

Solvent effects on the dipole moments and photo physical properties of laser dye

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The absorption and emission spectra of fluorescent laser dye namely, 4,4''-bis-2-butyloctyl-oxy)-P-quaterphenyl have been recorded at room temperature in solvents of different polarities. The excited state dipole moments (μ_e) have been estimated from Lippert's, Bakhshiev's and Kawski-Chamma-Viallet's equations using the variation of Stoke's shift with the solvent dielectric constant and refractive index. The geometry of the molecule has been fully optimized and the μ_g has also been calculated theoretically by Gaussian 03 software using B3LYP/6-31g* level of theory. The μ_g and μ_e have been calculated by means of solvatochromic shift method. It has been observed that μ_e is higher than μ_g , indicating a substantial redistribution of the π -electron densities in a more polar excited state for the selected laser dye. Further, the changes in the dipole moment ($\Delta\mu$) has been calculated both from solvatochromic shift method and microscopic empirical solvent polarity parameter (E_T^N) and values are compared.

Keywords: Solvatochromic shift method, Stoke's shift, Solvent polarity parameter, Ground state dipole moments, Excited state dipole moments, Laser dye, DFT

1 Introduction

The absorption and fluorescence characteristics of organic compounds under the effect of a solvent have always been a subject of interest¹⁻⁵. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes. This can result in the change of dipole moment at the excited state. The dipole moment of an electronically excited molecule is an important property which sheds light on the electronic and geometrical structure of the molecule. 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 solvatochromic method is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. 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, indoles, purines, and fluorescein and in few laser

dyes⁶⁻¹⁹. In the last few years, fluorescent compounds like thiophene, have become a strong interdisciplinary research field. These studies range from fabrication of electronic and optoelectronic devices to the selective detection of biosensors. These organic molecules are important materials having novel electronic and photonic properties which find its use in many technological applications. Organic molecules have become the hot cake of today due to its properties like broad tunability, high quantum efficiency and broad spectral band width.

In this paper, we report the solvent effects on absorption and emission spectra, and estimation of ground and excited state dipole moments of a laser dye by solvatochromic shift method. Theoretical studies on ground state (μ_g) dipole moments using DFT (B3LYP/6-31g* method) is also reported²⁰. However, there are no reports available in literature on the determination of μ_g and μ_e values of the molecule investigated.

2 Experimental

2.1 Materials

The solute 4,4''-bis-2-butyloctyl-oxy)-P-quaterphenyl was obtained from Koch laboratory,

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England. The molecular structure of this laser dye is given in Fig. 1. The solvents used in the present study are cyclohexane, hexane, benzene, tetrachloro ethane, tetrahydro furan, dichloro ethene, dichloro methane, dimethyl formamide, dimethyl sulphoxide, butanol, propanol and ethanol. All the solvents were obtained from S-D-Fine Chemicals Ltd., India, which were of spectroscopic grade. The required solutions were prepared at fixed concentration of solute $1 \times 10^{-5} \text{M}$ in each solvent.

2.2 Spectroscopic measurements

The absorption spectra were recorded using Hitachi 50–20 UV–VIS spectrophotometer. Fluorescence intensities of the solutions were measured on Hitachi F-2000 Spectrofluorimeter with perpendicular geometry. All these measurements were carried out at room temperature (300 K).

2.3 Theoretical calculations of ground state dipole moments

The ground state dipole moment (μ_g) of the laser dye was calculated by quantum chemical calculations. All the computations were carried out using the Gaussian 03 program²⁰ on a Pentium-4 PC. The basis sets at the levels of theory B3LYP/ 6-31 g* was used for calculations and corresponding optimized molecular geometries were shown in Fig. 2. The values of ground state dipole moments obtained from *ab initio* calculations using DFT. Ground state optimized molecular geometries of 4,4''-bis-2-

butyloctyl-oxy)-P-quaterphenyl is shown in Fig. 3. The arrow indicates the direction of the dipole moment.

2.4 Experimental calculations of excited state dipole moments

The three independent equations used for the estimation of excited state dipole moments of the selected laser dye are as follows:

Lippert's equation²¹:

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\epsilon, n) + \text{Constant} \quad \dots (1)$$

Bakshiev's equation²²:

$$\bar{\nu}_a - \bar{\nu}_f = m_2 F_2(\epsilon, n) + \text{Constant} \quad \dots (2)$$

Kawski-Chamma-Viallet's equation²³:

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_3 F_3(\epsilon, n) + \text{Constant} \quad \dots (3)$$

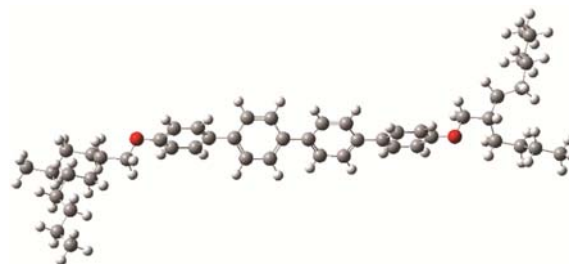
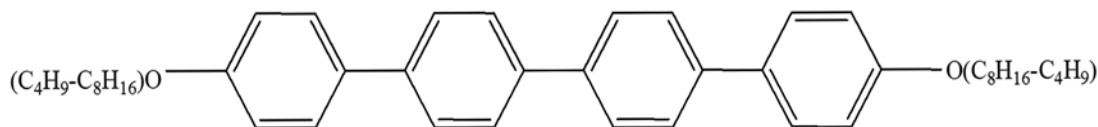


Fig. 2 — Optimized geometries of laser dye.



4,4''-Bis(2-butyl-octyloxy)-p-quaterphenyl (BIBUQ)

Fig. 1 — The molecular structure of laser dye.

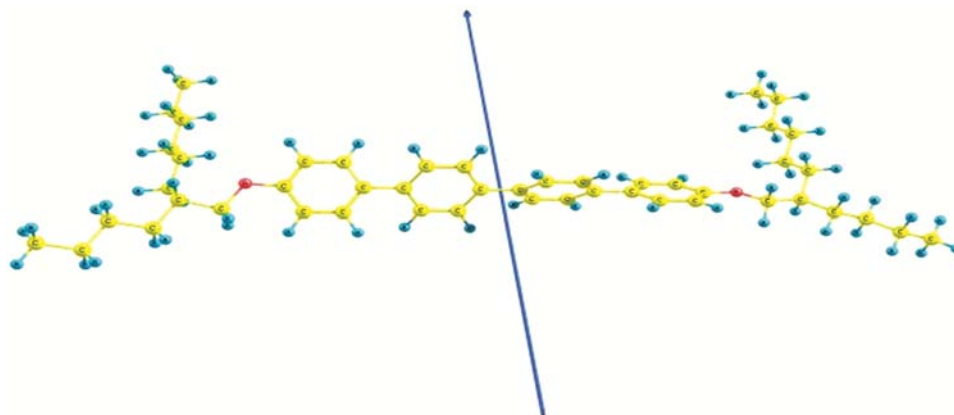


Fig. 3 — Ground state optimized molecular geometry of laser dye. The arrow indicates the direction of the dipole moment.

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

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

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

$$F_3(\varepsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \quad \dots (6)$$

Where $\bar{\nu}_a$ and $\bar{\nu}_f$ 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 (4-6), it follows that $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\varepsilon, n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_2(\varepsilon, n)$

and $\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ versus $F_3(\varepsilon, n)$ should give linear graphs with slopes m_1 , m_2 and m_3 respectively and are given as:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad \dots (7)$$

$$m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad \dots (8)$$

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad \dots (9)$$

Where μ_g and μ_e are the ground and excited state dipole moments of the solute molecule. 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 Eqs (8-9).

$$\mu_g = \frac{m_3 - m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2} \quad \dots (10)$$

$$\mu_e = \frac{m_3 + m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{1/2} \quad \dots (11)$$

and

$$\mu_e = \left[\frac{m_3 + m_2}{m_3 - m_2} \right] \mu_g \quad \text{for } (m_3 > m_2) \quad \dots (12)$$

2.5 Molecular-microscopic solvent polarity parameter (E_T^N)

The empirical polarity parameter E_T^N proposed by Richards³ gave towering results with solvatochromic shift of dipolar molecules. The results correlate better with microscopic solvent polarity E_T^N rather than the traditionally used bulk solvent polarity functions involving dielectric constant (ε) and refractive index (n) as in the later error estimation of Onsager cavity radius 'a' has been minimized. In E_T^N the error estimation of the Onsager cavity radius has been minimized, it also includes intermolecular solute/solvent hydrogen bond donor/acceptor interactions along with solvent polarity. The theoretical basis for the correlation of the spectral band shift with E_T^N was proposed by Reichardt and developed by Ravi *et al.*²⁴, according to Eq. (13).

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_b} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + \text{Constant} \quad \dots (13)$$

Where $\Delta\mu_b = 9\text{D}$ and $a_B = 6.2 \text{ \AA}$ are the change in dipole moment on excitation and Onsager cavity radius respectively of molecule and $\Delta\mu$ and a are the corresponding quantities for the solute molecule of interest. A dimensionless normalized scale E_T^N was introduced in order to avoid the use of non SI unit kcal/mol in $E_T(30)$ solvent polarity scale and is defined by Eq. (13), using water ($E_T^N = 1$) and tetramethylsilane (TMS = $E_T^N = 0$) as extreme reference solvents [3].

$$E_T^N = \frac{E_T(\text{Solvent}) - E_T(\text{TMS})}{E_T(\text{Water}) - E_T(\text{TMS})} = \frac{E_T(\text{Solvent}) - 30.7}{32.4} \quad \dots (14)$$

The change in dipole moment ($\Delta\mu$) can be evaluated from the slope of the stokes shift versus E_T^N plot and is given by Eq. (15):

$$\Delta\mu = (\mu_e - \mu_g) = \sqrt{\frac{mX81}{(6.2/a)^3 11307.6}} \dots (15)$$

where 'm' is the slope obtained from the plot of Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus microscopic solvent polarity (E_T^N) using Eq. (15). The Onsager radius of the molecule can be calculated by the method suggested by Edward²⁵.

3 Results and Discussion

The typical absorption and emission spectra of laser dye as shown Fig.4 in acetonitrile solvent. The spectral shifts ($\bar{\nu}_a - \bar{\nu}_f$) and ($\bar{\nu}_a + \bar{\nu}_f$) of the selected laser dye and solvent polarity function values $F_1(\epsilon, n)$, $F_2(\epsilon, n)$ and $F_3(\epsilon, n)$ for various solvents are presented in Table 1. We have used twelve solvents for laser dye with dielectric constants varying from 2.200 to 47.240. Figure 5 shows the graph of ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_1(\epsilon, n)$, ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_2(\epsilon, n)$, $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_3(\epsilon, n)$ and ($\bar{\nu}_a - \bar{\nu}_f$) versus E_T^N . 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 ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_1(\epsilon, n)$, ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_2(\epsilon, n)$ and

$1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus $F_3(\epsilon, n)$ correlation is established for a large number of solvents and the correlation coefficients are larger than 0.96 which 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 moment (μ_g) values obtained from Eq. (10) are presented in

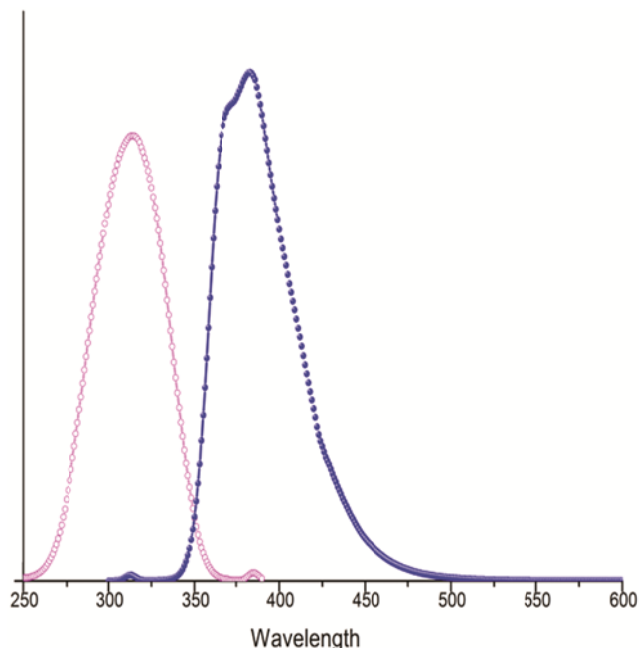


Fig. 4 — Typical absorption and emission spectra of laser dye.

Table 1 — Solvatochromic data of laser dye in different solvents.

Solvents	λ_a (nm)	λ_f (nm)	$\Delta\theta = \theta_a - \theta_f$ (cm^{-1})	$(\theta_a + \theta_f)/2$ (cm^{-1})	$F_1(\epsilon, n)$	$F_2(\epsilon, n)$	$F_3(\epsilon, n)$	E_T^N
Cyclohexane	312	378	5596.26	29253.15	-0.002	-0.003	0.2875	0.006
Hexane	311.2	377	5608.48	29329.44	0.0134	0.0253	0.2684	0.009
Benzene	312.1	379.6	5697.49	29192.27	0.0046	0.01	0.343	0.111
TCE	312	383	5941.62	29080.47	0.193	0.5498	0.6009	0.16
THF	310.6	382.1	6024.59	29183.45	0.2092	0.5495	0.5519	0.207
DCE	311.9	384.5	6053.76	29034.68	0.2228	0.6301	0.6166	0.269
DCM	312	385	6077.26	29012.65	0.2182	0.5952	0.5859	0.321
DMF	312.7	385.1	6012.25	28973.41	0.2754	0.8409	0.7216	0.404
DMSO	312.9	386.2	6065.77	28926.21	0.2636	0.8426	0.7451	0.444
Butanol	311.3	384.3	6102.02	29072.35	0.2639	0.753	0.6482	0.602
Propanol	311.5	383.6	6033.91	29085.78	0.2728	0.765	0.6396	0.617
Ethanol	310.7	384.4	6170.82	29099.98	0.289	0.8133	0.6524	0.654
Solvents	311.2	377	5608.48	29329.44	0.0134	0.0253	0.2684	0.009
Cyclohexane	312.1	379.6	5697.49	29192.27	0.0046	0.01	0.343	0.111
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$F_1(\epsilon, n)$:Lip pert's polarity function, $F_2(\epsilon, n)$:Bakhshiev's polarity function,

$F_3(\epsilon, n)$:Kawski-Chamma-Viallet's polarity function, E_T^N : Microscopic solvent polarity function

Table 3. The value of Onsager cavity radius for 4,4''-bis-2-butyloctyl-oxy)-P-quaterphenyl was calculated by molecular volumes and the Parachor²⁵ method and is also listed in Table 3.

The excited state dipole moments of the laser dye, estimated by computing the values of ground state dipole moment (μ_g) obtained from Eqs (7-9) are presented in Table 3. Also the (μ_g) and (μ_e) values obtained from Eqs (10) and (11), the ratio of (μ_g) and (μ_e) obtained from Eq. (12) are presented in Table 3. The theoretically calculated (*ab initio* calculations

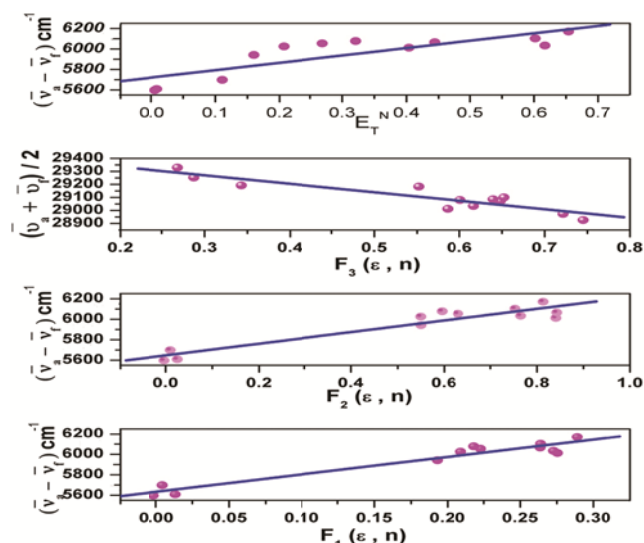


Fig. 5 — The variations of Stoke's shift with $F_1(\epsilon, n)$ and $F_2(\epsilon, n)$, arithmetic means of Stoke's shift with $F_3(\epsilon, n)$ and Stoke's shift with E_T^N for laser dye.

Table 2 — Statistical treatment of the correlations of solvents spectral shifts of laser dye.


Compound	Correlation	Slopes 'm'	Correlation co-efficient 'R'	Number of data
Laser dye	Lippert's	1704.77	0.97	12
	Bakshiev's	568.096	0.95	12
	Chamma-Viallet's	651.719	0.91	12
		720.262	0.84	12

Table 3 — Ground and excited state dipole moments of laser dye.

Compound	Radius 'a' (Å)	μ_g^a (D)	μ_g^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	μ_e^f (D)	$\Delta\mu^g$ (D)	$\Delta\mu^h$ (D)	$(\mu_e/\mu_g)^i$
Laser dye	5.5579	0.854	0.229	3.343	5.624	3.343	3.343	3.114	1.928	14.5869

Debye (D) = $3.33564 \times 10^{-30} \text{ cm} = 10^{-18} \text{ esu cm}$.

^a Calculated by Gaussian software; ^b ground states dipole moments calculated using Eq. (10); ^c experimental excited state dipole moment calculated from Eq. (11); ^d experimental excited state dipole moment calculated from Lippert's equation; ^e experimental excited state dipole moment calculated from Bakshiev's equation; ^f experimental excited state dipole moment calculated from Chamma-Viallet's equation; ^g change in dipole moments for μ_e^c and μ_g^b ; ^h change in dipole moments calculated from Eq. (15) and ⁱ ratio of excited state and ground state dipole moments values calculated using Eq.(12).

using DFT) ground state dipole moment values are presented in Table 3. The values of experimental and theoretical ground state (μ_g) dipole moment are good in agreement^{4,12,26-28} for our used chemical systems as shown in Table 3. It may be noted that the measured values of (μ_g) and (μ_e) for laser dye differ from each other. It may also be noted that the discrepancies occur between the estimated values of (μ_e) for laser dye. 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 Kawski-Chamma-Viallet's correlations²¹⁻²³. 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 at the excited state would be due to the marked difference in the charge distribution with that of the ground state distribution. This in turn, provides stronger interaction with polar solvents in the excited state. The observed variations in the dipole moments can be understood from their resonance structures as shown in Fig. 6.

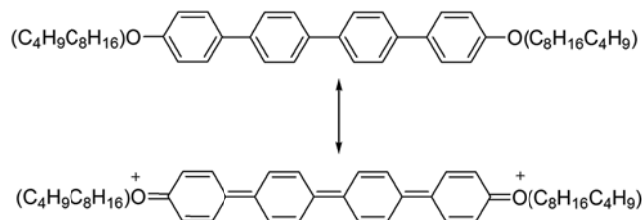


Fig. 6 — Possible resonance structure of laser dye.

5 Conclusions

We have studied the photo physical properties of laser dye. It has been found that excited state dipole moment (μ_e) is greater than ground state dipole moment (μ_g) for the selected laser dye. The increase in dipole moment in the excited states range about 1 to 3 D. This demonstrates that the molecule is more polar in excited states than in ground states for all the solvents studied. The ground state dipole moments results are correlated 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 the molecule. Also Eq. (12) 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 solute.

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