Excited state electric dipole moments of two exalite dyes from solvatocromic shift measurements

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Excited state electric dipole moments of two exalite dyes from solvatocromic shift measurements

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The determination of excited state electric dipole moment through solvatochromic shifts of two Exalite dyes, namely, E-392A, E-398 have been carried out using fluorescence shifts and have been found to be less than those calculated through absorption shifts. It is felt that the one calculated using shifts in emission are more reliable. The results are presented and discussed. A qualitative estimate of the orientation of dipole moments in ground and excited state are also presented and discussed.

Keywords: Electric dipole moment; Solvatochromic shifts; Onsager cavity radius; Solvent dielectric medium; Exalite dyes

1. Introduction

The use of solvatochromic shifts for the determination of the dipole moment of electronically excited state of a molecule has been important for an understanding of their structure in that state [1–24,25]. These studies have gained importance due to the fast progress in photo science, especially, the studies on dyes, which are fluorescent. The insight into the understanding of the optical aspects of a material can be had through the excited state dipole moment value. The value of the dipole moment in the excited state can be estimated from several methods. The stark effect on the rotational spectra, solvatochromic shifts in absorption or fluorescence or a combination of both, are a few of them. The electro optical method [26,27], which uses the principle of fluorescence anisotropy and stark splitting of rotational levels of 0,0 vibrational band although gives accurate values, apart from being complicated, has difficulty in its application to large molecules such as dyes. The solvatochromic shift method, in general, although does not give accurate values of the dipole moments of a molecule, they give fairly acceptable values. The dipole moment values obtained using the solvatochromic shifts can improve by the proper choice of solvents and a method,

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Table 1. Fluorescence solvatochromic shifts for two dyes (cyclohexane as reference solvent 1).

Solvents	E-392A		E-398	
	ν_s in cm^{-1}	$\Delta\nu_{1-2}$ in cm^{-1}	ν_s in cm^{-1}	$\Delta\nu_{1-2}$ in cm^{-1}
Cyclohexane	26208	–	25316	–
Benzene	25707	321	25157	189
Ethylether	25906	122	25380	−64
DMF	25707	321	25062	254
Acetonitrile	25853	175	25252	64
Butanol	25839	189	25284	32
Methyl-cyclohexane	25974	54	25413	−97
Acetone	25839	189	25252	64

for example, use of slightly polar solvents, which are having almost same refractive indices, and use of fluorescence shifts rather than absorption data wherever available. Especially, in case of dyes which are used in lasers, which are mostly fluorescent, the fluorescence data in different solvents is expected to give better estimates of dipole moments in the excited state than the absorption data in view of the fact that fluorescence shifts are larger compared to those in absorption. The improved estimate of the dipole moment means a better understanding of the electron charge distribution, which plays an important role in giving insight into photochemical reaction, quantum yield etc. [8].

The use of a particular method to determine the dipole moment in the excited state, out of the several methods [10–22] available which use solvatochromic shifts is usually decided by looking into the available data of solute molecule in its ground state, like Onsager cavity radius, orientation of the dipole moment in its ground state etc. and capability to give fluorescence/absorption. In the case of dyes, the orientation of dipole moment with respect to its symmetry axis is difficult to comprehend and so also the accurate value of the Onsager cavity radius. However, there are methods available to estimate cavity radius. Thus, usually one employs those methods in which the Onsager cavity radius is used along with solvent shifts, preferably with fluorescence shifts in the absence of orientation of the dipole moment in the ground state. Nadaf *et al.* [19] have used one such method due to Ayachit *et al.* [12] and have estimated the excited state dipole moment of Exalite dyes, namely, E-392A, E-398 through absorption shifts. In view of the reasons mentioned above and explained later in this text, the authors have taken up the estimation of the dipole moment of these dyes again, using the fluorescence data available in the literature [20]. The solvents used along with their solvent shifts with respect to cyclohexane for two dyes are presented in table 1. The results of these studies along with the results available are discussed and are presented in this article. This study was felt more warranted as the dipole moment of such short-lived species in the excited state are often found useful in the design of non-linear optical materials, which bring photochemical transformations.

2. Theory and procedure

The displacement of electronic absorption and luminescence spectra are related to solvent interaction. These interactions can be non-specific, when they depend only on

multiple and polarizability properties of solute and solvent molecules. When a liquid solvent surrounds a molecule, each state of it is stabilized by an energy known as salvation energy. The medium i.e. solvent can affect the solute molecule by its viscosity and also by its polarity. The number of electronic states which are defined for a molecule are determined through Schrodinger wave equation $E\psi = H\psi$, where ψ being the wave function. The wave function gives the information regarding the nature of a state. By employing the quantum mechanical second order perturbation theory and using Onsager model, McRae [1] has given an equation for the frequency of maximum solute absorption/fluorescence in a solvent, ν_s and is as below:

$$\nu_s = \nu_0 + (A + B + C)f(n_s) + E[f(D_s) - f(n_s)] + F[f(D_s) - f(n_s)]^2 \tag{1}$$

where ν_0 is the corresponding vapor phase frequency of ν_s, $f(n_s) = (n_s^2 - 1)/(2n_s^2 + 1)$ is a function of solvent refractive index (n_s), $f(D_s) = (D_s - 1)/(2D_s + 1)$ is a function of solvent dielectric medium (D_s), $(A + B)$ is a measure of dispersive effect, and h and c are Planck's constant and velocity of light respectively. C is either $(\mu_e^2 - \mu_g^2)/hca_0^3$ or $(\mu_g^2 - \mu_g^2)/hca_0^3$ depending on whether ν_s is measured through absorption spectra or emission spectra respectively. Similarly, E is either $(\mu_g \cdot \Delta \mu_{g-e})/hca_0^3$ or $(\mu_e \cdot \Delta \mu_{e-g})/hca_0^3$ depending upon the spectra under study, with μ_e, μ_g being dipole moment in the excited state and ground state respectively with $\Delta\mu_{e-g} = \mu_e - \mu_g$ and a_0 is the Onsager cavity radius. The last term in equation (1) and $(A + B)$ can be neglected due to their small contribution towards shift.

With this, Suppan formulated the equation cited below for the difference in frequency in absorption for two different solvents 1 and 2, which is

$$-\Delta\nu_{1-2} = \left[\frac{(\mu_g \cdot \Delta\mu_{g-e})}{hca_0^3}\right]\Delta[f(D_s) - f(n_s)]_{1-2} + \left[\frac{(\mu_e^2 - \mu_g^2)}{hca_0^3}\right]\Delta f(n_s)_{1-2}.$$

The above equation for fluorescence will be, (with a_e being the cavity radius in the excited state),

$$-\Delta\nu_{1-2} = \left[\frac{(\mu_g \cdot \Delta\mu_{g-e})}{hca_e^3}\right]\Delta[f(D_s) - f(n_s)]_{1-2} + \left[\frac{(\mu_g^2 - \mu_e^2)}{hca_e^3}\right]\Delta f(n_s)_{1-2}.$$

The above equation was written by Ayachit *et al.* [12] in the form,

$$[(X/C_1) + (Y/C_2)] = 1. \tag{2}$$

Here, $X = [\Delta[f(D_s) - f(n_s)]_{1-2}]/-\Delta\nu_{1-2}$ and $Y = [\Delta f(n_s)_{1-2}]/-\Delta\nu_{1-2}$, with $C_1 = hca_0^3/(\mu_g \cdot \Delta \mu_{g-e})$ and $C_2 = hca_0^3/(\mu_e^2 - \mu_g^2)$ in case of absorption studies and $C_1 = hca_0^3/(\mu_e \cdot \Delta \mu_{g-e})$ and $C_2 = hca_0^3/(\mu_g^2 - \mu_e^2)$ in fluorescence studies (Nadaf *et al.* [19] have mentioned the equation corresponding to fluorescence, while using the absorption data, however, it seems they have used the correct equation in their calculations.)

The values of C_1 and C_2 can be obtained using either a graphical method or a least square fit. The values of X and Y are of the order of 10^{-4} and hence it forces to plot the graph of quantities which are greater by a factor 10^4, which may lead to points being scattered leading to erroneous values of C_1 and C_2. Hence in the present study, C_1 and C_2 have been calculated using a least squares fit.

3. Results and discussion

The solvatochromic shifts are the experimental evidence for the change in energies of levels of a solute due to change in the matrix. Emission spectra are usually more informative than the absorption spectra as emission state arise out of energy of more relaxed excited states. In view of this, the quantities determined using solvatochromic shifts become more important for the description of the intramolecular charge transfer in molecular excited states [2–7] and inter molecular charge transfer in exciplexes [23,24]. The shifts observed are dependent on the nature of solvent (polar or non-polar), dielectric constant etc. This is evident from the fact that, in certain cases the shift in fluorescence spectrum is not necessarily accompanied by a shift in the absorption spectra, if exists it need not be in proportion to the one observed in fluorescence. There are examples for shifts in fluorescence to occur with no shifts in the absorption spectrum of a solute [25].

Since the excited state of a molecule is much different from its ground state, it may be more or less depending upon the transition involved, the ground state dipole moment may slightly change from solvent to solvent, but the excited state may be much different. Thus it is expected that little changes in absorption, while large in the fluorescence spectrum with change in solvent. In the different equations used for the determination of excited state dipole moments, one or more assumptions are made in obtaining the simplified equation from the original McRae's equation [1]. The estimations carried out using absorption shifts will thus not be that reliable compared with that calculated with emission spectra.

If the difference of excited state of a solute in vacuum and the excited state of a polar solvent is greater than the difference of excited state of a solute molecule in vacuum and the excited state of non-polar solvent, the fluorescence as one goes from polar to non-polar show a blue shift (π^*–π transition) and if it is reverse the shift will be red (π^*–n transition). In the present study, the fluorescence shifts for two dyes indicate that the transitions involved are of the first type. The values determined for dipole moments in the excited state in the earlier work through absorption and in this work (presented later in the text) are in conformity with this observation.

When a molecule gets electronically excited (by having different dipole moment and orientation), the electron will be raised to a new electronic level in much less time than it takes for the whole molecule to rearrange itself with solvent environment. Thus, immediately upon excitation, the molecule can be assumed to be in the same environment in the excited state as in the ground state and hence one can safely assume $a_e = a_0$. In the present work, the values of μ_e are calculated by assuming $a_e = a_0$.

In table 2 the values of X and Y for fluorescence are presented, calculated for two dyes in different solvents along with the values of C_1 and C_2. In this table are also given the a_0 values used in the earlier work. In table 3 are presented the calculated values of μ_e using fluorescence shift and μ_g values available in the literature from two different methods. In this table are also given the μ_e values reported in the earlier work using solvatochromic shift in absorption.

From table 3, it is clear that the dipole moments in the excited state are much higher than the ground state dipole moment for the two dyes under study, but less than the values reported in earlier work using shifts in the absorption spectra. The values of μ_e calculated by using the data of solvatochromic shift in emission and absorption are so large that they can be considered outside the experimental errors. Thus, one can

Table 2. Values of X and Y obtained through fluorescence data.

Solvents	E-392A		E-398	
	$X \times 10^4$	$Y \times 10^4$	$X \times 10^4$	$Y \times 10^4$
Cyclohexane	–	–	–	–
Benzene	0.26539	1.4707	0.5384	2.978
Ethylether	27.58849	−4.286	−52.5906	8.170
DMF	17.1821	0.0825	21.7134	0.1042
Acetonitrile	35.049	−3.3319	95.834	−9.1109
Butanol	28.0919	−0.9723	165.918	−5.7345
Methyl-cyclohexane	0.8826	−1.3648	−0.134	0.2072
Acetone	30.2036	−2.4908	89.263	−7.3557
C_1	17.217E-4		24.65E-4	
C_2	3.776E-4		1.791E-4	
a_0	5.2579 Å		6.0271 Å	

conclude that the values of dipole moments calculated for a molecule in their excited state differs depending upon type of the shifts, namely, fluorescence or absorption, used.

One more notable point is the large difference in between the μ_e and μ_g values, which is clearly indicative of change in the molecular structure of a dye on excitation. Of course the large solvatochromic shifts in the present study are consistent with this observation. This indicates that on excitation the orientation of the dipole moment has considerably changed. This change in the orientation in the dipole moment (θ) can be measured using equation (2), by writing,

$$(\mu_e \cdot \Delta\mu_{g-e}) = \mu_e^2 - \mu_e\mu_e \cos\theta = \frac{hca_0^3}{C_1}$$

$$\text{i.e. } \theta = \cos^{-1}\left[\frac{\mu_e^2 - hca_0^3/C_1}{\mu_e\mu_g}\right]. \tag{3}$$

The values of θ thus calculated are reported in table 3. Although, these values are less than earlier values, these are still large in themselves in conformity with an earlier conclusion drawn regarding the change in molecular structure on excitation. Using the value of θ, one can calculate the values ζ and Φ, which are the orientation of dipole moment of a molecule in its ground and excited states respectively with respect to the direction of charge transfer, as defined in the following figure 1.
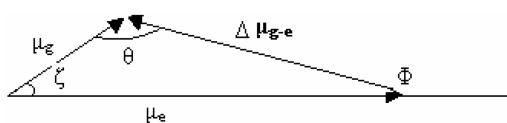
The relation between θ, ζ and Φ can be obtained using C_1 and C_2 values. The relation is,

$$\Phi = 180 - \tan-1\left\{\left[-\frac{(C_1 + C_2)}{C_1}\tan(180 - \zeta)\right]\right\} \text{ and } \theta = \Phi - \zeta.$$

The values θ, ζ and Φ calculated for the two dyes are given in table 4, which also clearly indicate the large change in the molecular structure in the excited state. These orientations are very sensitive to the value of a_0 and hence cannot be given much importance quantitatively unless the method is free from a_0, which is not the case here and hence the values θ, ζ and Φ reported here are to be considered as indicative of the trend.

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Table 3. Values of μ_g, μ_e and θ (angle between μ_g and μ_e) from different methods.

Dye	μ_g in D From eqn (3) Ref. [19]	μ_e in D From absorption data [Ref. 19]	θ in deg. From absorption data [Ref. 19]	μ_e in D From fluorescence data present work	θ in deg. present work	μ_g in D from eqn (4) Ref. [19]	μ_e in D From absorption data [Ref. 19]	θ in deg. From absorption data [Ref. 19]	μ_e in D From fluorescence data present work	θ in deg. present work
E-392A	5.8369	15.63	81	10.515	73.6	6.094	15.73	81	10.66	71.7
E-398	6.7369	19.93	81	16.97	75.95	6.9299	19.99	80	17.053	75.10

Figure 1.   Orientation of b_e, g_o and Δg_{o-e}.

Table 4.   Values of θ, ζ and Φ in degrees.

Dye	θ in deg. present work	ζ in deg. present work	Φ in deg. present work
E-392A	73.69	39.8	113.49
E-398	75.95	37.68	113.48

Acknowledgements

References

[1] E.G. McRae. *J. Phys. Chem.*, **61**, 562 (1957).
[2] M.B. Ledger, P. Suppan. *Spectrochim. Acta*, **23A**, 641 (1967).
[3] P. Suppan. *J. Chem. Soc.*, **4**, 3125 (1968).
[4] M. Ito, K. Inuzuka, M. Imanishi. *J. Am. Chem. Soc.*, **82**, 1317 (1960).
[5] P. Suppan, C. Tsiams. *Spectrochim. Acta*, **36A**, 364 (1980).
[6] D.K. Deshpande, M.A. Shashidhar, K. Suryanarayana Rao. *Z. Phy. Chem., Leipzig*, **262**, 588 (1981).
[7] L.S. Prabhumirashi, D.K. Narayan Kutty, A.S. Bhide. *Spectrochim. Acta*, **39A**, 663 (1983); L.S. Prabhumirashi. *Spectrochim. Acta*, **39A**, 91 (1983).
[8] K.M.C. Davis. In *Molecular Association*, R. Foster (Ed.), p. 151, Academic Press, New York (1975).
[9] E. Lippert. *Z. Electrochem.*, **61**, 962 (1957).
[10] L.S. Prabhumirashi, S.S. Kunte. *Spectrochim. Acta*, **42A**, 441 (1986).
[11] P. Suppan. *Chem. Phys. Lett.*, **94**, 272 (1983).
[12] N.H. Ayachit, D.K. Deshpande, M.A. Shashidhar, K. Suryanarayana Rao. *Spectrochim. Acta*, **42A**, 585 (1986); **42A**, 1405 (1986).
[13] C.N.R. Rao, S. Singh, V.P. Senthilanthan. *Chem. Soc. Rev.*, **5**, 297 (1976).
[14] N.H. Ayachit. *Chem. Phys. Lett.*, **164**, 272 (1989).
[15] N.H. Ayachit. *Proceedings Indian Academy of Sciences* (*Chem. Sci.*), **101**, 269 (1989).
[16] N.H. Ayachit. *Asian Chem. Lett.*, **3**, 167 (1999).
[17] N.H. Ayachit. *Asian J. Phys.*, **9**, 349 (2000).
[18] P. Suppan. *J. Photochem. Photobio.*, **50**, 293 (1990).
[19] Y.F. Nadaf, D.K. Deshpande, A.M. Karaguppikar, S.R. Inamdar. *J. Photosci.*, **9**, 29 (2002).
[20] Mamdouh S. Masoud, Alaa E. Ali, Medhat A. Shaker, Mohamed Abdul Ghani. *Spectrochim. Acta*, **61A**, 3102 (2005).
[21] T. Abe, I Iweibo. *Bull. Chem. Soc.*, Japan, **58**, 3415 (1985); T. Abe. *Bull. Chem. Soc.*, Japan, **41**, 1260 (1985).
[22] N.H. Ayachit, G. Neeraja Rani. *Phys. Chem. Liq.* (In press) (2006).
[23] Z. R. Crabowski, K. Rothiewicz, A. Siemiarezuk, D. J. Cowley, W. Baumann. *Nouv. J. Chem.*, **3**, 443 (1979).
[24] H. Beans, H. Knibbe, A. Weller. *J. Chem. Phys.*, **47**, 1183 (1967).
[25] A.J. Pesce, C.G. Rosen, T. Pasby. *Fluorescence Spectroscopy*, Marcel Dekker, New York (1971).
[26] W. Laptay. *Excited States*, Vol. 1, p. 129, Academic Press, INC, New York (1974).
[27] W. Baumann. In *Physics Mathematics and Chemistry*, B.W. Roossiter, J.F. Hamilton (Eds), Vol. 38, p. 45, John Wiley & Sons (1989).