v}_a + \bar{v}_f)$ versus F_3 (ε, n) respectively. A linear progression was done and the data was fit to a straight line, corresponding values of the slopes are given in Table 2. In most cases $(\bar{v}_a - \bar{v}_f)$ versus F_1 (ε, n) and $(\bar{v}_a - \bar{v}_f)$ versus F_2 (ε, n) correlation is established for a larger number of solvents than $\frac{1}{2}(\bar{v}_a + \bar{v}_f)$ versus F_3 (ε, n) correlation. In most cases

the correlation coefficients are larger than 0.92 and indicate a good linearity for m_1, m_2 and m_3 with selected number of Stokes shift data points. Generally, the deviation from linearity may be due to specific solute solvent interactions.

The ground state dipole moments of two coumarins were estimated by using Guggenheim method [25]. The values obtained from this method are 6.162 D and 6.261D for C_1 and C_2 respectively and also ground state (μ_g) dipole moment values obtained from Eq. 12 are presented in Table 3. The values of Onsager cavity radii of the C_1 and C_2 molecules were calculated by molecular volumes and the Parachor [29] and are listed in Table 3.

The excited state (μ_e) dipole moments of the two coumarins, estimated by computing the values of ground state (μ_g) dipole moments obtained from Guggenheim method, in Eqs. 9–11 are presented in Table 3. Also the (μ_g) and (μ_e) values were obtained from Eqs. 12 and 13. The ratio of (μ_g) and (μ_e) obtained from Eq. 14 are presented in Table 3. The experimental (from Eq. 2) and theoretically calculated (*ab initio* calculations using DFT) values are presented in Table 3. The experimental and theoretical ground state (μ_g) dipole moment results are good in agreement for our used chemical systems as shown in Table 3 [3, 15, 24]. The difference in the ground state dipole moment is due to the necessity of knowing the radius of the solute molecule in Eq. 12 as compared to experimental and theoretical values obtained from Eq. 2 and *ab initio* calculations using DFT. It may be noted that the measured values of (μ_g) and (μ_e) for C_1 and C_2 differ from each other. The higher values of (μ_e) in the case of C_2

Table 2 Statistical treatment of the correlations of solvents spectral shifts of C_1 and C_2

A- Lippert Correlation; B-Bakshiev Correlation; C-Chamma Viallet Correlation

Coumarins	Slope			Correlation coefficient			Number of data		
	A	B	C	A	B	C	A	B	C
C_1	1517.509	559.963	953.498	0.927	0.914	0.927	9	9	9
C_2	6808.792	3394.794	3629.719	0.812	0.859	0.784	7	7	7

Table 3 Ground and excited state dipole moments of C_1 and C_2

Coumarins	Radius 'a' (A^o)	$\mu_g{}^a$ (D)	$\mu_g{}^b$ (D)	$\mu_e{}^c$ (D)	$\mu_e{}^d$ (D)	$\mu_e{}^e$ (D)	$\mu_e{}^f$ (D)	$(\mu_e/\mu_g)^g$
C_1	3.771	6.162	6.2270	4.0527	2.9364	3.4631	2.331	2.330
C_2	3.622	6.261	6.3848	7.2055	5.4353	5.5800	4.144	4.145

[a] The experimental ground states dipole moments calculated from Guggenheim method

[b] Calculated by B3LYP functional with 6–31 g* basis using DFT

[c] The experimental excited state dipole moments calculated from Lippert's equation

[d] The experimental excited state dipole moments calculated from Bakshiev's equation

[e] The experimental excited state dipole moments calculated from Chamma-Viallet's equation

[f] The excited states dipole moments calculated using Eq. 13

[g] The ratio of excited state and ground state dipole moments values calculated using Eq. 14

may be attributed to the structural difference between the molecules. It may be noted that the discrepancies occur between the estimated values of (μ_e) for the two coumarins. These differences between the values of (μ_e) may be in part, due to the various assumptions and simplifications made in the use of Lippert's, Bakshiev's and Chamma Viallet's correlations [26–28]. The large magnitude of Stoke's shift indicates that the excited state geometry could be different from that of the ground state. The general observation is that there is an increase in Stoke's shift with increase in solvent polarity which shows that there is an increase in the dipole moment on excitation.

The Solvatochromic data can be used to identify the spectra, namely π- π*, n-π*, etc. It can be noticed from Table 1 that, with increase in the solvent polarity, the fluorescence emission peak undergoes a bathochromic shift, confirming a π-π* transition. The shift of the fluorescence wavelengths towards longer wavelengths could be caused, if the excited state charge distribution in the solute is markedly different from the ground state charge distribution, and is such as to give a stronger interaction with polar solvents in the excited state.

Conclusion

We have studied the photophysical properties of C_1 and C_2. It has been found that excited state dipole moment (μ_e) is greater than ground state dipole moment (μ_g) for both the coumarins. The increase in dipole moment in the excited singlet states range between about 2.5 to 3 D. This demonstrates these two coumarins are more polar in excited states than in ground states for all the solvents studied. The excited state dipole moments were observed less in Bakshiev's relation as compared to Lippert and Chamma-Viallet's relations. The ground state dipole moments results are correlated (experimental and theoretical) in our used chemical systems. It may be noted that there is a difference in the ground state and excited state dipole moments. It is

worthwhile to stress that the discrepancies observed may due to approximations made in both methods to estimate ground state and excited singlet state dipole moments for two coumarins. Also Eq. 14 can be used to estimate the value of excited state dipole moment by pre-knowledge of the value of ground state dipole moment, without the necessity of knowing the Onsager radius of the solutes.

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