

# Dipole Moments of Coumarin 500 Dye in Aqueous Ethanol: Solvatochromic and Computational Study

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**Abstract:** The photo-physical study of Coumarin 500 polar laser dye in aqueous ethanol was carried out experimentally as well as computationally. We observed a hypsochromic shift in both the absorption and fluorescence emission spectra with increasing solvent polarity indicating the  $n \rightarrow \pi^*$  transition. The dipole moments calculated by the Bilot-Kawski, Lippert-Mataga, Kawski-Chamma-Viallet and Bakhshiev methods have been compared with the theoretical values obtained by DFT studies. It is observed that the excited state dipole moment is higher than the ground state dipole. The ground and excited state geometry optimization of the C500 was carried out using Gaussian 09 software by applying CAM-B3LYP/6-311++G(d,p) basis set in gas phase.

**Index Terms** — Solvatochromism, Aqueous Ethanol, DFT calculations, Dipole moments.

## I. INTRODUCTION

Solvatochromism is one of the simplest and popular methods used to determine the dipole moments of fluorescent organic molecules. Shift in both absorption and emission spectra induced by solvent effect has been interesting parameter to study electronic distribution in the excited states of molecules and helpful in the design of novel molecules for specific applications [1]. Coumarins have attracted significant attention due to their widespread applications such as laser dyes, fluorescent probes for protein studies, fluorescent indicators, estimation of enzymes, dye-sensitized solar cells, biosensors, etc [2]. A solvent is characterized by its polarity, relative permittivity ( $\epsilon$ ), refractive index ( $n$ ), and viscosity ( $\eta$ ) which show significant effect on organic molecules. It is possible to tune these solvent properties by mixing two (binary) or three (ternary) solvents in different proportions [3-21].

Solvatochromism of the coumarin derivatives has been mainly studied by electronic absorption and fluorescence spectroscopy. It reflects changes in the spectroscopic and optical properties and consequently, in the electronic structure of a molecule with a change of solvent media. The excitation and emission spectra of a dye are often altered by solvents and provide information on the behavior of the excited state in comparison to the ground state. Using the spectral shift data as a function of solvent polarity, the spectral transition ( $\pi \rightarrow \pi^*$ ,  $\pi^* \rightarrow n$ , etc.) can be identified. As a function of solvent polarity, the  $\pi^* \rightarrow n$ , and  $\pi \rightarrow \pi^*$  bands exhibit blue and red shifts, respectively [22]. The present research work aims to determine the ground and excited state dipole moments of C500 in aqueous ethanol at different compositions.

## 2. EXPERIMENTAL METHODS

Commercially available Coumarin 500 Laser dye (Fig. 1a) was obtained from Exciton Inc., USA, and was used as received. Spectroscopic grade ethanol procured from Spectrochem Pvt. Ltd. Mumbai, chemicals, and double distilled water (Milli-Q) with the highest available purity were used to prepare aqueous mixtures of solvents. Absorption spectra were recorded using a dual beam UV-VIS NIR spectrophotometer (JASCO, Model V-670) in the wavelength range of 200-800 nm. A spectrofluorometer (JY Horiba, Model Fluoromax4) was used to record the emission spectra. The ground and excited state geometries of C500 were optimized in the gas phase employing Gaussian 09 software [23] using density functional theory (DFT) and time-dependent density functional theory (TD-DFT), respectively.

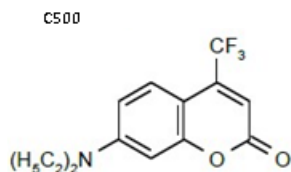


Fig. 1. (a) Molecular structure of C500 Laser Dye.

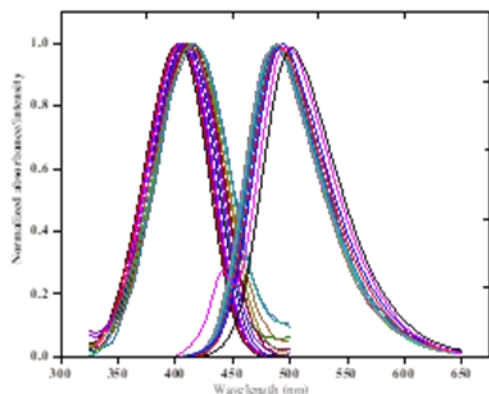


Fig. 1(b) Absorption and Emission spectra of C500 in aqueous ethanol.

### 3. THEORETICAL BACKGROUND FOR THE EVALUATION OF DIPOLE MOMENT

The electronic distribution of a molecule can be determined by analyzing its ground and excited state dipole moments. We have used the following solvatochromic shift approaches for the measurement of dipole moments of C500 polar laser dye.

#### 3.1. Bilot and Kawski method

Bilot and Kawski used quantum mechanics to figure out how dipole moments in the ground ( $\mu_g$ ) and singlet excited ( $\mu_e$ ) states can be measured using different solvents of varying polarities. They achieved this by measuring the absorption ( $\nu_a$ ) and fluorescence ( $\nu_f$ ) band shifts in these different solvents [25]. According to Bilot-Kawski, the difference and sum of absorption and fluorescence maxima ( $\text{cm}^{-1}$ ) depend linearly on solvent polarity function  $f(\epsilon, n)$  and the expressions are as shown in equations (1) and (2)

$$\bar{\nu}_a - \bar{\nu}_f = -m_2(f(\epsilon, n) + 2g(n)) + const \quad (1)$$

$$\bar{\nu}_a + \bar{\nu}_f = m_1 f(\epsilon, n) + const \quad (2)$$

where,  $m_1$  and  $m_2$  are the slopes from the relation (1) and (2), respectively. If the solvent polarity of the solute can be studied with refractive index ( $n$ ) and permittivity of distinct solvents ( $\epsilon$ ), then  $f(\epsilon, n)$  and  $g(n)$  can be described as

$$f(\epsilon, n) = \frac{2n^2+1}{n^2+2} \left[ \frac{\epsilon-1}{\epsilon-2} - \frac{n^2-1}{n^2+2} \right] \quad (3)$$

$$\text{and } g(n) = \frac{3(n^4-1)}{2(n^2+2^2)} \quad (4)$$

If the polarizability of the solute is isotropic with the  $\left(\frac{2\alpha}{a^3}\right)$ , where ' $\alpha$ ' is an isotropic polarizability and ' $a$ ' the Onsager cavity radius of the solute then according to the reaction field theory of Onsager

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (5)$$

and

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (6)$$

where, ' $c$ ' denotes the speed of light in a vacuum, and ' $h$ ' is Planck's constant. If the solute's symmetry does not change throughout the electronic transition, then  $\mu_g$  and  $\mu_e$  are considered to be parallel and are given by [8,9].

$$\mu_g = \frac{m_1 - m_2}{2} \left[ \frac{hca^3}{2m_1} \right]^{1/2} \quad (7)$$

$$\mu_g = \frac{m_1 + m_2}{2} \left[ \frac{hca^3}{2m_1} \right]^{1/2} \quad (8)$$

or

$$\frac{m_1 + m_2}{m_2 - m_1} \mu_g; \quad (\mu_e = \mu_g) \quad (9)$$

#### 3.2. Lippert -Mataga, Bakhshiev and Kawski-Chamma-Viallet methods

Lippert-Mataga, Bakhshiev and Kawski-Chamma-Viallet solvatochromic techniques may also be used to determine the ground and singlet excited state dipole moments using the equations reported by Lippert-Mataga (Eq.10) [25, 26], Bakhshiev (Eq.11) [27] and Kawski-Chamma-Viallet (Eq.12) [28, 29].

$$\bar{\nu}_a - \bar{\nu}_f = m f_{LM}(\epsilon, n) + const \quad (10)$$

$$\bar{\nu}_a + \bar{\nu}_f = m f_B(\epsilon, n) + const \quad (11)$$

and

$$(\bar{\nu}_a + \bar{\nu}_f)/2 = -m f_{KCV}(\epsilon, n) + const \quad (12)$$

where,  $\bar{\nu}_a, \bar{\nu}_f$  are the absorption and fluorescence maxima wave numbers in ( $\text{cm}^{-1}$ ), respectively,  $m_{L-M}, m_B, m_{K-C-V}$  are slopes derived from linear graphs (Fig.3) and  $f_{LM}(\epsilon, n), f_B(\epsilon, n)$  and  $f_{KCV}(\epsilon, n)$  are solvent polarity function defined by Eqs. (13)-(15).

$$f_{L-M}(\epsilon, n) = \left[ \frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1} \right] \quad (13)$$

$$f_B(\epsilon, n) = \frac{2n^2+1}{n^2+2} \left[ \frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right] \quad (14)$$

$$f_{K-C-V}(\epsilon, n) = \frac{2n^2+1}{2(n^2+2)} \left[ \frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2} \right] + \frac{3(n^4-1)}{(2n^2+2)^2} \quad (15)$$

The graph of  $\bar{\nu}_a-\bar{\nu}_f$  vs  $f_{BK}(\epsilon, n)$ ,  $\bar{\nu}_a+\bar{\nu}_f$  vs  $\phi(\epsilon, n)$ ,  $\bar{\nu}_a-\bar{\nu}_f$  vs  $f_{LM}$ ,  $f_B$  and  $(\bar{\nu}_a+\bar{\nu}_f)/2$  vs  $f_{KCV}$  of C500 laser dye in aqueous ethanol exhibits linear patterns with the respective slopes  $m_{L-M}$ ,  $m_B$ ,  $m_{K-C-V}$  as given in the following equations

$$m_{L-M} = \frac{2(\mu_e-\mu_g)^2}{hca^3} \quad (16)$$

$$m_B = \frac{2(\mu_e-\mu_g)^2}{hca^3} \quad (17)$$

$$m_{K-C-V} = \frac{2(\mu_e-\mu_g)^2}{hca^3} \quad (18)$$

### 3.3. Onsager cavity radius

The value of Onsager cavity radius “a” of C500 dye was determined by using Eq. (19) [30]

$$\alpha = \left[ \frac{3M}{4\pi\rho N_A} \right]^{1/3} \quad (19)$$

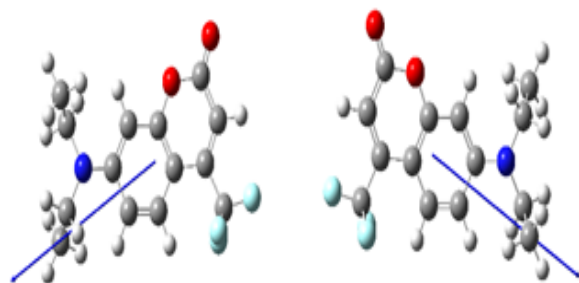
where,  $\rho$  is density of solute molecule, M, its molecular weight and  $N_A$ , the Avogadro’s number.

### 4. Computational details

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at the level CAM-B3LYP/6-311G++(d,p) level vacuum were used to optimize the ground and excited state geometries of the fluorescent C500 molecule [31]. All the calculations were carried out in the gas phase. The optimized structures of C500 in both the ground and excited state along with dipole moment vector are given in Fig. 2.

## 5. RESULTS AND DISCUSSION

The spectral characteristics of C500 laser dye were analyzed in aqueous mixture to estimate the solvent effect on electronic transition. Table 1 summarizes the solvent properties of C500 dye in different composition of aqueous ethanol solvents



(a) Ground state

(b) Excited state

Fig. 2. Optimized geometry with dipole moment vector of C500

such as the relative permittivity ( $\epsilon$ ), refractive index ( $n$ ), solvent polarity parameters  $f(\epsilon, n)$  and  $\phi(\epsilon, n)$  from different solvent correlation approaches.

### 5.1. Solvent effects on absorption and fluorescence spectra

As the solvent polarity increases, the fluorescence emission maxima shift toward the higher wavelength. From Fig. 1 (b) it is observed that as the solvent polarity increases both the absorption and fluorescence emission spectra show a bathochromic shift indicating the occurrence of the  $n \rightarrow \pi^*$  transition. Table 1 summarizes experimentally determined values of absorption maxima ( $\bar{\nu}_a$ ), emission maxima ( $\bar{\nu}_f$ ), Stokes shift ( $\bar{\nu}_a-\bar{\nu}_f$ ) and  $(\bar{\nu}_a+\bar{\nu}_f)$  values of C500 in aqueous ethanol. Table 1 summarizes the mole fractions of aqueous ethanol, refractive index ( $n$ ), relative permittivity ( $\epsilon$ ), absorption and fluorescence emission maxima and solvent polarity parameters  $f(\epsilon, n)$  and  $\phi(\epsilon, n)$  from Bilot-Kawski,  $f_{L-M}(\epsilon, n)$  of Lippert-Mataga,  $f_B(\epsilon, n)$  of Bakhshiev and  $f_{KCV}(\epsilon, n)$  of Kawski-Chamma-Viallet methods.

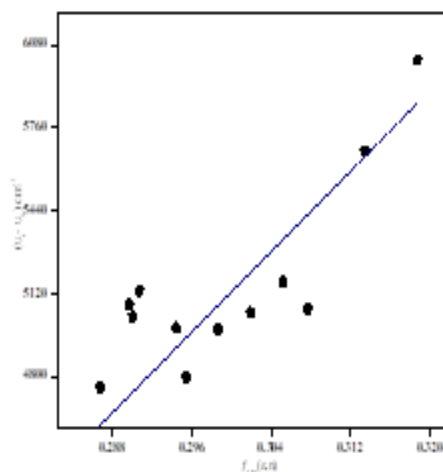


Fig. 3. Graph of  $f_{BK}(\epsilon, n)$  vs.  $\bar{\nu}_a-\bar{\nu}_f$  for C500 laser dye in aqueous ethanol.

Table 1. Mole fractions of aqueous ethanol, refractive index ( $n$ ), relative permittivity ( $\epsilon$ ), sum and difference of absorption and fluorescence emission maxima ( $\bar{\nu}_a+\bar{\nu}_f$  and  $\bar{\nu}_a-\bar{\nu}_f$ ) and solvent polarity parameters calculated from various methods

Sl. No	Mole fraction of Ethanol	n	$\epsilon$	$\bar{\nu}_a - \bar{\nu}_f$ (cm <sup>-1</sup> )	$\bar{\nu}_a + \bar{\nu}_f$ (cm <sup>-1</sup> )	B-K method f(ε, n)	Φ(ε, n)	L-M Method f <sub>L-M</sub> (ε, n)	Bakhshiev Method f <sub>B</sub> (ε, n)	KCV Method f <sub>KCV</sub> (ε, n)
1	1.00	1.3632	23.50	4759.03	45492.23	1.0074	1.636	0.287	0.856	2.307
2	0.91	1.3603	24.99	5078.69	45811.89	1.0043	1.626	0.290	0.864	2.316
3	0.84	1.3611	25.58	5032.48	45600.43	1.0028	1.626	0.290	0.867	2.318
4	0.73	1.3661	28.05	5131.80	45373.25	0.9968	1.632	0.291	0.878	2.328
5	0.66	1.3622	30.80	4986.90	45390.94	0.9932	1.619	0.294	0.888	2.339
6	0.55	1.3660	34.33	4797.98	45202.02	0.9877	1.622	0.295	0.899	2.349
7	0.41	1.3649	39.42	4982.34	45142.98	0.9828	1.615	0.299	0.911	2.361
8	0.31	1.3628	45.65	5045.31	45205.95	0.9786	1.606	0.302	0.923	2.374
9	0.23	1.3604	53.52	5165.55	45085.71	0.9749	1.597	0.305	0.934	2.385
10	0.17	1.3565	57.75	5062.66	45062.66	0.9740	1.587	0.308	0.939	2.391
11	0.11	1.3516	64.11	4689.31	44450.74	0.9729	1.575	0.311	0.945	2.398
12	0.07	1.3458	67.29	5670.09	44962.82	0.9733	1.562	0.313	0.947	2.402
13	0.03	1.3400	70.76	5276.13	44723.87	0.9737	1.549	0.316	0.950	2.406
14	0.00	1.3354	76.18	6021.90	45391.98	0.9734	1.539	0.319	0.954	2.411

Table 2. Experimentally and computationally determined values of ground and excited state dipole moments of C500.

### 6. CONCLUSION

Generally, the refractive index and relative permittivity of solvents play a key role in the shift in the spectral range whereas in specific types of interaction, the shifts are caused due to hydrogen

In order to calculate the dipole moments in the ground and excited states using solvatochromic shift approach based on spectral shift and solvent polarity is given by Bilot and Kawski [Eqs. (1) & (2)]. Using Eqs. (7) and (8), the slopes  $m_1$  and  $m_2$  by the Bilot-Kawski method (Fig. 3) are employed to compute the ground ( $\mu_g$ ) and

Solute	Solvent	Method	$\mu_g$	$\mu_e$	$\mu_e/\mu_g$	$\Delta\mu$
C500	Binary Mixture of Ethanol +Water at different compositions	Bilot-Kawski Method	3.50	12.68	3.62	9.18
		Lippert-Mataga Method	--	8.22	--	--
		Bakhshiev Method	--	6.00	--	--
		Kawski-Chamma-Viallet Method	--	3.55	--	--
C500 (Literature)	Aprotic solvents Alcohols Liquid crystals	Gaussian09 software	5.42	7.44	1.37	2.02
		--	3.7	6.2	1.67	2.5
			2.2	4.8	2.18	2.6
			1.2	2.9	2.42	1.7

bonding, n-donor and excited state dipole moments.

singlet excited state ( $\mu_e$ ) dipole moments.

Table 2 depicts the experimentally measured and computationally determined values of ground and excited state dipole moments of C500. The ground state dipole moment ( $\mu_g$ ) obtained from the Bilot-Kawski method is 3.50D whereas it is 12.60D for the excited state ( $\mu_e$ ). The values of  $\mu_e$  calculated from Lippert-Mataga and Bakshiev method are 8.22D and 6D, respectively. Also, theoretically calculated  $\mu_g$  and  $\mu_e$  by using Gaussian 09 software are 5.42D and 7.44D, respectively. From these values it is clear that the C500 molecule is more polar in excited state than

the ground state. The experimentally determined ground and excited state dipole moments of C500 were compared with those obtained from the different methods. The dipole moments calculated by these methods are comparable to those calculated by the Gaussian 09 software.

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