



# Estimation of ground and excited state dipole moment of laser dyes C504T and C521T using solvatochromic shifts of absorption and fluorescence spectra



Jana Basavaraja<sup>a</sup>, H.M. Suresh Kumar<sup>a,\*</sup>, S.R. Inamdar<sup>b</sup>, M.N. Wari<sup>b</sup>

<sup>a</sup> Department of Physics, Siddaganga Institute of Technology, Tumkur 572 103, India

<sup>b</sup> Laser Spectroscopy Programme, Department of Physics, Karnatak University, Dharwad 580 003, India

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## ABSTRACT

The absorption and fluorescence spectra of laser dyes: coumarin 504T (C504T) and coumarin 521T (C521T) have been recorded at room temperature in a series of non-polar and polar solvents. The spectra of these dyes showed bathochromic shift with increasing in solvent polarity indicating the involvement of  $\pi \rightarrow \pi^*$  transition. Kamlet–Taft and Catalan solvent parameters were used to analyze the effect of solvents on C504T and C521T molecules. The study reveals that both general solute–solvent interactions and specific interactions are operative in these two systems. The ground state dipole moment was estimated using Guggenheim's method and also by quantum mechanical calculations. The solvatochromic data were used to determine the excited state dipole moment ( $\mu_e$ ). It is observed that dipole moment value of excited state ( $\mu_e$ ) is higher than that of the ground state in both the laser dyes indicating that these dyes are more polar in nature in the excited state than in the ground state.

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## 1. Introduction

Coumarin is a member of benzopyrone family of compounds, which consist of a benzene ring joined to a pyrone ring. Coumarins are well known laser dyes in the blue-green spectral region and they establish a family of dyes, which are applicable in physics, chemistry, biology and medicine [1–7]. The strong solvent dependence of various substituted coumarins was exploited for photo initiators, probes, photosensitizing agents in the biological study and photodimerization in polar and non-polar solvents in chemistry [8]. Coumarins are also widely used as fluorescent indicators [9], sunburn preventives [10], for estimation of enzymes, [11] etc.

The study of effect of solvents on absorption and fluorescence characteristics of organic compounds has been a subject of interesting investigations, since, the physical and chemical processes are influenced by the properties of solvents in which they carried out [12,13]. It is observed that the spectral shift such as blue shift or red shift occurs due to effects of various solvents with polar or non-polar nature [14–16], at different temperature [17,18] and at different pH values [19]. Also, the fluorescence characteristics can be altered by the substitution at various positions in the parent coumarin molecule. From the literature survey, we noticed that the substituted coumarins have electron donating and withdrawing groups attached at different positions and these substituents alter their spectral shifts in various solvents [20–23]. In general, electron donating

substituent tends to enhance the fluorescence intensity while electron withdrawing substituents tend to diminish it. These spectral changes impart a substantial alteration of the optical properties of the solute, for example, change in degree of polarization, quantum yield, excited state lifetime, excited state dipole moment, etc.

One of the important physical parameters of any organic molecules, which describe the distribution of electrons around them is quantitatively known as dipole moment. In the ground and excited state, the dipole moments are different due to change in electron density in these states. The ground state ( $\mu_g$ ) and excited ( $\mu_e$ ) state dipole moments of organic (dyes) molecules reveal information on electronic and geometrical structure of the molecule in the excited state. A prior knowledge of the dipole moment of electronically excited species is often useful in the design of non-linear optical materials and elucidation of the nature of the excited state as well as the course of any photochemical transformation [24].

Several methods are used to determine the dipole moment of the singlet excited state, namely electronic polarization of fluorescence [25], electric dichroism [26], microwave conductivity [27] and Stark splitting [28,29]. Solvatochromism is the simplified and popular method, employed to determine the excited state dipole moment. Because, it shows a linear correlation between the wave number of the absorption and fluorescence maxima with solvent polarity functions  $f(\epsilon, n)$ . Therefore, this method is informative and proves fruitful in studying the excited state behavior of the molecules [30–36]. As a part of our research on laser dyes, in the present paper, we have studied the effect of solvent polarity on absorption and fluorescence characteristics of two coumarin laser dyes: C504T and C521T and estimated the ground and

\* Corresponding author.

E-mail address: [sureshkumarhm@rediffmail.com](mailto:sureshkumarhm@rediffmail.com) (H.M. Suresh Kumar).

excited state dipole moments by correlating the spectral shifts with solvent polarity scale  $f(\epsilon, n)$  and microscopic polarity scale  $E_T^N$  [37,38].

## 2. Material and methods

The coumarin laser dyes C504T and C521T obtained from Exciton, USA are of scintillation grade and were used without further purification. The molecular structures of these dyes respectively are given in Fig. 1. All the solvents used were of HPLC grade, transparent and non-fluorescent in the range of excitation and fluorescence emission (SD Fine Chemicals Ltd., India). The absorption spectra were recorded using Hitachi F2000 absorption spectrophotometer and fluorescence spectra were recorded using JY Horiba Scientific Fluoromax-4S Spectrofluorometer. All the measurements were carried out at room temperature keeping dye concentration very low at about  $2 \times 10^{-5}$  M to avoid the self-absorption.

### 2.1. Estimation of ground state dipole moment

The ground state dipole moment of C504T and C521T was calculated using Guggenheim's method [39]. Dilute solutions of the concentration about  $10^{-5}$  M prepared in toluene solvent were used for the studies. The dipole moment of the dye in the ground state was calculated using the equation

$$\mu_g^2 = \frac{27kT}{4\pi N(\epsilon_1 + 2)(n_1^2 + 2)} \times \Delta \quad (1)$$

where  $\Delta = [(\frac{\epsilon_{12}-\epsilon_1}{C})_{C \rightarrow 0} - (\frac{n_{12}^2-n_1^2}{C})_{C \rightarrow 0}]$  is the difference between the extrapolated intercepts of the plots of  $(\frac{\epsilon_{12}-\epsilon_1}{C})$  versus  $C$  and  $(\frac{n_{12}^2-n_1^2}{C})$  versus  $C$  with respect to infinite dilution ( $C \rightarrow 0$ ). The quantities  $k, N, \epsilon, n, C$  and  $T$  are the Boltzmann's constant, Avogadro's number, dielectric constant, refractive index, concentration in M/L and absolute temperature, respectively. The suffixes 1 and 12 refer to the solvent and solution respectively. The dielectric constant of dilute solutions used in this method was measured in a suitably fabricated cell of small capacitance where the accurate determination of small changes in the capacitance is possible. The small capacitance was measured with the help of Forbes Tinsley (FT) 6421 LCR Data Bridge at 10 kHz frequency. The refractive index of the solutions was determined using Abbe's refractometer. All these measurements were carried out at room temperature.

The ground state dipole moment ( $\mu_g$ ) of the dyes was also determined theoretically by quantum mechanical calculations. All the computations were carried out using Gaussian 03 program [40] on a Pentium-4 PC. The basis sets at the levels of theory B3LYP/6-31 g\* were used for calculations.

### 2.2. Estimation of excited state dipole moment

#### 2.2.1. Theory

Lippert and Mataga [30,31] obtained the expressions based on Onsager's reaction field theory, in which the fluorophore is assumed to be a point dipole residing at the center of a spherical cavity with radius

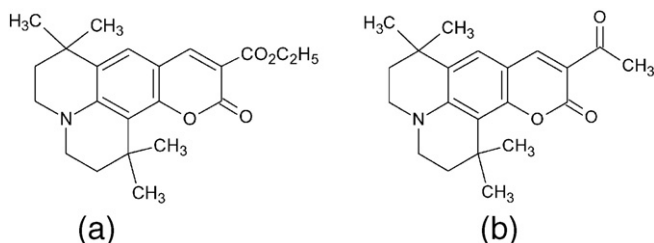


Fig. 1. Molecular structures of (a) C504T and (b) C521T.

' $a$ ' in the homogeneous and isotropic dielectric medium. These equations break down due to two factors; when the solute-solvent interactions such as non-specific or specific interactions (hydrogen bonding acceptors/donors) are not considered, since these interactions also contribute significantly. The other one is the cavity radius which is difficult to estimate for non-spherical molecule [41]. Bakshiev [32] and Bilot-Kawski [33,34] obtained a simplified equation based on quantum mechanical second order perturbation theory of absorption ( $\bar{\nu}_a$ ) and fluorescence ( $\bar{\nu}_f$ ) band shift in different solvents of varying dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) relative to the band position of a solute molecule, these equations are:

According to Bakshiev,

$$(\bar{\nu}_a - \bar{\nu}_f) = m_1 F_1(\epsilon, n) + \text{constant} \quad (2)$$

and Bilot-Kawski,

$$\frac{(\bar{\nu}_a + \bar{\nu}_f)}{2} = m_2 F_2(\epsilon, n) + \text{constant} \quad (3)$$

where  $\bar{\nu}_a$  and  $\bar{\nu}_f$  are the absorption and fluorescence maxima,  $n$  and  $\epsilon$  are the refractive index and the dielectric constants of the solvents, respectively.  $F_1(\epsilon, n)$  &  $F_2(\epsilon, n)$  are solvent polarity functions given by Eqs. (4) and (5), respectively.

$$F_1(\epsilon, n) = \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 1} \right] \frac{(2n^2 + 1)}{(n^2 + 1)} \quad (4)$$

$$F_2(\epsilon, n) = \left[ \frac{2n^2 + 1}{2(n^2 + 2)} \left( \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 1} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right] \quad (5)$$

Plots of  $(\bar{\nu}_a - \bar{\nu}_f)$  and  $(\frac{\bar{\nu}_a + \bar{\nu}_f}{2})$  against the bulk solvent polarity functions  $F_1(\epsilon, n)$  and  $F_2(\epsilon, n)$  for different solvents yield the slopes  $m_1$  and  $m_2$  respectively and are given below:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (6)$$

$$m_2 = \frac{-2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (7)$$

where  $h, c$  and  $a$  are Planck's constant, the velocity of light and Onsager's cavity radius of the molecule, respectively.  $\mu_g$  and  $\mu_e$  are ground and excited state dipole moments.

The angle  $\varphi$  between the dipole moments  $\mu_e$  and  $\mu_g$  is

$$\cos \varphi = \frac{1}{2\mu_e \mu_g} \left[ (\mu_e^2 + \mu_g^2) - \frac{m_1}{m_2} (\mu_e^2 - \mu_g^2) \right] \quad (8)$$

Assuming that the symmetry of the investigated solute molecule remains unchanged upon electronic transition and, the ground and excited state dipole moments are parallel, based on Eqs. (6) and (7), one can obtain

$$\mu_g = \frac{m_2 - m_1}{2} \left( \frac{hca^3}{2m_1} \right)^{1/2} \quad (9)$$

$$\mu_e = \frac{m_1 + m_2}{2} \left( \frac{hca^3}{2m_1} \right)^{1/2} \quad (10)$$

The other method employing empirical solvent polarity  $E_T^N$  scale proposed by Reichardt [37] correlates the spectral shift better than the traditionally used bulk solvent polarity function because in bulk solvent polarity function, polarizability, hydrogen bonding effect and complex

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