

# Effect of binary solvent mixtures (DMSO/water) on the dipole moment and lifetime of coumarin dyes

B.R. Gayathri, J.R. Mannekutla, S.R. Inamdar \*

*Laser Spectroscopy Programme, Department of Physics, Karnatak University, Dharwad, Karnataka 580 003, India*

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## Abstract

Absorption and fluorescence spectra of four coumarin laser dyes, Coumarin 440 (C440), Coumarin 450 (C450), Coumarin 466 (C466) and Coumarin 151 (C151), have been recorded in binary mixtures of DMSO and water at room temperature (298 K) to study the solvent effect and to evaluate the ground and excited state dipole moments using solvatochromic shift method. The anomalous feature in the complex systems of these mixtures due to the structural heterogeneities is discussed. The effect of solvent polarity parameters of binary mixture on the ground and excited state dipole moments was examined. Experimental results indicate that the dipole moments in the excited state, for all the molecules investigated, are higher than the corresponding values in the ground state. The ground and excited state dipole moments of these probes have also been computed from *ab initio* calculations and compared with those obtained experimentally. Fluorescence lifetimes of all the probes measured using time domain fluorescence spectrometer employing time correlated single photon counting technique, show a nonlinear variation with the composition of binary mixture.

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**Keywords:** Binary solvent; Stokes shift; Solvatochromic shift; Dipole moment; Lifetime

## 1. Introduction

In recent years, due to fast progress in photochemistry, studies of electric dipole moments in the excited states have gained greater importance. The excitation of a molecule by a photon causes redistribution of the electron density and correspondingly a change in the dipole moment. A non-equilibrium state is created as the solvent environment cannot follow the sudden change in the dipole moment. During the relaxation of the solvent towards a new equilibrium state, the interaction energy between the solvent and solute changes and hence the fluorescence band of the probe molecule shifts [1]. This results in an increase or decrease of the excited state dipole moment as compared to that in the ground state. Similarly, when a solute molecule in a polar solvent is excited optically, its dipole moment in the excited state changes due to modified charge

distribution. A change in solvent is generally accompanied by a change in polarity, dielectric constant or a change in the polarizability of the surrounding medium. These parameters can easily be altered by mixing two solvents in different proportions. Hence, the study of binary solvent system and its role in biochemical processes has spurred the measurement of some excess properties. The mixtures of several solvents have been extensively used as media for carrying out physico-chemical investigations of organic molecules [2–4]. The dielectric behavior is one of the key ways of characterizing polar liquid environments as reaction media. It is found that the dielectric properties of the polar mixtures depart significantly from what one might expect on the basis of ideal mixing [5]. In hydrogen bonding systems such as alcohol–water mixtures, intermolecular correlations are strong, and consequently the dielectric properties [6,7] of the mixtures are usually not simply related to those of the individual components [8]. The use of solvent mixtures also facilitates a systematic variation of polarities [9] and thus, a binary mixture with different

\* Corresponding author. Tel.: +91 836 2215289; fax: +91 836 2771275.  
E-mail address: [him\\_lax3@yahoo.com](mailto:him_lax3@yahoo.com) (S.R. Inamdar).

proportions of the component solvents affects the excited state differently. Upon mixing, new solvent–solvent and solute–solvent interactions often create solvent properties that were not present in the pure solvents. Many mixtures of water with organic solvents show properties that deviate from ideality. For the system consisting of water and dimethyl sulphoxide (DMSO), extreme deviations from additivity are observed for a wide range of properties, such as dielectric constant, density, viscosity and adiabatic and isothermal compressibility [10]. Analysis of these mixtures are hindered by the fact that it represents one more complicated binary systems, namely an associating component plus a second component, capable of forming hydrogen bonds with the first. DMSO and its aqueous solutions are among the most widely used solvents in organic chemistry, chemical technology and cell biology [11,12]. DMSO ((CH<sub>3</sub>)<sub>2</sub>SO) is a polyfunctional molecule with a polar S=O group and two hydrophobic groups. Hence, its structure enables it to solubilize a variety of compounds [4]. A systematic analysis of binary solvent effect is, therefore, informative and proves useful in studying the excited state behavior of the molecule.

Coumarins are a family of molecules that have been studied extensively because of their application as laser dyes and their substantial state-dependent variation in static dipole moment. Indeed, the latter gives rise to characteristically large Stokes shift, sometimes of the order of 100 nm [13]. The knowledge of absorption and fluorescence characteristics of these compounds with different substituents under varying conditions of solvents, temperature and pH is crucial in understanding the working of tunable dye-lasers and operating them at maximum efficiency. The coumarin molecules as such in aqueous solution are non-fluorescent, but they do become highly fluorescent on substitution [14]. The emission characteristics of a fluorophore depend upon the position and nature of the substituent as well as the nature of the surrounding medium [15,16]. The magnitude of the spectral changes due to substituent/solvent is linked to the structural aspects of the molecule and serves as a tool for its detailed investigations. The wide spread occurrence of coumarins and their variety of applications such as fluorescent indicators and whiteners in detergent products, sunburn preventives, as laser dyes, for the estimation of enzymes, for studying biological systems and also in other interesting areas have given importance to the study of their fluorescence characteristics ([14] and references therein). These molecules form an important class of laser dyes in the blue-green spectral region.

Most of the methods available for the determination of dipole moment of the singlet-excited state are based on the spectral shift caused externally by electrochromism [17] or internally by solvatochromism [18]. In both these techniques Lippert–Mataga equation [19,20] is used, which is based on the spectral shift of absorption and fluorescence maximum and solvent polarity parameters dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ). A thermo-chromic method [21], similar in principle, where the variation of

dielectric constant and refractive index is brought about by temperature changes, is also employed. The solvatochromic method to determine the excited state dipole moments is preferred due to simplicity of the experimental procedure and ease of data analysis.

In this paper, the ground and excited state dipole moments of a set of 7-amino coumarin dyes viz., C440, C450, C466 and C151 in polar solvent mixtures of dimethyl sulphoxide (DMSO) and water following solvatochromic shift technique is presented for the first time. The experimental results are compared with the theoretical ground and excited state dipole moments obtained from *ab initio* calculations [22] using DFT and CIS method, respectively. Further, fluorescence lifetime of these probes at each solvent mixture to check the excited state behavior of all the probes under study were also measured. The paper is divided into five sections. The theory relevant to the present study is given in Section 2, the experimental techniques are described in Section 3 followed by results and discussions in Section 4. Conclusions from the present work are given in Section 5.

## 2. Theory

The bulk dielectric constant ( $\epsilon$ ) and refractive index ( $n$ ) of a solvent strongly affect [23–25] the dipole moment of the solute molecules. An interaction with environment affects various electronic states in a different way. The interaction between the solute and solvent molecules depends upon dielectric constant, refractive index of the solvent and the dipole moment of the solute molecules.

By employing quantum-mechanical second-order perturbation theory [26], following equations have been obtained for the absorption ( $v_a$ ) and emission ( $v_f$ ) band shifts (in wave numbers) in different solvents of varying permittivity ( $\epsilon$ ) and refractive index ( $n$ ):

$$v_a - v_f = m_1 f(\epsilon, n) + \text{const.} \quad (1)$$

$$v_a + v_f = -m_2 \phi(\epsilon, n) + \text{const.} \quad (2)$$

with

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

being the solvent polarity function and

$$\phi(\epsilon, n) = f(\epsilon, n) + 2g(n), \quad (4)$$

where

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

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (6)$$

and

$$m_2 = \frac{2(\mu_c^2 - \mu_g^2)}{hca_0^3} \quad (7)$$

The parameters  $m_1$  and  $m_2$  occurring in Eqs. (1) and (2) for the difference ( $v_a - v_f$ ) and the sum ( $v_a + v_f$ ) of the wave numbers, which are linear functions of the solvent polarity parameters  $f(\epsilon, n)$  and  $\phi(\epsilon, n)$ , can be determined from the slopes of the straight lines. In Eqs. (6) and (7)  $\mu_c$  and  $\mu_g$  represent the dipole moments in the excited and ground state, respectively,  $h$  being Planck's constant,  $c$  the velocity of light in vacuum and  $a_0$  is the cavity radius of the solute molecule. The cavity radius  $a_0$  of the solute molecules were calculated from the molecular volumes of the laser dyes using the relation [24].

$$a_0 = \left( \frac{3M}{4\pi\delta N} \right)^{1/3} \quad (8)$$

where  $M$  is the molecular weight of the solute,  $\delta$  is the density of the solute molecule and  $N$  is the Avagadro's number.

If the ground and excited states are parallel, based on the Eqs. (6) and (7), the following equations are obtained:

$$\mu_g = \frac{m_2 - m_1}{2} \left[ \frac{hca_0^3}{2m_1} \right]^{1/2} \quad (9)$$

$$\mu_c = \frac{m_2 + m_1}{2} \left[ \frac{hca_0^3}{2m_1} \right]^{1/2} \quad (10)$$

### 3. Experimental

The laser dyes C440 and C450 were obtained from Exciton Inc. (USA) and C466 and C151 were obtained from Lambda Physik Inc. (Germany). All the four dyes were used as received. The molecular structure of all the molecules is given in Fig. 1. The solvents used in the present study are binary mixtures of DMSO (HPLC, Spectrochem, India) with triple distilled water (VITSIL, Model VQDD, India) in different proportions. The steady-state absorption and emission spectra were recorded using Hitachi U-3310 UV–vis double beam ratio spectrophotometer and Hitachi F-2000 spectrophotometer, respectively, at room temperature (298 K). The refractive indices of the solvent mixtures were measured using Abbe's refrac-

tometer (ATAGO-3T, Japan) and the dielectric constant values were obtained from the literature [27]. In order to avoid the possible self-quenching or inner filter effects, the concentration of the solute was kept quite low. The recorded absorption and fluorescence wavelengths are accurate within  $\pm 1$  nm.

Fluorescence lifetimes were determined using time correlated single photon counting (TCSPC) technique [28]. The 370 nm second harmonic light pulses were derived from the output of tunable Ti-sapphire femtosecond laser (Coherent, Mira) with repetition rate of 3.8 MHz. The emission was collected with a resolution of 4 nm at magic angle through a monochromator equipped with a holographic grating with 1200 grooves/mm. The TCSPC system with thermoelectrically cooled photomultiplier tube (Hamamatsu H7422) detector has been obtained from Edinburg Instruments (LifeSpec-Red). The instrument response function of TCSPC system was  $\sim 180$  ps. The fluorescence decays were deconvoluted from the instrument response function (IRF) using the software F900.

### 4. Results and discussion

The observed spectral data of coumarins are listed in Tables 1 and 2 along with dielectric constant ( $\epsilon$ ), refractive index ( $n$ ) and solvent polarity functions  $f(\epsilon, n)$  and  $\phi(\epsilon, n)$ . Figs. 2–5 show the variation of Stokes shift  $v_a - v_f$  with solvent polarity function  $f(\epsilon, n)$  and the variation of  $v_a + v_f$  with  $\phi(\epsilon, n)$  observed in the case of C440, C450, C466 and C151, respectively. A linear progression was done and the data were fit to a straight line whose slopes were taken as  $m_1$  and  $m_2$ . Upon changing the polarity of binary solvent mixture from lower to higher polarity the difference in Stokes shift of about  $1031 \text{ cm}^{-1}$  (64.70–77.56),  $944 \text{ cm}^{-1}$  (68.73–77.56),  $615 \text{ cm}^{-1}$  (64.7–77.56) and  $1894 \text{ cm}^{-1}$  (48.11–77.56) were observed for C440, C450, C466 and C151, respectively. The quantities inside the parenthesis indicate the range of variation of dielectric constant of solvent mixture. A red shift in the magnitude of Stokes shift as observed from Tables 1 and 2, indicates a charge transfer transition [18]. The increase in the Stokes shift with increasing solvent polarity, indicates that there is an increase in the dipole moment on excitation. The fluorescence emission peak undergoes a bathochromic shift with increase in the polarity of the mixture, confirming a  $\pi \rightarrow \pi^*$  transition. The shift in the fluorescence peaks towards longer wavelengths could be due to markedly different excited state charge distribution of the solute than that in ground state and leads to a stronger interaction with polar solvents in the excited state [14]. In the case of 7-amino coumarins electron donating nature of the amino group and the electron accepting nature of the carbonyl group results in the first excited singlet state  $S_1$  having greater dipole moment. The experimental results indicate that the excited state dipole moments of these laser dyes are higher than those in the ground state and are consistent with the inferences of Gustavsson et al. [29].

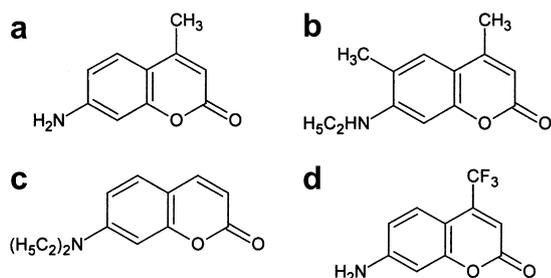


Fig. 1. The molecular structures of (a) C440, (b) C450, (c) C466 and (d) C151.

Table 1  
Spectroscopic data along with calculated values of  $f(\epsilon, n)$  and  $\phi(\epsilon, n)$  for C440, C450 and C466

Mole fraction of DMSO	Molecule	$\nu_a$ (cm <sup>-1</sup> )	$\nu_r$ (cm <sup>-1</sup> )	$\nu_a - \nu_r$ (cm <sup>-1</sup> )	$n$	$\epsilon$	$f(\epsilon, n)$	$\phi(\epsilon, n)$	$\nu_a + \nu_r$ (cm <sup>-1</sup> )
0.503	C440	28,409	23,041	5368	1.406	64.70	0.884	1.435	51451
0.372	C466	25,740	21,459	4281					47,199
	C440	28,571	22,989	5583	1.387	68.73	0.892	1.419	51,560
	C450	26,918	22,422	4496					49,339
0.275	C466	25,674	21,231	4443					46,905
	C440	28,736	22,936	5800	1.370	71.47	0.899	1.402	51,671
	C450	27,137	22,422	4716					49,559
0.202	C466	25,707	21,277	4430					46,984
	C440	28,818	22,883	5935	1.359	73.34	0.903	1.392	51,702
	C450	27,248	22,371	4877					49,619
0.145	C466	25,641	21,142	4499					46,783
	C440	28,944	22,883	6060	1.351	74.49	0.906	1.384	51,827
	C450	27,322	22,272	5051					49,594
0.098	C466	25,740	21,097	4643					46,837
	C440	29,028	22,831	6197	1.344	76.03	0.908	1.378	51,859
	C450	27,360	22,321	5038					49,681
0.06	C466	25,707	21,053	4654					46,760
	C440	29,070	22,883	6186	1.340	77.02	0.910	1.373	51,953
	C450	27,360	22,321	5038					49,681
0.0	C466	25,740	21,008	4732					46,748
	C440	29,283	22,883	6399	1.330	77.56	0.913	1.363	52,166
	C450	27,663	22,222	5440					49,885
	C466	25,806	20,964	4842					46,771

Table 2  
Spectroscopic data along with calculated values of  $f(\epsilon, n)$  and  $\phi(\epsilon, n)$  for C151

Mole fraction of DMSO	$\nu_a$ (cm <sup>-1</sup> )	$\nu_r$ (cm <sup>-1</sup> )	$\nu_a - \nu_r$ (cm <sup>-1</sup> )	$n$	$\epsilon$	$f(\epsilon, n)$	$\phi(\epsilon, n)$	$\nu_a + \nu_r$ (cm <sup>-1</sup> )
1.000	25,940	20,921	5020	1.473	48.11	0.845	1.484	46,861
0.828	26,076	20,661	5414	1.454	54.07	0.859	1.474	46,737
0.695	26,316	20,534	5782	1.436	58.46	0.869	1.461	46,850
0.503	26,490	20,450	6040	1.406	64.70	0.884	1.435	46,940
0.372	26,596	20,450	6146	1.387	68.73	0.892	1.419	47,046
0.275	26,774	20,408	6366	1.370	71.47	0.899	1.402	47,182
0.202	27,027	20,450	6577	1.359	73.34	0.903	1.392	47,477
0.145	27,137	20,450	6687	1.351	74.49	0.906	1.384	47,587
0.098	27,211	20,408	6803	1.344	76.03	0.908	1.378	47,619
0.060	27,211	20,408	6803	1.340	77.02	0.910	1.373	47,619
0.000	27,322	20,408	6914	1.330	77.56	0.913	1.363	47,731

The variation of Stokes shift with solvent polarity functions is linear in the presence of general solvent effect. This linear dependence exhibits good correlation in the case of DMSO–water binary mixture. These observations are in agreement with the characteristics of the binary solvent mixture [27]. However, the deviations from the linearity observed in some cases imply the existence of short-range specific solute–solvent interactions, such as hydrogen bonding and the tendency of polar solvent molecules to form aggregates [26]. These are also related to the extent of interactions between the solute and the solvent molecules, which lead to the energy difference between the ground and the excited states. The prominent hydrophilic nature of DMSO makes it capable of forming strong and persistent hydrogen bonds to water [30,31] and often held

responsible for the strong non-ideal mixing behavior [32–34]. The largest deviation from ideal mixing occurs around 33% mole of DMSO, thus suggesting the existence of stoichiometrically well-defined 1DMSO:2water complexes. Even the viscosity of the mixed solvent at this composition also shows a maximum value of about 4.4 cP at 293 K, which is about 4.4 and 1.8 times those of pure water and pure DMSO, respectively. A number of molecular dynamics (MD) simulations [32,35] and neutron diffraction experiments [36] have identified the structure of the 1DMSO:2water complex and linked many of the structural and dynamical features of DMSO–water mixtures to the presence of such aggregates. Borin and Skaf [37] have proposed, using MD simulations, a second distinct type of aggregate consisting of two DMSO linked by a central

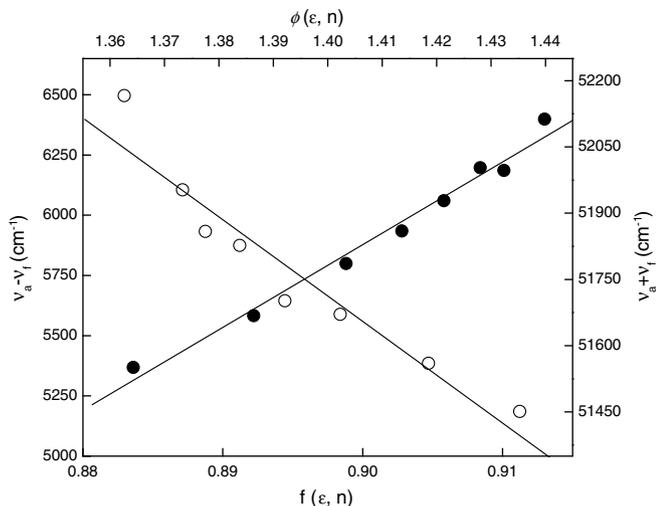


Fig. 2. Plot of  $v_a - v_f$  vs.  $f(\epsilon, n)$  (●) and  $v_a + v_f$  vs.  $\phi(\epsilon, n)$  (○) for C440.

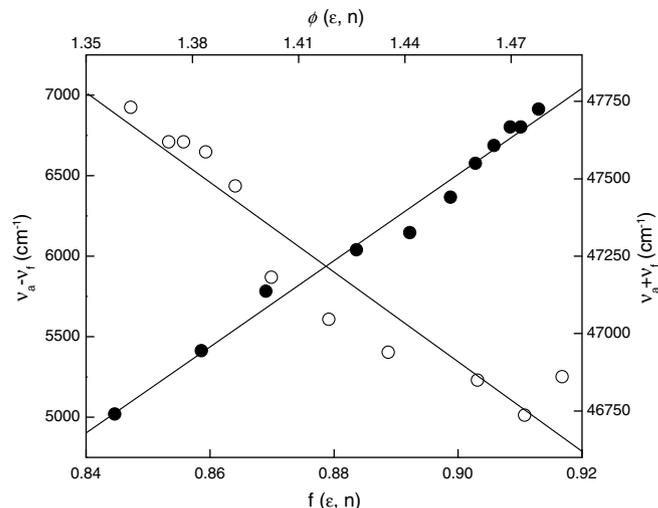


Fig. 5. The variation of  $v_a - v_f$  with  $f(\epsilon, n)$  (●) and variation of  $v_a + v_f$  with  $\phi(\epsilon, n)$  (○) for C151.

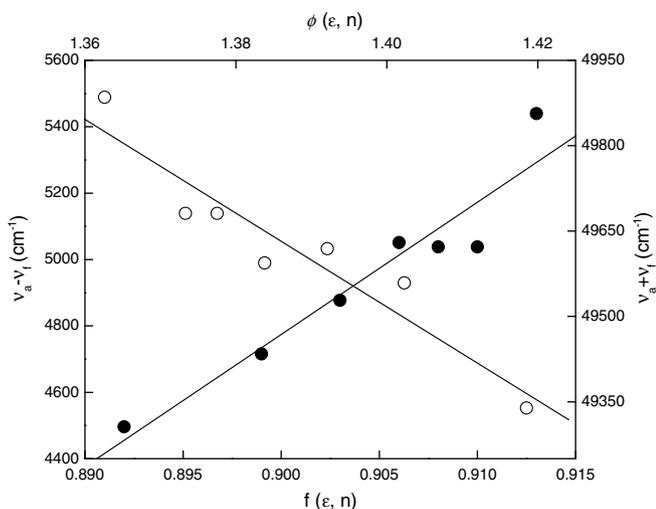


Fig. 3. Plot of  $v_a - v_f$  vs.  $f(\epsilon, n)$  (●) and  $v_a + v_f$  vs.  $\phi(\epsilon, n)$  (○) for C450.

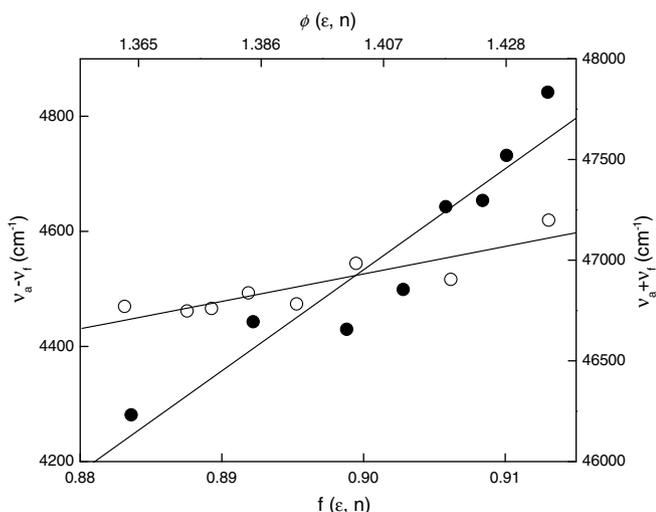


Fig. 4. The variation of  $v_a - v_f$  with  $f(\epsilon, n)$  (●) and variation of  $v_a + v_f$  with  $\phi(\epsilon, n)$  (○) for C466.

water molecule through hydrogen bonding, which is expected to be the predominant form of molecular association between DMSO and water in DMSO-rich mixtures.

Fig. 6(a–d) shows the dependence of the absorption maximum (A), fluorescence maximum (B) and Stokes shift (C) of coumarins on the composition of aqueous DMSO solution. The magnitude of the Stokes shift in the case of all the coumarins increases in the binary solutions with increasing concentration of water. Further, we find that absorption maxima are blue shifted in the case of C440 and C151 irrespective of mole fraction of DMSO in the mixture. In the case of C450, absorption maxima are red shifted for a mole fraction of DMSO in the range 1.0–0.372 whereas in the range of 0.275–0.0 the absorption maxima are blue shifted. However, in the case of C466, absorption maxima are red shifted for a mole fraction of DMSO in the range 1.0–0.372 and for the range 0.372–0.0 absorption maxima remains almost constant. The emission maxima of all the coumarins are red shifted in DMSO–water binary mixture with increasing solvent polarity. The observed red shift in the emission peaks of all the coumarins indicates that the excited states of the coumarins are more stabilized by polar solvents [38]. A large spectral shift observed in the emission spectra in comparison with absorption spectra leads to higher dipole moment in the excited state than in the ground state. Similar observations have been reported in the case of C307 and C522B [39]. However, the less pronounced absorption shift observed with the solvent polarity implies that the ground state energy distribution is not affected to a greater extent possibly due to the less polar nature of the dye molecule in the ground state rather than the excited state [18]. Previous reports indicated a blue shift with increasing polarity of the solvent for the probe cresyl violet, resorufin and merocyanine 540 (MC540) [40,41]. In the present study, the probes C440 and C151 possess hydrogen bonding functional groups like C=O and  $-\text{NH}_2$  and are

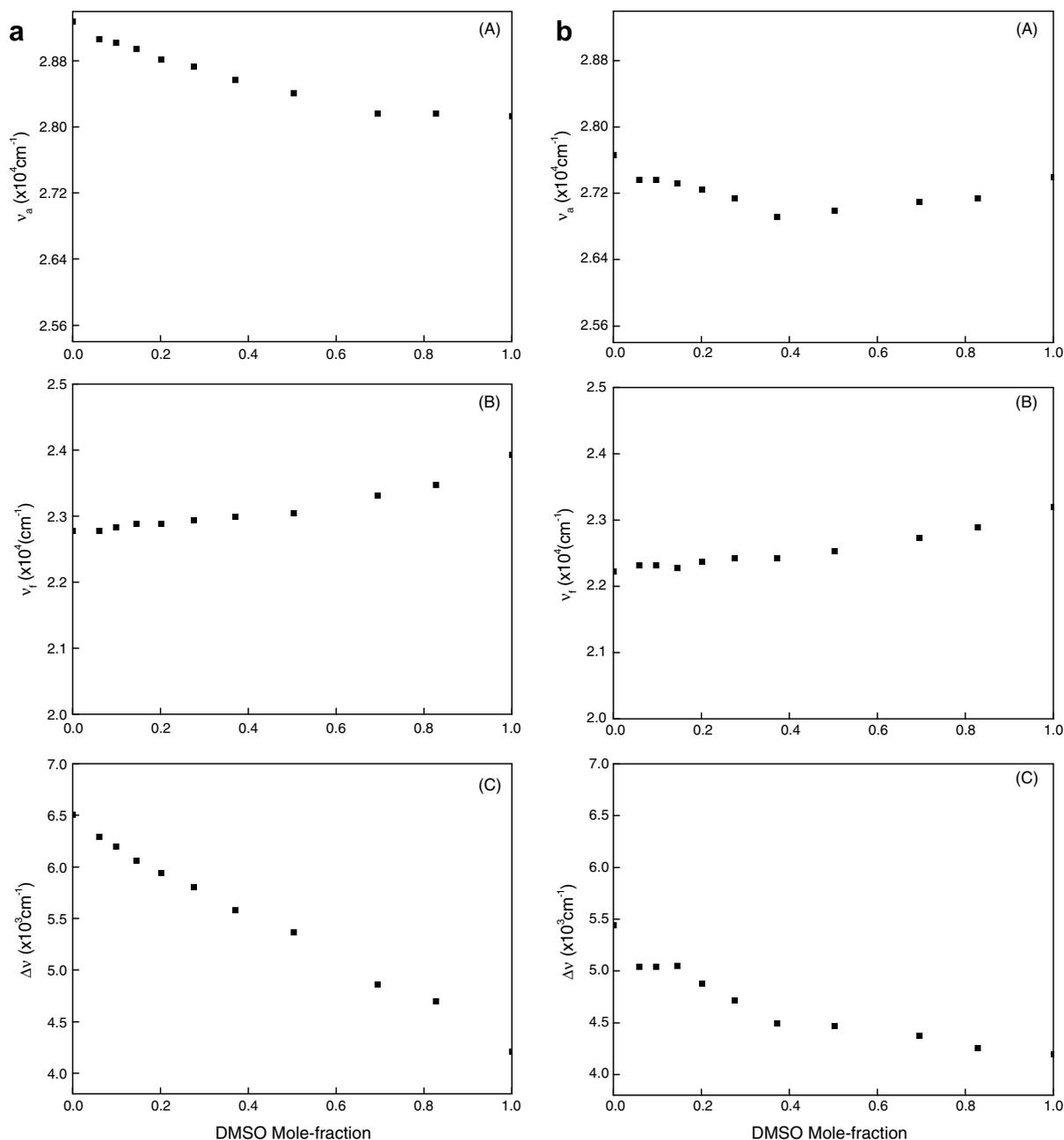


Fig. 6. Absorption maximum (A), fluorescence maximum (B) and Stokes shift (C) of (a) C440, (b) C450, (c) C466 and (d) C151 in all mole fractions of DMSO.

normally expected to form hydrogen bonds with binary mixture of DMSO–water resulting in a blue shift in the absorption spectrum as the polarity of the mixture increases. The polarity of the mixture increases with the increasing concentration of water and so is the hydrogen-bonding characteristic of the mixture. Moreover,  $-\text{CF}_3$  group present in C151 is also partially responsible for the observed blue shift [42]. The observed blue shift in the absorption maxima in polar solvents such as DMSO–water mixture reveals that the C440 and C151 are more stabilized in the ground state. It may be noted that as the mole fraction of DMSO decreases, the nature of the mixture changes from polar aprotic to polar protic. In polar aprotic solvents,

the observed red shift indicates the reorientation of solvent molecule around the excited state dipole gives rise to a minor effect whereas, in case of polar protic solvents, the ground state is more stabilized by intermolecular hydrogen bonding between the hydroxyl group of the solvents and hydrogen bonding functional group of the solute, resulting in blue shift [43]. In the same way, C450 exhibits red shift in polar aprotic solvent mixture and later as the polarity of the solvent mixture increases, the primary amino group  $-\text{NH}$  of the solute forms stronger hydrogen bonds with hydroxyl group of water resulting in a blue shift.

Fig. 7 shows the typical absorption and fluorescence spectra of C151 in aqueous DMSO solutions. It is clear

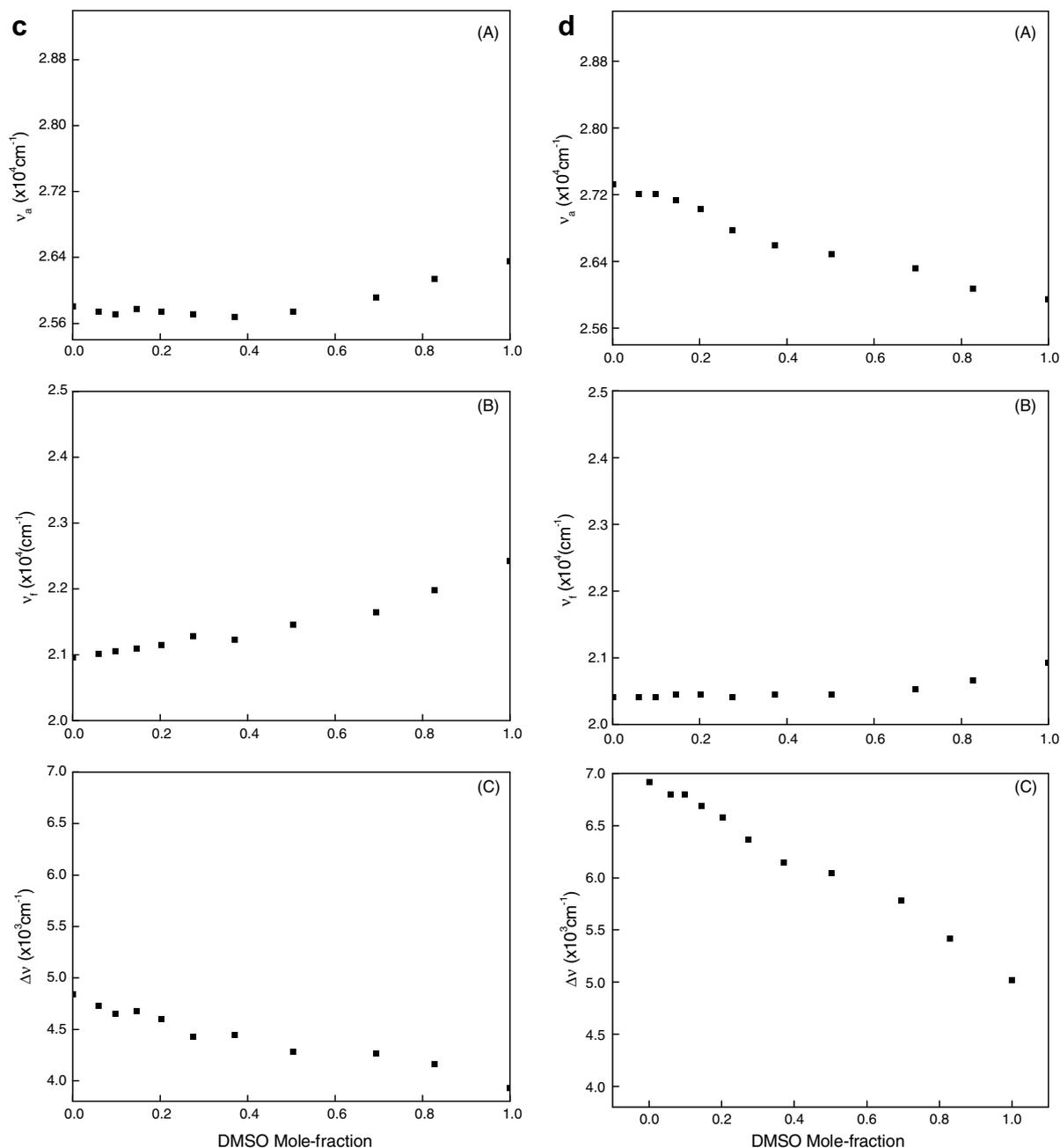


Fig. 6 (continued)

that both the absorption and fluorescence maxima are very sensitive to the mole fraction and shift to longer or shorter wavelengths with increasing value of mole fraction of DMSO depending on the probe used. A typical fluorescence decay of C151 in aqueous DMSO binary solutions at different mole fractions is shown in Fig. 8. The fluorescence lifetimes of all the coumarins are listed in Table 3. It may be noted that lifetime in binary solutions depend strongly upon the composition and not on the viscosity, and the variation of fluorescence lifetime with the mole fraction of DMSO is found to be nonlinear. The fluorescence lifetimes of C440, C450 and C151 by and large appear to be constant in various compositions. However,

the lifetimes of C466 gradually decrease with decrease of DMSO in water. The fluorescence lifetime values of C466, which has a side chain of *N*-diethyl group, were found to be longer in DMSO (2.27 ns) compared to water (0.24 ns). The unusually long lifetime in DMSO and short lifetime in water do not seem to follow a trend of either viscosity or dielectric constant or refractive index of the solvents. On the other hand, in the case of C440 and C450, in which an amino group replaces the *N*-diethyl group showed an opposite trend. These results indicate that the *N*-diethyl group is likely to be the perturbation site for the DMSO/water interaction. The substantial difference in the lifetime values of C466 in DMSO and water may

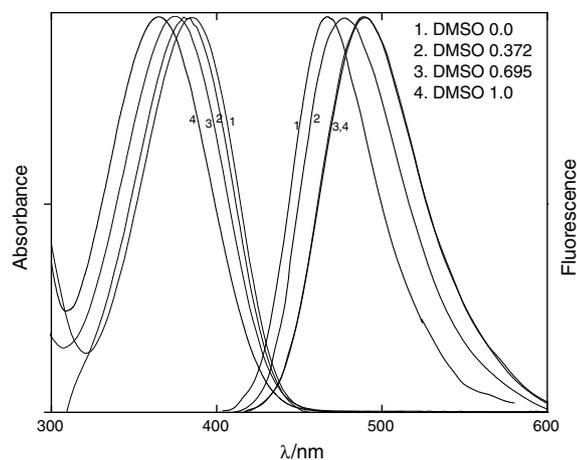


Fig. 7. Typical absorption and fluorescence spectra of C151 obtained for different mole fraction of DMSO. Curves 1, 2, 3 and 4 are with the mole fraction 0.0, 0.372, 0.695 and 1.0, respectively.

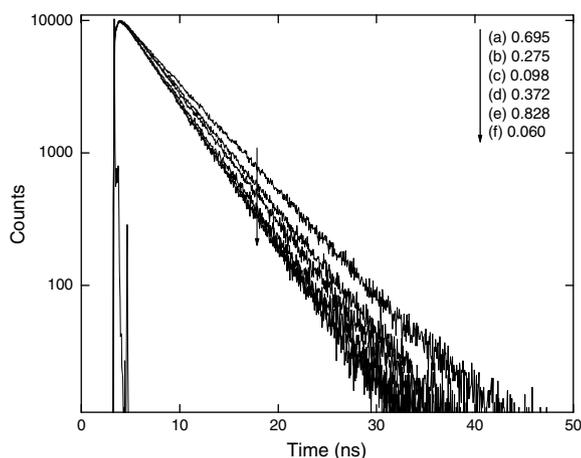


Fig. 8. Typical fluorescence decay curves of C151 in aqueous DMSO solution obtained at 370 nm. Curves a, b, c, d, e and f are with the mole fraction 0.695, 0.275, 0.098, 0.372, 0.828 and 0.06, respectively.

Table 3  
Fluorescence lifetime of probe molecules in DMSO–water mixture

DMSO mole fraction	Lifetime (ns)			
	C440	C450	C466	C151
1.000	2.65	3.33	2.27	4.66
0.828	3.47	3.36	1.73	3.99
0.695	3.84	3.12	1.26	5.21
0.503	4.07	3.77	0.70	4.80
0.372	3.49	3.82	0.58	4.16
0.275	4.40	4.17	0.44	4.62
0.202	3.97	3.70	0.36	4.56
0.145	3.75	4.44	0.39	4.03
0.098	3.97	4.28	0.31	4.45
0.060	3.94	4.42	0.29	3.86
0.000	4.27	4.60	0.24	3.85

be due to the interaction between  $-\text{N}(\text{C}_2\text{H}_5)_2$  group of C466 with binary solvent mixture as also noted in a previous study by Koti and Periasamy [44] for styrylthiazoloquinoline (STQ) dye in methanol and dichloromethane

solvent mixtures. The modified solvent arrangement around the dye leads to the perturbation of radiative and/or non-radiative rates of the dye–solvent complex in opposite ways. Hence, it is reasonable to conclude that there is a specific interaction between the dye with the solvent and the standard model of photophysics does not appear to hold for this dye. In the case of C151, in addition to amino group at the seventh position, the electronegative  $-\text{CF}_3$  group present in the fourth position may also affect the fluorescence lifetime.

The cavity radii of the solutes,  $a_0$ , correlation coefficient,  $r$  and the corresponding experimentally determined absolute values of the ground and excited state dipole moments of the coumarin dyes are given in Table 4. It is seen that, the changes in the dipole moments upon electronic excitation are small suggesting that the emission of these dyes originates from a state, which although more polar than the ground state, is probably a locally excited intramolecular charge transfer (ICT) state. The charge transfer accompanying the excitation in the lowest excited singlet state usually results in the excited molecule having a greater dipole moment than in its ground state [45]. This is evident from Fig. 9 showing the resonance structure of the molecules. Upon excitation, the carbonyl becomes highly elec-

Table 4

Cavity radius ( $a_0$ ), correlation coefficient ( $r$ ) and calculated values of ground ( $\mu_g$ ) and excited ( $\mu_e$ ) state dipole moments for C440, C450, C466 and C151

Solute molecule	$a_0$ (in Å)	Correlation coefficients ( $r$ )		$\mu_g$ (D)	$\mu_e$ (D)
C440	3.37	0.99 <sup>a</sup>	0.96 <sup>b</sup>	4.23	7.20
				6.34 <sup>c</sup>	8.00 <sup>d</sup>
C450	3.71	0.95 <sup>a</sup>	0.95 <sup>b</sup>	5.62	8.58
				5.80 <sup>c</sup>	7.39 <sup>d</sup>
C466	3.71	0.98 <sup>a</sup>	0.96 <sup>b</sup>	3.15	6.35
				6.89 <sup>c</sup>	8.19 <sup>d</sup>
C151	3.46	0.99 <sup>a</sup>	0.95 <sup>b</sup>	3.63	6.88
				6.10 <sup>c</sup>	7.12 <sup>d</sup>

<sup>a</sup> Correlation coefficient in the case of  $v_a - v_f$  vs  $f(\epsilon, n)$ .

<sup>b</sup> Correlation coefficient in the case of  $v_a + v_f$  vs  $\phi(\epsilon, n)$ .

<sup>c</sup> Calculated from B3LYP functional with 6-31g\* basis.

<sup>d</sup> Excited state dipole moment using CI singles (CIS) method.

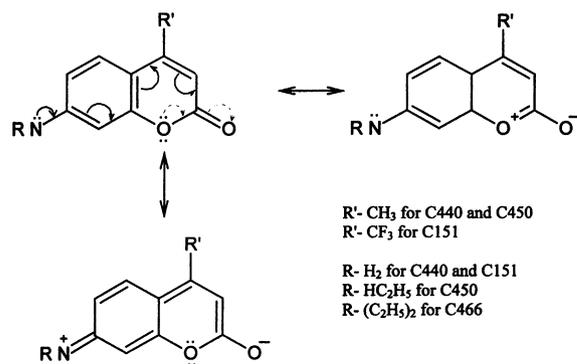


Fig. 9. Resonance structures of C440, C450, C466 and C151.

trophilic, whereas the amino groups become strong electron donor. It may also be possible that the amino group is more electron donating group than methyl group as is observed from the resonance structures. The ground and excited state dipole moments of all the coumarins were also obtained from *ab initio* calculations using DFT [22] and CIS method, respectively. The results are listed in Table 4 for comparison. The ground state optimized geometries

of all the probes obtained using B3LYP functional with 6-31g\* basis are shown in Fig. 10(a–d). The arrow in the figure indicates the direction of dipole moment in the ground state. It is evident from Table 4 that the ground state dipole moments obtained from Solvatochromic shift method are smaller than those obtained from *ab initio* calculations for C440, C466 and C151. Several reports have shown similar disagreement between theoretical and

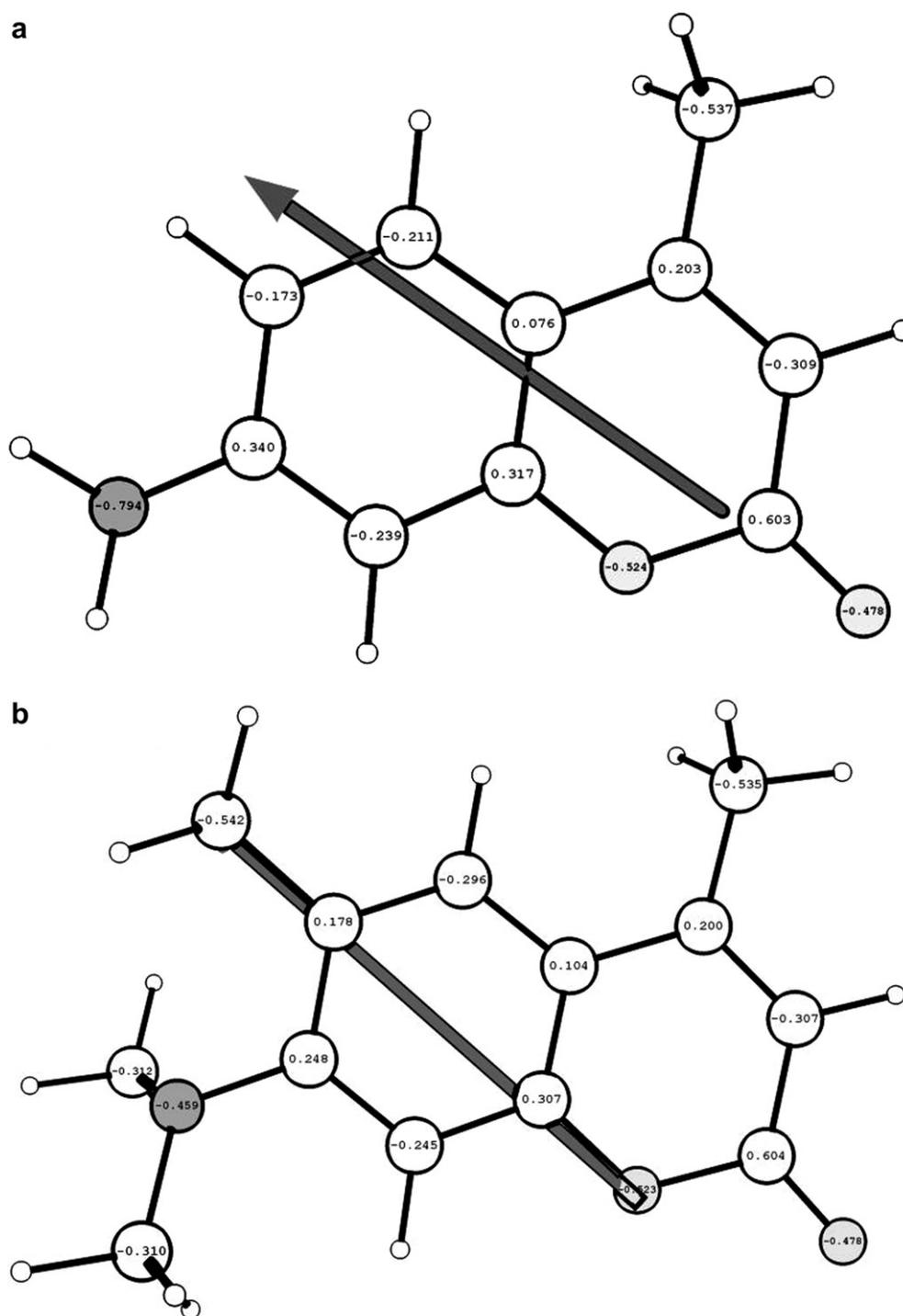


Fig. 10. Ground state optimized structures of coumarins obtained using B3LYP functional with 6-31g\* basis is shown along with the distribution of charges in case of (a) C440, (b) C450, (c) C466 and (d) C151. The arrow indicates the direction of dipole moment.

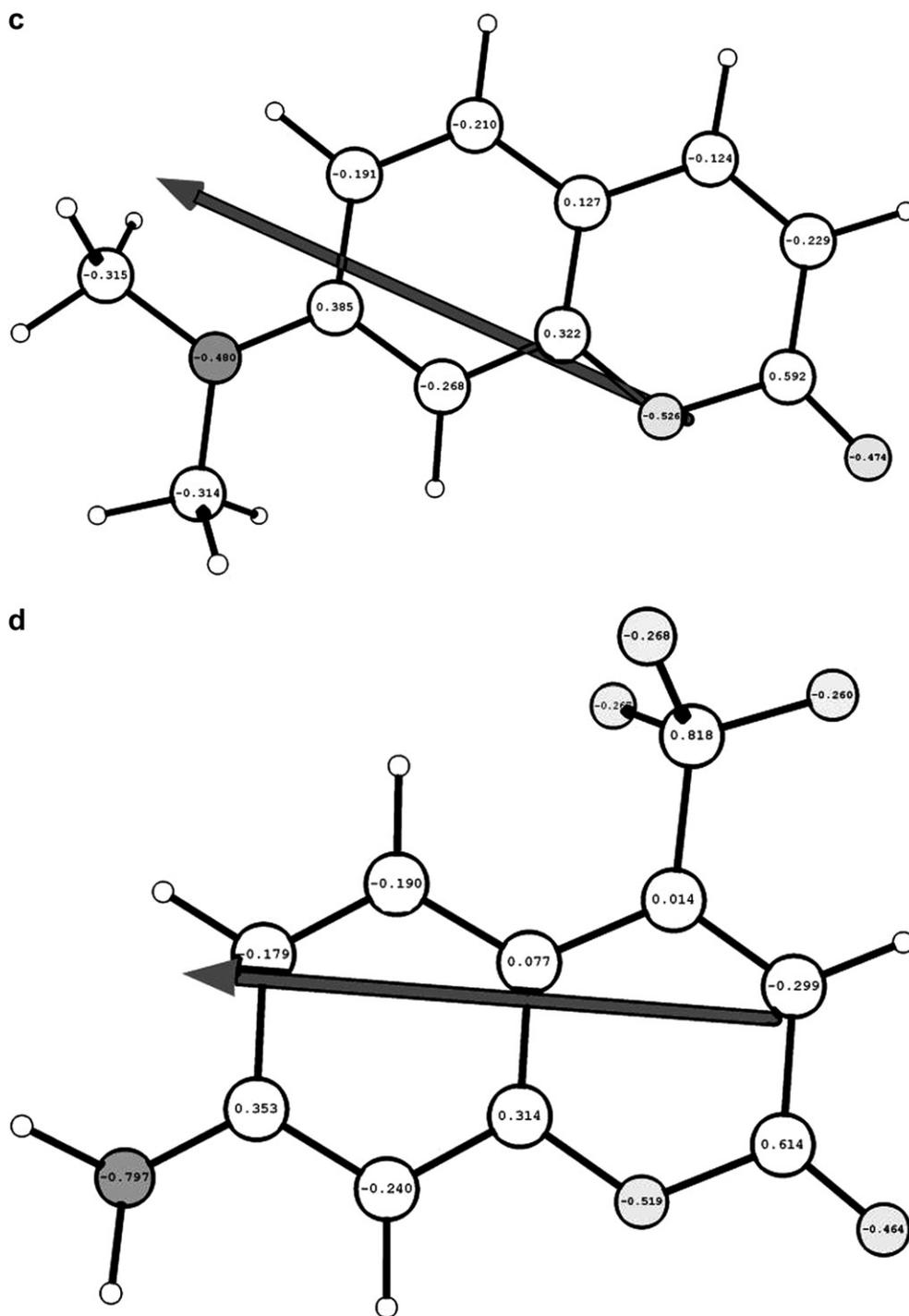


Fig. 10 (continued)

experimental values [46]. However, a fair agreement has been observed in case of C450 between experimental and theoretical values. The excited state dipole moments were computed using CIS method to estimate the minimum of the lowest excited singlet state and optimized using 6-31g\*. Nevertheless, the results obtained with this agree well with the experimental ones.

Ravi et al. [9] have studied excited state dipole moment of C151 (6.07 D) by solvatochromic method in different solvents and in binary mixtures of acetonitrile–benzene.

The solvents were chosen in such a way that those with possible strong H-bonding with the dyes were excluded. The excited state dipole moments were estimated from the experimentally determined value of the difference in the excited and ground state dipole moment ( $\Delta\mu$ ). The ground state dipole moments were obtained from semi-empirical quantum chemical procedures such as Austin Model 1 (AM1) method. The microscopic solvent polarity parameter such as  $E_N^T$  or  $E_{30}^T$  were used rather than the bulk solvent polarity parameters. In the present work, bulk

solvent parameters and highly polar solvent mixture were used to calculate both ground and excited state dipole moments. The excited state dipole moment of C151 is found to be 6.87 D, which is in good agreement with theoretically estimated excited state dipole moment 7.02 D [9]. Although there is a difference in the ground state dipole moments obtained using the DFT method and experimental technique, the excited state dipole moments obtained from CIS method are in consistence with experimental results indicating that the polar mixture of DMSO–water binary mixture is also suitable for the measurement of dipole moments.

## 5. Conclusion

In conclusion, the ground and excited state dipole moments of four coumarin laser dyes C440, C450, C466 and C151 in binary solvent mixture of DMSO–water were determined using solvatochromic shift method. The shifts in the emission peaks with solvent polarity changes are more pronounced than those of absorption peaks indicative of higher dipole moments in the excited state than in the ground state. Further, it also suggests that the dipole moments in the excited state of these dyes originate from a state, which is more polar compared to ground state. The estimation of the ground and excited state dipole moment of dye molecules is important as it controls the tunability of its emission energy as a function of solvent polarity. Further, by mixing miscible solvents in different proportions the polarity of the solvents could be controlled. In turn, using the homogeneous mixtures of these solvents a desired tenability can also be achieved. The theoretically estimated ground state dipole moment is in good agreement with experimental value in case of C450 though there are variations in the case of C440, C151 and C466. The excited state dipole moment values of all the molecules calculated with CIS method are found to agree well with those determined experimentally. The fluorescence lifetimes measured using TCSPC technique show a nonlinear variation indicating the strong dependence of lifetime on the composition of the binary mixture. The fluorescence lifetime of C466 also establishes that *N*-diethyl group present in the solute is likely to perturb the DMSO/water interaction.

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