ORIGINAL PAPER

Rotational Diffusion and Solvatochromic Correlation of Coumarin 6 Laser Dye

U. S. Raikar · C. G. Renuka · Y. F. Nadaf · B. G. Mulimani · A. M. Karguppikar

Abstract Rotational diffusion of coumarin 6 (C6) laser dye has been examined in *n*-decane and methanol as a function of temperature. The rotational reorientation of this probe has been measured in these solvents. It is observed that the decrease in viscosity of the solution is responsible for the decrease in the rotational relaxation time of the probe molecule. The molecule C6 has long reorientation times in *n*-decane solvent as compared to methanol over all temperatures. It is found that the coumarin 6 rotates slower in *n*-decane than in methanol especially at higher values of viscosity over temperature. Two methods are chosen to determine the ground state and excited state dipole moments. The change in dipole moments is estimated from Bakhshiev-Chamma-Viallet equations and, the ground and excited state dipole moments from Kawski et al. equations, by using the variations of the Stokes shifts with the dielectric constant and refractive index of the solvent. Our results are quite reliable which are solvatochromic correlation obtained using solvent polarity functions. The reported results show that excited state dipole moment is greater than ground state dipole moment, which indicates that the excited state is more polar than the ground state.

U. S. Raikar (✉) · C. G. Renuka · A. M. Karguppikar
Department of physics, Karnataka University,
Dharwad 580003, India
e-mail: usraykar_kud@yahoo.co.in

Y. F. Nadaf
Government Arts and Science College,
Karwar, India

B. G. Mulimani
Vice-Chanceller Gulberga University,
Gulberga, India

Introduction

Molecules rotating in liquids experience friction on account of continuous interaction with their neighbors. A desire to understand this friction has been one of the motivating factors in carrying out rotational diffusion studies of molecules in liquids. Rotational diffusion of medium-sized molecules provide useful means to probe solute-solvent interactions which play a major role in determining the physicochemical properties of solutions. A better insight into the nature of solute-solvent interaction is possible by modeling the friction using various continuum-based theories. Generally, the friction experienced by the nonpolar probes in polar/nonpolar solvents is purely mechanical or hydrodynamic friction dominated by short range repulsive forces between the molecules. Mechanical friction can be modeled by using the hydrodynamic theories [1]. Polar probe in polar solvents experiences dielectric friction in addition to mechanical friction. Dielectric friction can be modeled by using the continuum theories of Nee-Zwanzig [2] and Vander Zwan theories [3]. Since, our understanding of many aspects of solution phase dynamics has grown impressively over past decade, it may look surprising that our understanding of friction in even the simple case of solute rotation is still at qualitative level. To be sure, some aspect of solvent friction can be easily understood in terms of hydrodynamic theories, which derive from extrapolating the behavior of macroscopic objects down to the molecular level. The general approach is to measure the rotational reorientation time of a solute molecule in a liquid experimentally and model its rotation using the diffusion based theories of Stokes-Einstein and Debye (SED) [1, 4].

According to SED theory the reorientation times of a solute molecule is proportional to its volume, bulk viscosity of the solvent and inversely related to temperature. The SED theory describes the rotational diffusion of medium sized molecules accurately when the coupling between the solute and the solvent is purely mechanical or hydrodynamic in nature. This theory associates molecular-level friction with bulk viscosity in such a way as to provide reasonable estimates of the rotation times of molecules in solution.

Eisenthal and Drexhage in 1969 [5] made the first direct measurement of orientation relaxation of a large dye molecule in solution. They used a picoseconds laser to excite the Rhodamine 590 laser dye (Rh6G) in ethylene glycol and probed the polarization of the absorbance as a function of time. In a subsequent paper Chuang and Eisenthal [6] studied Rh6G in various protic, polar solvents, notably linear alcohols.

Various techniques are available for the determination of excited state dipole moments. Among the most popular is the Lippert-Mataga equation [7–8]. In this technique absorption and fluorescence shifts followed, using the solvent polarity described by, dielectric constant (ε) and refractive index (n). Other methods such as microwave dielectric absorption [9], stark splitting of rotational level [10–11] and microwave conductivity [12] are considered to be accurate in determining the excited state dipole moments. The dipole moments of an excited state of a molecule provide informations on the electronic and geometrical structure of molecule in the short lived state. Knowledge of this state of molecule is quite useful in designing non-linear optical material, elucidating the nature of the excited state and in determing the course of a photochemical transformation, where the ground state dipole moments of a chemical system can also be measured. Experimental determination of these parameters based on the analysis of the solvatochromism of absorption and fluorescence maximum is quite popular. The ground and excited state dipole moments have determined using different methods by Koti et al. [13], Karunakaran et al. [14], Aaron et al. [15], Nadaf et al. [16] and Ghazy et al. [17]. In the present study, we have determined rotational diffusion of C6 in n-decane and methanol solvents. The ground state and excited state dipole moments of coumarin 6 using solvatochromic data by Bakhshiev-Chamma-Viallet [18–19] and Kawski et al. [20–21] methods have been studied.

Coumarin dyes are a very good media for efficient broadband dye laser in the blue-green region [22]. While coumarin itself does not fluorescence, substitute coumarins are often fluorescing. The lasing properties of substituted coumarins have led to a renewed interest in their spectral characteristics, which are still not well understood [23, 24]. These compounds are widely used as dye lasers, indicators of biophys-

ical process, in biomedical applications and optical brighteners [25–28].

Determination of dipole moments

Sanjay Kumar et al. [29] and Acemioglu et al. [30] were investigated dipole moments using different techniques. In this paper we determined the dipole moments using solvatochromic shift data, employing two methods.

Method I

Bakhshiev [18] and Chamma-Viallet [19] equations are used to estimate the ground and excited state dipole moments of molecules using absorption and fluorescence band maxima. The changes in dipole moments of molecules on excitation can be estimated using the following two relations

$$\bar{v}_a - \bar{v}_f = S_1 F_1(D, n) + C_1 \tag{1}$$

$$\frac{1}{2}(\bar{v}_a + \bar{v}_f) = S_2 F_2(D, n) + C_2 \tag{2}$$

According to Bakhshiev Eq. (1) and Chamma and Viallet Eq. (2) the solvent polarity parameters $F_1(D, n)$ and $F_2(D, n)$ are expressed as

$$F_1(D, n) = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] \times \frac{2n^2+1}{n^2+2} \tag{3}$$

$$F_2(D, n) = \frac{2n^2+1}{2(n^2+2)} \times \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] + \frac{3(n^4-1)}{2(n^2+2)^2} \tag{4}$$

where $\bar{v}_a$, $\bar{v}_f$ are the absorption and fluorescence maxima (in cm^{-1}) respectively, D and n are the dielectric constant and the refractive index of the solvent.

From the above equations it follows that $(\bar{v}_a - \bar{v}_f)$ versus $F_1(D, n)$ and $1/2(\bar{v}_a + \bar{v}_f)$ versus $F_2(D, n)$ should give linear graphs with slopes S_1 and S_2

$$S_1 = \frac{2(\mu^* - \mu)^2}{hca^3} \tag{5}$$

and

$$S_2 = \frac{-2(\mu^{*2} - \mu^2)}{hca^3} \tag{6}$$

where μ and μ^* denote the ground and excited state dipole moments of the solute molecule and 'a' is the Onsager cavity

radius. From the Equations (1, 2, 5 and 6), the ratio of the dipole moments is given by the relation

$$\frac{\mu^*}{\mu} = \frac{|S_1 - S_2|}{|S_1 + S_2|} \tag{7}$$

The parameters $F_1(D, n)$ and $F_2(D, n)$ are calculated using Equations (3) and (4) for the solvents.

Method II

Based on the quantum mechanical perturbation theory [20, 31] of the absorption and fluorescence band shifts (in wavenumbers) in the solvents of different permittivity (ε) and refractive index (n), the following equations are obtained [17]

$$\bar{\nu}_a - \bar{\nu}_f = m_1 f(\varepsilon, n) + const \tag{8}$$

$$\bar{\nu}_a + \bar{\nu}_f = -m_2 [f(\varepsilon, n) + 2g(n)] + const \tag{9}$$

where

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \tag{10}$$

is solvent polarity parameter and

$$g(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \tag{11}$$

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{12}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{13}$$

where μ_g and μ_e are the dipole moments of the ground and excited states respectively. h is Planck's constant and c is the velocity of light in vacuum. The parameters m_1 and m_2 are obtained from the absorption and fluorescence band shifts ($\bar{\nu}_a - \bar{\nu}_f$ and $\bar{\nu}_a + \bar{\nu}_f$) and solvent polarities from above equations. If the ground and excited states are parallel, the following expressions are obtained on the basis of relations (12) and (13) [21, 32]

$$\mu_g = \frac{m_2 - m_1}{2} \left[\frac{hca^3}{2m_1} \right]^{1/2} \tag{14}$$
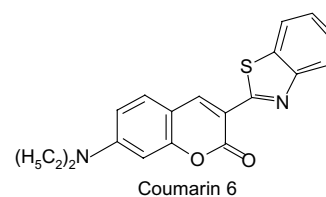
Fig. 1 Molecular structure of Coumarin 6

$$\mu_e = \frac{m_1 + m_2}{2} \left[\frac{hca^3}{2m_1} \right]^{1/2} \tag{15}$$

and

$$\mu_e = \frac{m_1 + m_2}{m_2 - m_1} \mu_g; \quad (m_2 > m_1) \tag{16}$$

The Onsager radius 'a' of the solute molecule can be determined by using atomic increment method [33]. Note that the solvent polarity function $f(\varepsilon, n)$ is different from Lippert-Mataga function [7, 34].

Experimental

Coumarin 6 was obtained from Aldrich Chemical Co., and used without further purification. The molecular structure of C6 is given in Fig. 1. Reorientation times of C6 are measured using steady-state depolarization method in *n*-decane and methanol solvents of spectroscopic grade. The steady-state anisotropy $\langle r \rangle$ is related to the experimentally measured intensities by the following equation

$$\langle r \rangle = \frac{I_{\text{II}} - I_\perp}{I_{\text{II}} + 2GI_\perp} \tag{17}$$

where I_{II} and $I_\perp$ are the polarized fluorescence intensities parallel and perpendicular with respect to the excitation radiation respectively. G is an instrumental factor that corrects for the polarization bias in the detection system and is given by

$$G = \frac{I_{\text{HV}}}{I_{\text{HH}}} \tag{18}$$

where I_{HV} is the fluorescence intensity when the excitation polarizer is kept horizontal and the emission polarizer vertical and I_{HH} is the fluorescence intensity when both the polarizers are kept horizontal.

Steady-state fluorescence anisotropies are measured using Hitachi F2000 Spectrofluorimeter. The sample was excited at 442 nm and emission was monitored from 450 to 540 nm.

The measurement of $\langle r \rangle$ involves recording four spectra one each for I_{11} and $I_{\perp}$ two for the G-factor. Each anisotropy measurement was repeated 5–6 times and for every trail, the G-factor was determined. The fluctuations in the measured values of $\langle r \rangle$ in the required wavelength range are within the limits of experimental error for a given probe/solvent combination. The experiments were performed in the range of 298–342°K for n-decane and 298–333°K for methanol solvents. Reorientation times can be obtained from the measured steady-state anisotropies by the following Perrin relation if the decay of fluorescence and the decay of anisotropy are single exponential [35].

$$\tau_r = \frac{\tau_f}{\left[\left(\frac{r_0}{\langle r \rangle} \right) - 1 \right]} \qquad (19)$$

where r_0, τ_f and τ_r are limiting anisotropy, fluorescence lifetime and reorientation time respectively. The limiting anisotropy r_0 value was determined by measuring the steady-state anisotropies of the probe in glycerol at low temperature. As glycerol having high viscosity in this condition, all rotational motions are frozen.

Fluorescence lifetimes were measured using an IBH (Scotland, UK) fluorescence spectrometer based on Time-Correlated-Single-Photon-Counting technique [36]. The sample was excited by laser pulse of 408 nm, 1 MHz repetition rate, from a diode laser of pulse width of ~ 100 ps. The fluorescence was detected by a PMT based detection module [37] (model TBX4, IBH, Scotland, UK) placed at right angles to the excitation path. The temperature of the sample was controlled with a cold finger arrangement, using a temperature controller (model 2216 e, IBH, Scotland, UK). In this apparatus, the desired sample temperature was maintained within $\pm 1°$ with the help of temperature controller.

The solvents used for determination of dipole moments are, n-hexane, cyclohexane, dioxane, ethyl ether, ethyl acetate, toluene, acetone, acetonitrile named as various solvents and, n-decanol, n-nonanol, n-octanol, n-pentanol, 2-propanol, n-propanol as alcohol series, which are of spectroscopic grade. The electronic absorption spectra are recorded on Hitachi model U-3200 spectrophotometer and fluorescence spectra are taken by using Hitachi model F-2000 spectrofluorimeter at room temperature.

Results and discussion

Absorption and fluorescence emission spectra of molecule were recorded in solvents of different solvent parameters of dielectric constant (ε) and refractive index (n). Figure 2 shows the typical absorption and fluorescence spectra of C6 obtained in acetone solvent. The value of Stokes shift
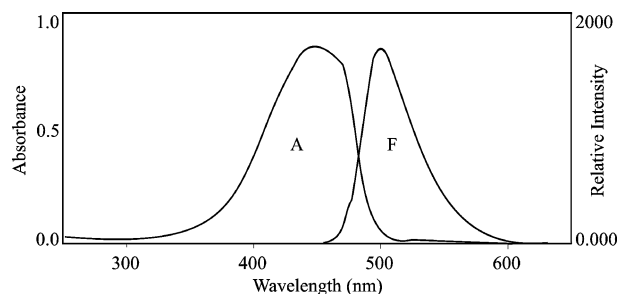
Fig. 2   Absorption (A) and fluorescence (F) spectra of C6 in acetone

between absorption and emission maxima is indication of charge transfer during excitation. The large magnitude of the Stokes shift indicates that the excited state geometry could be different from that of ground state.   The general observation is, there is an increase in the Stokes shift values with increasing solvent polarity, which shows that there is an increase in the dipole moment on excitation. The reported values of reorientation times of C6 in n-decane and methanol solvents as a function of temperature, which were obtained from the measured values of $\langle r \rangle$, r_0 and τ_f using the Equation (19) are given in Tables 1 and 2 respectively, made several interesting observations. The r_0 value for C6 is 0.366. Dutt et al. [38] have reported rotational diffusion of C6 in DMSO and n-octanenitrile solvents in various temperatures and follows the single exponential for fluorescence and anisotropy decay. Raikar et al. [39] have also reported of C30 in n-octanenitrile and n-butanol solvents at different temperatures and follows single exponential trend. In the present work florescence decay of C6 in n-decane and methanol as well as the anisotropy decay are single exponentials throughout the temperature range used in the study. Hence use of Equation (19) to obtain reorientation times from the measured values of $\langle r \rangle$, r_0 and τ_f are justified. We have plotted the observed rotational relaxation time of the probe with viscosity and temperature of solvents, shown in

Table 1   Steady-state anisotropy, fluorescence lifetime (τ_f) and reorientation times (τ_r) of C6 in n-decane as a function of temperature

Temperature °K	η^a/mPa s	$\langle r \rangle$	τ_f (ns)	τ_r (ps)
298	0.838	0.0126	2.559	91.2
303	0.784	0.0125	2.559	91.2
308	0.748	0.0119	2.556	86.3
313	0.707	0.0112	2.552	69.1
318	0.670	0.0096	2.550	60.4
323	0.635	0.0085	2.548	57.2
328	0.597	0.0080	2.545	52.3
333	0.556	0.0074	2.543	52.3
338	0.518	0.0074	2.540	52.3
342	0.482	0.0068	2.538	48.3

^{a}Viscosity data from ref [40].

Table 2 Steady-state anisotropy, fluorescence lifetime (τ_f) and reorientation times (τ_r) of C6 in methanol as a function of temperature

Temperature °K	η^a/mPa s	$\langle r \rangle$	τ_f (ns)	τ_r (ps)
298	0.544	0.0106	2.318	69.4
303	0.536	0.0095	2.289	61.4
308	0.516	0.0086	2.254	54.8
313	0.502	0.0084	2.220	52.3
318	0.468	0.0081	2.187	49.4
323	0.437	0.0075	2.152	44.9
328	0.405	0.0074	2.121	43.8
333	0.371	0.0063	2.087	36.5

^{a} Viscosity data from ref [40].

Figs. 3(a) and 3(b). Plots are almost linear and confirm that rotational relaxation of C6 in solvents follows the simple hydrodynamic theory. Probe rotates faster in lower viscosities, i.e. rotation of probe increases with an decrease in viscosity of the solvents. (Viscosity varied by varying the temperature of the solvent). Thus, we may conclude that the viscosity is the main guide factor to determine the rotational relaxation time for the probe molecule in these solvents.

Figures 4(a) and 4(b) give a plots of τ_r versus η/T for C6 in *n*-decane and methanol solvents. The parameters for the solvents are given in Tables (1 and 2), have been fitted to linear function describing the relation of τ_r and η/T of the molecule which gives the correlation function (r) 0.99 for *n*-decane and 0.96 for methanol solvent indicating that the good relationship between τ_r and η/T for both solvent system. The slope, intercept and correlation factors of C6 in *n*-decane and methanol as shown in Figs. 4(a) and 4(b) are summarized in Table 3.

Reported readings from the Tables 1 and 2, indicate that, the molecule experience more friction at higher viscosities and less friction at lower viscosities. According to hydrodynamic theory, the rotational relaxation time of the probe is proportional to viscosity and inversely proportional to temperature (Debye-Stokes-Einestein equation). Thus, coumarin 6 experiences less friction in methanol as compared to *n*-decane especially at higher values of viscosity over temperature. This can be explained by considering the interaction of alcohol molecules with probe molecule, which results from hydrogen bonding. Methanol molecule can form hydrogen bonds with the probe molecule. This hydrogen bonding impede the rotation of the solute molecule. This bond must be broken before reorientation of the molecule. *n*-decane (nonpolar) is not forming any hydrogen bond with probe molecule. Its size is sufficiently larger than the methanol molecule. The effects of the size and volume of solute and solvent molecule on reorientation times can not be neglected. Large size and large volume of the solvent molecule definitely reduce the friction. So usual ex-
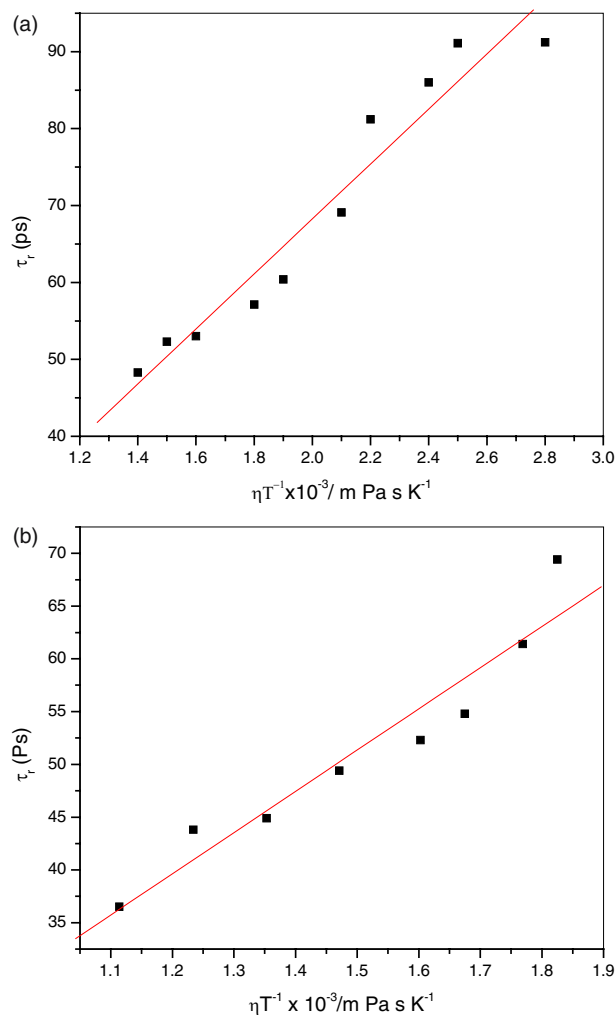

(a)

(b)
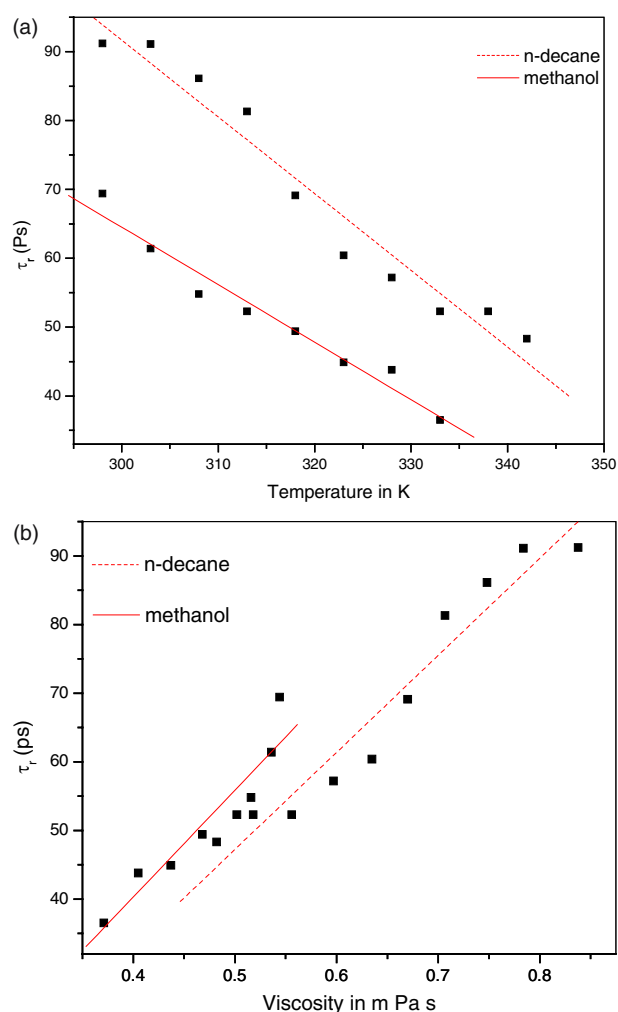
Fig. 3 (a) Plot of τ_r versus T for coumarin 6 in *n*-decane and methanol solvents. (b) Plot of τ_r versus η for coumarin 6 in n-decane and methanol solvents

pectation is that probe molecule rotates faster in *n*-decane than methanol. However with rise in temperature, the viscosity of methanol solvent molecule decreases and its bond with probe molecule are loosened. The cavities formed in this network of methanol solvent molecule become region of reduced friction and hence probe molecule can rotate faster in methanol than *n*-decane. Thus, viscosity is the main guiding factor to determine the rotational relaxation time of the probe in these solvents [42].

The wavenumbers of absorption and emission maxima of chosen molecule in various solvents are summarized in Table 4. In order to estimate the ratio (μ^*/μ) of ground to excited state dipole moments of the molecule, the parameters for solvent polarities F_1 or $f(\varepsilon, n)$, F_2 and $f(\varepsilon, n) + 2g(n)$ are calculated. For knowing the meanings of the solvent functions F_1, F_2, $f(\varepsilon, n)$ and $f(\varepsilon, n) + 2g(n)$ see Eqs. 3, 4, 10 and 11 respectively. Spectral shifts ($\bar{\nu}_a - \bar{\nu}_f$), $1/2(\bar{\nu}_a + \bar{\nu}_f)$ and ($\bar{\nu}_a + \bar{\nu}_f$) (cm^{-1}) of the molecule in different solvents

(a)

(b)

Fig. 4 (a) Plot of τ_r versus η/T for coumarin 6 in n-decane. (b) Plot of τ_r versus η/T for coumarin 6 in methanol

Table 4 Wavenumbers (cm^{-1}) for the absorption and emission[a] maxima of C6 molecule in different series of solvents

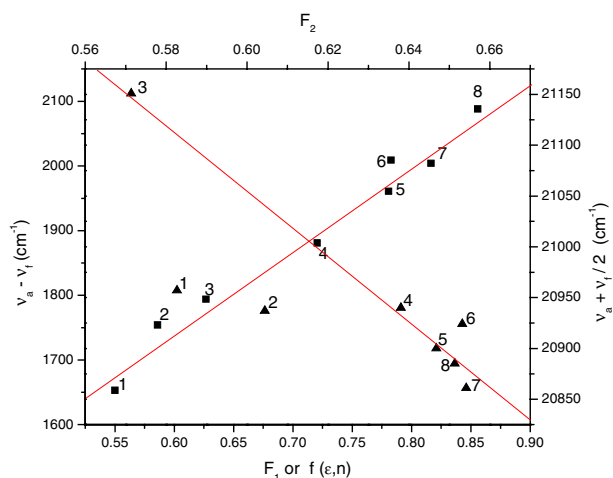| Solvents	Wavenumber (cm^{-1})	Solvents	Wavenumber (cm^{-1})
n-Hexane	23485 (21786)	n-Decane	21978 (20325)
Cyclohexane	23320 (21598)	n-Nonanol	21834 (20080)
Dioxane	22624 (20746)	n-Octanol	21834 (20040)
Ethyl ether	23255 (21141)	n-Pentanol	21821 (19920)
Ethyl acetate	22222 (20202)	n-Propanol	21881 (19929)
Toluene	22271 (20080)	2-Propanol	22016 (19929)
Acetone	22016 (20000)	Ethanol	21881 (19841)
Acetonitrile	22114 (19920)	Methanol	21929 (19841)

[a]given in parentheses.

giving the same meaning but notations used in the methods are different, which are represented in figures as F_1 or $f(\varepsilon, n)$, F_2 and $f(\varepsilon, n) + 2g(n)$. The slopes $S_1 = m_1$, S_2 and m_2 of the fitted lines shown in the results of statistical treatment of Bakhshiev, Chamma-Viallet and Kawski's correlations, i.e. the slopes, intercepts and correlation coefficients values are reported in Table 5. The ratios of dipole moments (μ^*/μ) are determined from the slopes of Bakhshiev and Chamma-Viallet correlation.

The Figs. 5 and 6 show spectral shifts (in cm^{-1}) $(\bar{\nu}_a - \bar{\nu}_f)$ versus F_1 or $f(\varepsilon, n)$ Bakhshiev or Kawski's correlation, $1/2(\bar{\nu}_a + \bar{\nu}_f)$ versus F_2 Chamma-Viallet, and $(\bar{\nu}_a + \bar{\nu}_f)$ versus $f(\varepsilon, n) + 2g(n)$ Kawski's correlation of C6 in alcohol solvents which give the slopes of $S_1 = m_1 = 1337.653$, $S_2 = 3222.069$ and $m_2 = 3225.353$ cm^{-1}. Taking the slopes (S_1 and S_2) of graphs from Figs. 5 and 6, and using the Equation (7), we obtained, the $\mu* = 0.425$ μ (D). Similarly the slopes m_1 and m_2 using Eqs. (14) and (15), we get $\mu_e = 5.351$ D, $\mu_g = 2.214$ D and the ratio of dipole moments i.e. 2.416 for C6 in alcohol solvents are reported in Table 6.

The above results suggest relatively more stable excited singlet-state relative to the ground state in C6 molecule. Stokes shifts versus solvent polarity functions should be linear in the presence of general solvent effects as a function of the dielectric constant and the refractive index. The deviations from the linearity imply the specific solute-solvent interaction [30]. These deviations are related to the extent of the interactions leads to the energy difference changes between the ground and the excited state dipole moments.
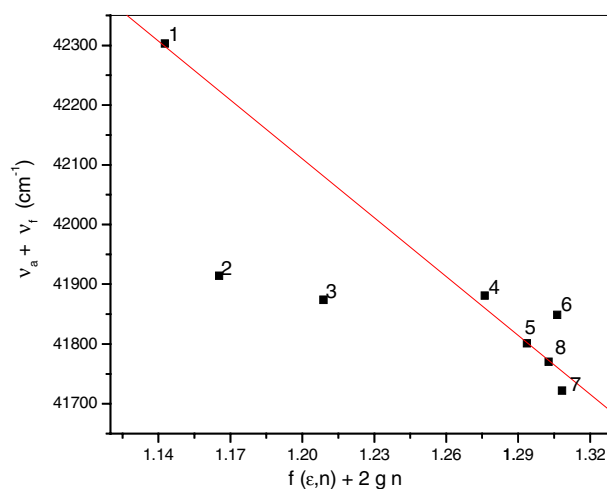
versus solvent polarity functions are shown in Figs. 5 and 6. A linear progression was carriedout using the software Origin 6.0 program and the data was fit to a straight line.

It is observed that the shifts of emission peaks with change in solvent polarity are more pronounced than the shifts of absorption peaks. This indicates that $\mu_e \gg \mu_g$ i.e. the dipole moment of a molecule increases on excitation. A red shift is observed with increasing in solvent polarity which suggests π-$\pi*$ transition.

Figures 5 and 6 show spectral shifts (in cm^{-1}) $(\bar{\nu}_a - \bar{\nu}_f)$, $1/2(\bar{\nu}_a + \bar{\nu}_f)$ and $(\bar{\nu}_a + \bar{\nu}_f)$ of C6 in alcohol solvents versus the solvent polarity functions F_1 (Eq. 3) and $f(\varepsilon, n)$ (Eq. 10)

Table 3 Linear regression result of rotational reorientation times of C6 in n-decane and methanol solvents

n-Decane				Methanol				$\tau_r$methanol
Slope ps °K/mPa s	Intercept (ps)	Correln. Coeff. (r)	No. of data	Slope ps °K/mPa s	Intercept (ps)	Correln. Coeff. (r)	No. of data	$\dfrac{\tau_r}{n\text{-decane}}$
32.121	−0.751	0.99	10	39.045	−7.220	0.96	8	1.215

Fig. 5 Plot of Bakhshiev, Kawski and Chamma-Viallet correlation $(\nu_a - \nu_f)$ (cm^{-1}) versus F_1 or f (ε, n) (■) and $1/2(\nu_a + \nu_f)$ (cm^{-1}) versus F_2 (▲) of C6 in alcohol solvents. (1) n-Decanol, (2) n-Nonanol, (3) n-Octanol, (4) n-Pentanol, (5) 2-Propanol, (6) n-Propanol, (7) Ethanol and (8) Methanol

Fig. 6 Plot of Kawski correlation $(\nu_a + \nu_f)$ (cm^{-1}) versus $f(\varepsilon, n) + 2g$ (n) of C6 in the same solvents as in the Fig. 5

From Table 5 it is seen that correlation co-efficients are varying from 0.878 to 0.989. The poor correlation between the Stokes shifts and solvent polarity function is attributed to the contribution of solute-solvent interaction. Bakhshiev and Chamma-Viallet correlation in series of various solvents show a slightly poor correlation. This scattering suggests specific interaction between solute and solvent interactions. In general, Bakhshiev, Chamma-Viallet in alcohol series and Kawski's correlations in both the series of solvents are linear (Table 5). Moreover the excited state dipole moments values compared with the ground state values are higher. It indicates that the excited state electronic change distribution should be substantially different from the ground state charge distribution.

Conclusion

Rotational relaxations of C6 as a function of temperature in n-decane and methanol solvents have been measured. The experimental rotational correlation times are well represented as linear function of η/T. Rotational relaxation studies of probe molecule serve as a means of understanding solute-solvent interactions. It has been observed that viscosity, size of the molecule and solvent, hydrogen bonding and other specific interactions between rotating probe molecule and surrounding solvent medium are affecting the nature of rotation of probe in the solvents. Solvent n-decane because of its relatively high viscosity and hence long reorientation time, the molecule C6 has slower rotation in n-decane than methanol. We have also determined experimentally the ratio of μ_e and μ_g for C6 molecule from solvatochromic Stokes shift data in two series of solvents. We found that the molecule has higher

Table 5 Statistical treatment of the correlation of solvents, spectral Stokes shifts of coumarin 6

Dye	Various solvents				Alcohol solvents			
	Slope (cm^{-1})	Intercept (cm^{-1})	Correlation Coefficient	No. of data	Slope (cm^{-1})	Intercept (cm^{-1})	Correlation Coefficient	No. of data
Bakhshiev correlations[a]								
S$_1$ = m$_1$								
C6	769.404	479.419	0.878	7	1337.653	941.773	0.989	8
Chamma-Viallet correlation								
S$_2$								
C6	4066.831	23716.922	0.986	5	3222.069	2299.970	0.982	6
Kawski et al correlation[a]								
m$_2$								
C6	3502.001	46664.238	0.905	8	3225.353	45989.038	0.981	6

[a]The Stokes shift and solvent polarity relation of Bakhshiev ($\bar{\nu}_a - \bar{\nu}_f$) Vs F_1 and Kawski et al. ($\bar{\nu}_a + \bar{\nu}_f$) Vs $f(\varepsilon, n)$ are same.

Table 6 Ground and excited state dipole moments, change in the dipole moment ($\Delta\mu$) of C6 molecule

Molecule	μ_e (D)[a]	μ_g (D)[a]	μ_e/μ_g[b]	$\Delta\mu$ (D)
C6	7.695[c]	5.817[c]	1.323 (0.789)	1.878
	[5.351]	[2.214]	2.416 (0.425)	3.137

[a] Values of ground and excited state dipole moments measured in alcohols solvents are given within [ ] parenthesis.

[b] Values measured by Bakhshiev-Chamma-Viallet methods are given within ( ) parenthesis.

[c] Reference [41].

dipole moment in the excited state than in the ground state. This demonstrates that the molecules in the excited state are more polar than the ground state.

References

1. Debye P (1929) Polar Molecules. Dover, New York
2. Nee TW, Zwanzig R (1970) J Chem Phys 52:6353–6363
3. vader Zwan G, Hynes JT (1985) J Phys Chem 89:4181–4188
4. Fleming GR (1986) Chemical applications of ultra fast spectroscopy. Oxford University Press, London
5. Eisenthal KB, Drexhage KH (1969) J Chem Phys 51:5720–5721
6. Chuang TJ, Eisenthal KB (1971) Chem Phys Lett 11:368–370
7. Lippert E (1995) Z Naturforsch 10a:541–545
8. Mataga N, Kaifu Y, Koizumi M (1956) Bull Chem Soc Jpn 29:465–470
9. Samanat A, Fessenden RW (2000) J Phys Chem A 104:8577–8582
10. Lombardi JR (1969) J Chem Phys 50:3780–3783
11. Lombardi JR (1970) J Am Chem Soc 92:1831–1833
12. Hass MP, Warman JM (1982) Chem Phys 73:35–53
13. Koti ASR, Bhattacharjee B, Haran NS, Das R, Periaswamy N, Sonawane ND, Rangnekar DW (2000) J Photochem Photobiol A 137:115–123
14. Karunakaran VK, Ramamurthy P, Joseph Rajan T, Ramkrishnan VT (2002) Spectrochim Acta 58:1443–1451
15. Aaron JJ, Tine A, Gaye MD, Parkanyi C, Boniface C, Bieze TWN (1991) Spectrochim Acta 47:419–430
16. Nadaf YF, Mulimani BG, Gopal M, Inamdar SR (2004) J Mol Stuct (Theochem) 678:177–181
17. Ghazy R, Azin SA, Shaheen M, El-Mekawey F (2004) Spectrochim Acta A 60:187–191
18. Bakhshiev NG (1964) Opt Speckrosk 16:821–832
19. Chamma A, Viallet P, Acad CR (1970) Sci Ser France 270:1901–1904
20. Kawski A (1966) Acta Phys Polon 29:507–518
21. Kawski A(1992) In Rabek JF (ed) Progress in photochemistry and photophysics, vol. 5, CRC Press Boca Raton, pp 1–47
22. Schimitschek EJ, Trias JA, Hammond PR, Henry RA, Atkins RL (1976) Optics Commun 16:313–316
23. Halstead JA, Reeves RR (1978) Opt Commun 27:273–276
24. Reynold GA, Drexhage KH (1975) Opt Commun 13:222–225
25. Parkanyi C, Antonious MS, Aaron JJ, Buna M, Tine A, Cisse L (1994) Spectrosc Lett 27:439–449
26. Shobini J, Mishra AK, Sandhya K, Chandra N (2001) Spectrochim Acta 57:1133–1147
27. Rang HP, Dale MM, Ritter J (1995) Molecular pharmacology, IIIrd Eds., Churchill Living Stone, New York
28. Madhavan GR, Balraj V, Mallesham B, Chakrabarti R, Lohray VB (2003) Bioorg Med Chem Lett 13:2547–2551
29. Kumar S, Jain SK, Rastogi RC (2001) Spectrochim Acta 57A:291–298
30. Acemioglu B, Arik M, Efeoglu H, Onganer Y (2001) J Mol Struct (Theochem) 548:165–171
31. Bilot L, Kawski A (1962) Z Naturforsch 17a:621–627
32. Kawski A (2002) Z Naturforsch 57a:255–265
33. Edward JT (1956) Chem Ind 774–777
34. Lippert E (1957) Z Elektrochem 61:962–975
35. Lakowich JR (1983) Principles of fluorescence spectroscopy. Plenum Press, New York
36. O'Connor DV, Philips D (1984) Time correlated single photon counting. Academic press, New York
37. Pal H, Palit DK, Mukarjee T, Mittal JR (1990) J Photochem Photobiol A 52:391–409
38. Dutt GB, Ramakrishna G, Raman S (2001) J Chem Phys 115:4732–4741
39. Raikar US, Renuka CG, Nadaf YF, Mulimani BG (2006) J Mol Struct 787:127–130
40. Lide DR (1996) CRC handbook of chemistry and physics, 76th Ed. CRC Press, New York
41. Raikar US, Renuka CG, Nadaf YF, Mulimani BG, Karguppikar AM (2006) Spectrochim Acta A (In Press)
42. Chakrabarty D, Chakraboty A, Seth D, Sarkar N (2005) J Phys Chem A 109:1764–1769