

Estimation of Ground and Excited State Dipole Moments of Coumarin 450 by Solvatochromic Shift Method

L. R. Naik* and N. N. Math

Department of Physics, Karnatak University, Dharwad - 580 003, India

The ground and excited state dipole moments of Coumarin 450 (C 450) laser dye were measured at room temperature in several solvents of varying dipole moments. The ground state dipole moment (μ_g) is estimated by using the modified Onsager model and the excited state dipole moments (μ_e) were estimated by the method of solvatochromism as well as by utilizing the microscopic solvent polarity parameter (E_T^N). Further, the deviation of some of the points from the linearity of the E_T^N versus Stokes shift indicates the existence of specific type of solute-solvent interaction. The excited state dipole moment of C 450 were found to be higher than those of the ground state and is interpreted in terms of the resonance structure of the molecule. A reasonable agreement has been observed between the values obtained by the method of solvatochromism and modified Onsager model. It is observed that, corresponding to cyclohexane solution, the fluorescence maxima shift towards the red region with increasing the polarity of the solvents, hence the transition involved are of $\pi - \pi^*$ type.

key words: Dipole moment, Stokes shift, solute-solvent interactions

INTRODUCTION

Determination of dipole moments of organic molecules in their ground and excited singlet states are of great interest because they can be used as a tool to study their configuration and/or conformers. Moreover, the values of the excited state dipole moments provide information about the changes of electronic distribution occurring upon photoexcitation. Recent studies have indicated that excited state dipole moment can be used in the design of non-linear optical materials, which have large hyper polarizabilities and in membrane research [1-4]. Electronic absorption and of fluorescence emission of coumarin dyes has been a constant field of interest because a better understanding of the excited state properties not only helps in the design of new molecules but also for the best performances of specific applications: laser dyes, probes for polymers, micellar and biological systems, etc. Because of intensive fluorescent property, substituted coumarins have been found useful as optical brightness, fluorescence indicators and even as sunburns preventives [5,6]. Due to their uses in analytical and biological system the steady state properties of coumarin derivatives has attained the importance [6]. A systematic analysis of the solvent effects is useful in determining the dipole moments of excited and ground state of the molecules. The dipole moments of a molecule in the ground state and the excited state depend on the electron distributions in these states. A change of solvent is

accompanied by a change in polarity, dielectric constant and change of polarizability of the surrounding medium. Thus the change of solvent affects the ground state and the excited state differently. And for this purpose, we have estimated the ground state dipole moment by a modified Onsager model and excited state dipole moment by solvatochromic shift method as well as by utilizing the microscopic solvent polarity parameter E_T^N . It is observed that, compared to cyclohexane solution, all other solutions exhibit red shift (bathochromic) both in absorption and fluorescence maxima. The bathochromic shift produced both in absorption and fluorescence with increasing solvent polarity, indicates that the transition involved are of $\pi \rightarrow \pi^*$ nature. It is to be noted that, C 450 exhibited marked red shift in the fluorescence maxima compared to the shift in absorption. It indicates that solvation is large in S_1 state compared to ground state, i.e., excited state dipole moment is high compared to ground state dipole moment.

EXPERIMENTAL

The coumarin 450 was obtained from Exciton, USA and used as without further purification. All solvents were of spectroscopic grade (Fluka or Merck) and were used as received. The purity of solvents was checked before use, by HPLC-MS method. The absorption and fluorescence emission spectra were recorded using UV-Visible absorption spectrophotometer (Model Hitachi 150-20) and fluorescence spectrophotometer (Model Hitachi F-2000) at room temperature. In order to reduce the effect of self-absorption, measurements were taken at low concentration (1×10^{-5} mol dm⁻³).

*To whom correspondence should be addressed.

E-mail : naik_36@rediffmail.com

Received May 11, 2005 Accepted July 8, 2005

RESULTS AND DISCUSSION

Ground state dipole moment

The theoretical ground state dipole moment of C 450 in polar solvents were estimated by using a modified Onsagar model [7], which reflects electronic states of molecules and interactions with the solvents and is expressed as

$$\mu_g = 0.0128 \left[\left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{(2\epsilon + n^2)(\epsilon + 2)M}{3\epsilon(n^2 + 2)d} \times T \right]^{\frac{1}{2}} \quad (1)$$

where, M is the molecular weight of the solute, d is density, ϵ is dielectric constant, n is the refractive index of the solvent and T is the absolute temperature.

Excited state dipole moment

The experimental first excited state dipole moment (μ_e) can be estimated on the basis of Onsager's theory of the reaction field from the solvatochromic shift method [8]. Several treatments have been proposed leading to different equations relating the Stoke's shift $\Delta\bar{\nu}$ to an appropriate solvent polarity function.

Lippert-Mataga's correlation between the solvent spectral

shifts and F_1 solvent polarity function [9 & references therein] is given by

$$\Delta\bar{\nu} = (\bar{\nu}_a - \bar{\nu}_f) = S_1 F_1(\epsilon, n) + C_1 \quad (2)$$

$$\text{where, } S_1 = \frac{2(\mu_e - \mu_g)^2}{cha^3} \quad (3)$$

Bakhshiev correlation between the solvent spectral shifts and F_2 solvent polarity function [9 & references therein] is given by

$$\Delta\bar{\nu} = (\bar{\nu}_a - \bar{\nu}_f) = S_2 F_2(\epsilon, n) + C_2 \quad (4)$$

$$\text{where, } S_2 = \frac{2(\mu_e - \mu_g)^2}{cha^3} \quad (5)$$

and Chamma and Viallet correlation between the solvent spectral shifts and F_3 solvent polarity function [9,10] is given by

$$\frac{\Delta\bar{\nu}}{2} = \frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -S_3 F_3(\epsilon, n) + C_3 \quad (6)$$

$$\text{where, } S_3 = \frac{2(\mu_e - \mu_g)^2}{cha^3} \quad (7)$$

Table 1. Solvent properties and polarity functions of C 450.

Solvent	Dielectric const (ϵ) at 25°C	Refractive index (n) at 25°C	Polarity function $F_1(\epsilon, n)$	Polarity function $F_2(\epsilon, n)$	Polarity function $F_3(\epsilon, n)$	$(E_T^N)^a$
Cyclohexane	2.01	1.424	0.0156	-0.0028	0.2862	0.150
Dioxane	2.21	1.420	0.0212	0.0420	0.3066	0.164
Ethyl acetate	6.02	1.370	0.2204	0.4901	0.4967	0.228
Propanol	20.21	1.383	0.2748	0.7826	0.6530	
Ethanol	23.40	1.359	0.2882	0.8074	0.6480	0.654
Methanol	32.63	1.326	0.3094	0.8552	0.6496	0.762
Acetonitrile	35.94	1.342	0.3054	0.8664	0.6662	0.472
Dimethyl formamide	36.71	1.427	0.2746	0.8364	0.7102	0.404
Ethylene glycol	38.69	1.429	0.2758	0.8408	0.7114	
Dimethyl sulfoxide	48.89	1.477	0.2644	0.8446	0.7448	
Water	78.54	1.331	0.3211	0.9136	0.6816	1.000

^aTaken from reference 14

Table 2. Solvent shift data for C 450.

Solvent	$\bar{\nu}_a$ (cm ⁻¹)	E_a kcal mol ⁻¹	$\bar{\nu}_f$ (cm ⁻¹)	E_f kcal mol ⁻¹	$(\bar{\nu}_a - \bar{\nu}_f)$ (cm ⁻¹)	$(\bar{\nu}_a - \bar{\nu}_f)/2$ (cm ⁻¹)
Cyclohexane	29069	83.11	325641	73.31	3428	27355
Dioxane	28490	81.46	24330	69.56	4160	26272
Ethyl acetate	27247	77.90	23094	66.03	4153	25170
Propanol	27174	77.69	23041	65.87	4133	25108
Ethanol	27293	78.03	22988	65.72	4305	25141
Methanol	27412	78.37	22779	65.13	4633	25096
Acetonitrile	28089	80.31	23529	67.27	4560	25809
Dimethyl formamide	27594	78.89	23419	66.96	4175	25506
Ethylene glycol	26652	76.20	22523	64.39	4129	24588
Dimethyl sulfoxide	27293	78.03	23041	65.88	4252	25167
Water						

$\Delta\mu = (\mu_e - \mu_g)$ is the difference between the excited and ground state dipole moments, h is the Planck's constant, c is the speed of light, a is the solute cavity radius and $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$, $F_3(\varepsilon, n)$ are the solvent polarity functions which can be expressed as

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

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

$$\text{and } F_3 = \frac{F_2}{2} + \frac{3(n^4 - 1)}{2(n^2 + 2)^2}$$

According to the Suppan equation [11] the value of the solute cavity radius a , was calculated from the molecular volume of C 450 and was found to be 3.62\AA^0 .

The ground and excited state dipole moments of C 450 can also be determined from the following equations (7) & (8) [12,13]

$$\mu_g = \frac{1}{2} \left(\frac{a^3 hc S_1}{2} \right)^{1/2} \left(\frac{S_3}{S_1} - 1 \right) \quad (8)$$

$$\mu_e = \frac{1}{2} \left(\frac{a^3 hc S_1}{2} \right)^{1/2} \left(\frac{S_3}{S_1} + 1 \right) \quad (9)$$

A plot of stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) (in cm^{-1}) versus F gives a straight line and S_1 , S_2 and S_3 are the slopes of the straight lines given by equations 2, 4 and 6. Substituting the values of S_2 and S_3 in equation 8 and 9; we get, $\mu_e = 5.98$ D and $\mu_g = 4.21$ D. Similarly substituting the values of slopes S_1 and S_3 in equation 8 and 9 we get $\mu_e = 4.43$ D and $\mu_g = 1.28$ D. These values differ from those obtained from the slopes S_2 and S_3 . It is clear that this difference arises because of the differences between the Lippert's and Bakhshiev's theories. The excited state dipole moment estimated from the relation 10 with the knowledge of ground state dipole moment calculated from the modified Onsagar model in different solvents is given in Table 3, and it is observed that excited state dipole moment is higher than the ground state dipole moment.

Excited state dipole moment of C 450 was estimated by using the values of $\Delta\mu$ from Lippert's, Bakhshiev' and Chamma-Viallet's equations with the ground state dipole moment by modified Onsagar model for all solvents.

Further excited state dipole moment can also be determined by using the following expression [14].

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_D} \right)^2 \left(\frac{a_D}{a} \right)^3 \right] E_T^N + \text{constant} \quad (10)$$

where, E_T^N is the microscopic solvent polarity function proposed by Reinhardt based on absorption wave number of a standard Betaine dye in the solvent, $\Delta\mu_D$ and a_D are the

change of dipole moment and Onsager cavity radius, respectively and $\Delta\mu$ and a are the corresponding quantities of the C 450. The equation 10 clearly illustrates that the Stokes shift changes linearly with the solvent polarity function E_T^N . Hence, the $\Delta\mu$ can be estimated from the slope S_4 of the plot of Stokes shift versus E_T^N using the reported values of $\Delta\mu_D = 9$ D of the Betaine dye and its Onsagers cavity radius $a_D = 6.2$ \AA^0 [15] and hence excited dipole moment μ_e can be determined using the values of ground state dipole moment μ_g estimated from the modified onsagar model. It is also significant to note that since a ratio of $\frac{a_D}{a}$ is involved, hence, the errors

involved in the estimation of Onsager radius may be obviated to some extent. The calculated dipole moments are comparable with the other coumarin dyes [15,16].

From the slopes S_1 , S_2 and S_3 with Onsager radius, a of the dye, excited state dipole moment were calculated using the equation 3, 5 and 7 substituting the ground state dipole moment estimated from modified Onsagar model. The estimated ground (μ_g) and excited state dipole moment (μ_e) are collected in Table 3, and it is observed that excited state dipole moment is higher compared to ground state and can be attributed to the existence of the possible resonance structure of the molecule (Fig. 1). It also indicates that the excited state electronic charge distribution should be substantially different from the ground state charge distribution.

The values of the slopes S_1 , S_2 and S_3 are obtained by plotting the Stokes shift versus the solvent polarity functions $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$ and $F_3(\varepsilon, n)$ respectively. The plots drawn using least square fit method are shown in Fig (2-4). It is to be noted that all the points lie on straight line except dioxane,

Table 3. Theoretical ground state and experimental values of excited state dipole moments of C 450.

Solvents	μ_g^a (D)	μ_e^b (D)	μ_e^c (D)	μ_e^d (D)
Cyclohexane	3.64	6.80	5.46	4.64
Dioxane	3.22	6.38	5.40	4.22
Ethyl acetate	2.73	5.89	4.50	3.73
Propanol	5.89	9.05	7.66	6.88
Ethanol	6.33	9.48	8.19	7.33
Methanol	7.74	10.80	9.50	8.74
Acetonitrile	8.36	11.52	10.12	9.36
Dimethyl formamide	6.93	10.08	8.70	7.93
Ethylene glycol	6.61	9.77	8.38	7.61
Dimethyl sulfoxide	6.97	10.12	9.23	7.97
Water	10.86	14.02	12.62	11.86

^aThe ground state dipole moments calculated from modified Onsager model.

^bThe excited state dipole moments calculated with $\Delta\mu$ from Lippert's equation.

^cThe excited state dipole moments calculated with $\Delta\mu$ from Bakhshiev's equation.

^dThe excited state dipole moments calculated with $\Delta\mu$ from (E_T^N) polarity equation.

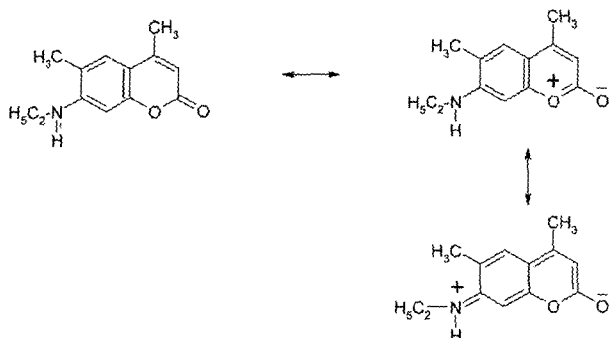


Figure 1. Possible resonance structures of the molecule.

acetonitril and methanol. The correlation coefficients are 0.73, 0.70 and 0.81 (Figs; 2, 3 and 4 respectively). The poor correlation between the Stokes shift and solvent polarity functions is attributed to the contribution of hydrogen bonding between the solute and polar solvents. If one

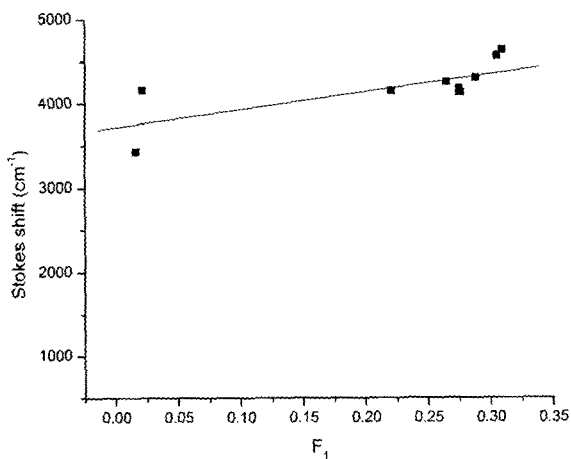


Figure 2. Plot of Stoke's shift versus $F_1(\epsilon, n)$ according to Lippert's relation.

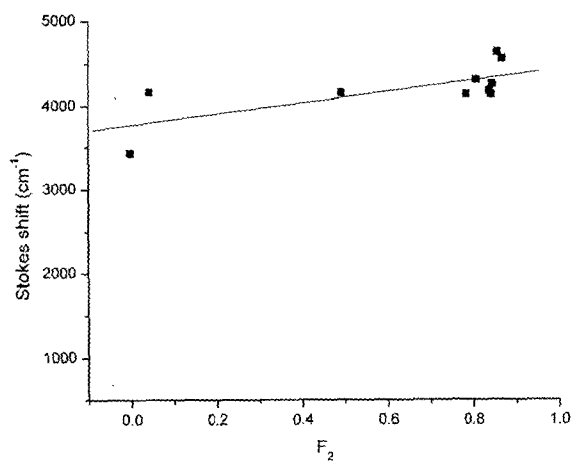


Figure 3. Plot of Stoke's shift versus $F_2(\epsilon, n)$ according to Bakhshiev's relation.

estimates the excited dipole moment from fluorescence spectroscopy technique and ground state dipole moments from the modified Onsagar model as shown in Table 3, it can be seen that Lippert's equation is more sensitive to the specific solute-solvent interactions while Bakhshiev equation is more sensitive to the general solvent effects [9], somehow Chamma-Viallet's equation does not indicate any trend regarding interactions.

The use of E_T^N as the solvent polarity function for solvatochromism studies of Stokes shifts can be efficient procedure to determine the excited state dipole moment of organic molecules [14]. The plot of solvent polarity function in terms of E_T^N versus Stokes shift is shown in Fig 5. with correlation coefficient of 0.76. If $\Delta\mu$ depends only on the solvent polarity function, the plot of Stokes shift versus E_T^N should have indicated a linear relationship for all solvents used. But in our case this has not been observed, as shown in Fig. 5, indicating specific solute-solvent interactions.

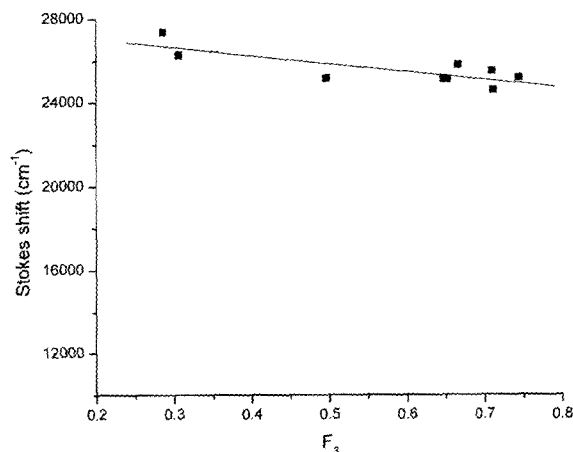


Figure 4. Plot of Stoke's shift versus $F_3(\epsilon, n)$ according to Chamma and Viallet's relation.

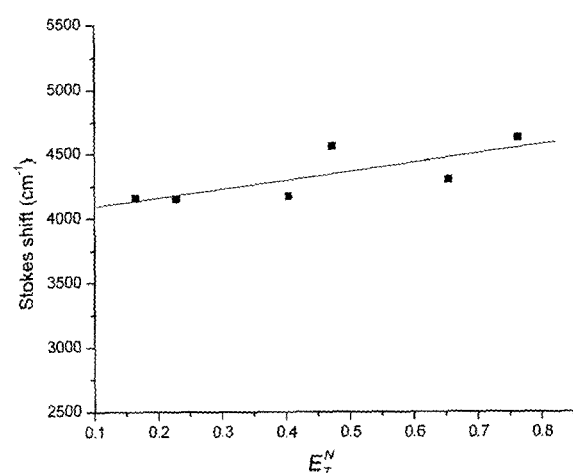


Figure 5. Plot of Stoke's shift versus E_T^N relation.

In the present study the excited state dipole moment obtained from Bakhshiev's equation and from E_T^N solvent polarity function are nearly reasonable, so to our opinion Bakhshiev's equation and E_T^N solvent polarity functions are better as compared to Lippert's equation.

It is worthwhile to stress that the use of E_T^N as the solvent polarity function for solvatochromism studies of Stokes shifts can be efficient procedure to determine the μ_e of organic molecules compared to the traditionally used bulk solvent polarity function involving relative permittivities and refractive index (Bakhshiev and Chamma & Viallet's equations). The dependence of Stokes shift on solvent polarity in Bakhshiev, Chamma and Viallet's expression seems to be less regular within polar solvents due to number of assumptions and simplifications made concerning the validity of their use and the errors associated in the estimation of the Onsager cavity radius.

CONCLUSION

In this study it is observed that, corresponding to cyclohexane solution, all other solutions exhibited red shift both in absorption and fluorescence maxima indicating a $\pi \rightarrow \pi^*$ transition. The deviation from the linear dependence of Stokes shift versus E_T^N indicated the existence of specific type solute-solvent interaction. The excited state dipole moment of Coumarin 450 is greater than ground state dipole moment.

ACKNOWLEDGEMENT

We thank change to Dr. D. K. Deshpande for helpful discussions.

REFERENCES

1. Basu, S. and Rohatgi-Mukherjee, K. K. (1983) Solvent effect on the emission spectra of Anthracene sulphonates and their excited state dipole moments. *J. Ind. Chem. Soc.*, **60**, 1147-1151.
2. Ravi, M. Samanta, A. Radhakrishnan, T. R. (1994) Excited state dipole moments from an efficient analysis of solvatochromic stokes shift Data. *J. Phys. Chem.*, **98**, 9133-9136
3. McRae, E. G. (1957) Theory of solvent effects on molecular charge separation studied by nanosecond time-resolved microwave conductivity. *J. Phys. Chem.*, **61**, 562-572.
4. Chemla, D. S. and Zyss, J. *Nonlinear optical properties of organic molecules and crystals*, Academic Press, New York, 1987.
5. Bush, T. E. and Scott, G. W. (1981) Fluorescence of Distyryl benzenes. *J. Phys. Chem.*, **85**, 144-146.
6. Maeda, M. *Laser Dyes*, New York, Academic Press., 1984.
7. Murthy, M. B. R. Dyasagar, B. S. and Patil, R. L. (2003) Measurements on polar liquids at a microwave frequency evaluation of molecular parameter-a new method. *PRAMANA, J. of Physics.*, **61**,4, 725-727.
8. Parkanyi, C. Antonious, M. S. Aaron, J. J. Buna, M. Tine and Cisse, A. (1994) Determination of the first excited singlet-state dipole moments of Coumarins by the solvatochromic method. *Spectro. Lett.*, **27**, 439-449.
9. Bilal Acemioglu, Mustafa Arik, Hasan Efeoglu, Yavuz Onganer. (2001) Solvent effect on the ground and excited state dipole moments of fluorescin. *J. Mol. Stru., (Theochem)*. **548**, 165-171.
10. Haas, M. P. and Warman, J. M. (1982) Photon-induced molecular charge separation studied by nanosecond time-resolved Microwave conductivity. *Chem. Phys.*, **73**, 35-53.
11. Suppan, P. (1983) Excited state dipole moments from absorption/fluorescence solvatochromic ratios. *Chem. Phys. Lett.*, **94**, 272-275.
12. Kawaski, A. (2002) On the estimation of excited state dipole moments from solvatochromic shifts of absorption and fluorescence spectra. *Z. Naturforsch.*, **57A**, 255-262.
13. Inamdar, S. R. Nadaf, Y. F. Mulimani, B. G. (2003) Ground and excited state dipole moments of exalite 404 and exalite 417 UV laser dyes determined from solvatochromic shifts of absorption and fluorescence spectra. *J. Mole. Struct., (Theochem)*, **624**, 47-51.
14. Kumar, S. Rao, V. C. Rastogi, R. C. (2001) Excited state dipole moments of some hydroxy coumarin dyes using an efficient solvatochromic method based on the solvent polarity parameter, . *Spectrochimica Acta Part A.*, **57**, 41-47.
15. Ravi, M. Soujanya, T. Samantha, A. Radhakrishna, T. P. (1995) Excited state dipole moments of some Coumarin dyes from solvatochromic method using the solvent polarity parameter, . *J. Chem. Soc. Farady. Trans.*, **91**, 2739-2742.
16. Giri, R. Rathi, S. S. Machwe, M.K. Murti, V. V. S. (1988) Effect of methoxy group and solvents on fluorescence of Coumarins. *Indian J. Pure and Appl. Phys.*, **26**, 445-448.

