Comparative Study of Excited State Dipole Moment of Coumarin Laser Dyes: Solvent and Substituent Effect

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Abstract: In the present work, an array of novel substituted 2H-chromen-2-one (coumarin derivatives abbreviated as C-337, C-480, C-540A) has been subjected to photophysical analysis. Although the influence of the electron donating groups such as amino, substituted amino, hydroxyl, alkoxy groups at position 7 of the coumarin ring system has been extensively studied, However, coumarin moieties with substituent at position 3 have not been explored much. Attempt is made to explain the effect of electron donating and electron accepting substituent on excited state and ground state dipole moment. The ground state (μ) and excited state (μ^*) dipole moment of C-337, C-480, C-540A coumarins are estimated from solvatochromic shift of absorption and fluorescence spectra as a function of the dielectric constant and refractive index using Bakhshiev and Kwaski-Chamma Vialletequ. μ^* and μ for all the reported coumarin are also calculated using Reichardt correlation method. The small angle is also reported between the ground and excited state dipole moment suggesting that they are almost parallel to each other. Excited state dipole moment is observed larger than ground state dipole moment for all the coumarins studied indicating substantial π-electron density redistribution.

Key words: Coumarin laser dyes, absorption and fluorescence spectroscopy, organic solvents, excited state, ground state, dipole moment.

1. Introduction

Substituted coumarin having excellent lasing parameters attracts renewed interest in the study of thespectral characteristics. Coumarin dyes are a very good media for efficient broad band dye lasers in the blue green region [1]. Coumarin class of laser dyes such as coumarin 1, i.e., 7-diethylamino-4-methyl coumarin was the first from which Sorokin and Lankard observed laser action, after that, more than hundred coumarin laser dyes came to existence. For getting maximum efficiency from tunable dye laser, one must understand the spectroscopic characteristics with varying conditions of temperature [2, 3], solvents [4-7], pH etc. for these molecules having different substituent. Besides, this coumarins are also used as indicators of biophysical process [8], optical

brightners [9], blood thinners [10], in enzymology [11], treating cancer affected cells [12], sun burn preventive [9] etc. Coumarin moiety as such is non-fluorescent, however, coumarins having substituent at different places show fluorescence. In general, electron donating substituents tend to enhance emission intensity while electron accepting or with drawing substituent tends to diminish it. Also the shift in position of the electronic bands of aromatic compounds due to substitution of the exocyclic group depends on the nature of the substituent group and its electronic interaction with the parent molecule. Substituent leads to a redistribution of charge in the ground as well as the excited state [13]. Some times more efficient conjugation takes place due to intra molecular charge transfer in the excited state. The substituent group provides additional levels for absorption and fluorescence to take place.

The spectral characteristics of these coumarin dyes

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are strongly altered by the nature of substituent, position of substituent on coumarin ring and its surrounding. As the substitution changes the excited state dipole moment of substituted coumarin molecule as well as location of absorption and fluorescence band, it improves solubility in organic solvents and modulate their resistance to chemical and photochemical protonation in certain environment. Present paper reports the effect of solvent and substituent in C-480, C-540A and C-337 coumarin molecules having almost identical structure with different substituent.

It is a known fact that dipole moment of molecule is different in ground and excited state because of the change in electron density. A prior knowledge of dipole moment of electronically excited state is often useful in design of non-linear optical materials and elucidation of any photochemical transformation. Also, the experimental data on dipole moment are useful in parameterization of quantum chemical methods.

The influence of solvents on fluorescence spectra may have several origins ranging from perturbation due to the solvent refractive index and dielectric constant to hydrogen bonding or even complexation between the fluorophore and the solvent. These factors can change the energy difference between the ground (S_0) and first excited state (S_1) and can shift the emission spectra. Hydrogen bonding and solvent polarity are the key factors in controlling pathways of energy dissipation following electronic excitation. Solvent moderated shifts of the energy levels may enhance or inhibit radiation less transition to the ground state via the proximity effect as discussed by Lim [14]. Different methods in literature are available for the estimation of excited state dipole moment such as externally cause spectral shift (electrochromism) or internally cause spectral shift (solvatochromism).

Methods such as electric fluorescence polarization [15], electric dichroism [16], microwave conductivity [17] and stark splitting [18] are generally considered as more accurate method but because of equipment and restriction on the molecules to be chosen for the study,

these methods are not used widely. However, the solvatochromic method is based on the shift of the UV-VIS absorption and fluorescence maxima in different solvents of varying polarity. A radiative transition (absorption or emission) connects a relaxed initial state to a Franck-Condon (FC) final state.

When the molecule is surrounded by a liquid solvent, each state is stabilized (or destabilized) by an energy *Es* which is the solvation energy. The difference in the solvation energy of the initial and final states in various solvents is observed as solvatochromic shifts. Because of change in excited state of molecule is different from the ground state, the change of dipole moment is greater in excited state than in ground state. The change in dipole moment of the C-480, C-540A and C-337 coumarin molecules in excited state with respect to ground state is determined by using following solvatochromism methods.

1.1 Method I

It has been suggested that Bakshiev [19] and Kawski-Chamma-Viallets [20] (Eqs. (1) and (2)) give the best results which are:

$$v_a - v_f = m_1 F_1 (\varepsilon, n) + \text{const.} \quad (1)$$
$$1/2(v_a + v_f) = m_2 F_2 (\varepsilon, n) + \text{const.} \quad (2)$$

where, v_a is an absorption maximum and v_f is an fluorescence maximum, wave number given in cm^{-1}.

The expressions for $F_1(\varepsilon, n)$ (Bakhshiev's polarity function) and $F_2(\varepsilon, n)$ (Kawski-chamma-Viallet polarity function) are given as:

$$F_1 (\varepsilon, n) = (2n^2 + 1/n^2 + 2) * ((\varepsilon - 1/\varepsilon + 2) - (n^2 - 1/n^2 + 2)) \quad (3)$$
$$F_2 (\varepsilon, n) = [(2n^2 + 1/2(n^2 + 2)) * ((\varepsilon - 1/\varepsilon + 2) - (n^2 - 1/n^2 + 2) + (3(n^4 - 1)/2(n^2 + 2)^2)] \quad (4)$$

In Eqs. (3) and (4), "n" is refractive index and "ε" is the dielectric constant of the solvents.

In Eqs. (1) and (2), expression for slopes m_1 and m_2 are given as:

$$m_1 = 2(\mu^* - \mu)^2/hca^3 \quad (5)$$
$$m_2 = 2(\mu^{*2} - \mu^2)/hca^3 \quad (6)$$

where, μ is ground state and μ^* is excited state dipole moment of the solute molecule; "h" is the Planck's constant, "c" is the velocity of light in vaccum, and "a" is the Onsagar cavity radius of the solute molecule. The values of the solute cavity radii (a) were calculated using the method of partial volume addition as suggested by Edward [21].

The ground and excited state dipole moments are estimated by means of the following equations. Assuming that the symmetry of the investigated solute molecule remains unchanged upon electronic transition, the angle between the ground and excited state dipole moments is small, and the cavity radius "a" is the same in both ground and excited state, based on Eqs. (5) and (6):

$$\mu = |m_2 - m_1|/2 \cdot [hca^3/2m_1]^{1/2} \qquad (7)$$
$$\mu^* = |m_2 + m_1|/2 \cdot [hca^3/2m_1]^{1/2} \qquad (8)$$

The slopes m_1 and m_2 can be determined by plotting the ($v_a - v_f$) Stokes shift and $1/2(v_a + v_f)$ against the bulk solvent polarity functions $F_1(\varepsilon, n)$ and $F_2(\varepsilon, n)$ respectively, for different solvents.

Generally, the dipole moment μ and μ^* are not parallel to each other but form an angle φ given as [6]:

$$\cos\varphi = 1/2\mu\mu^*((\mu^2 + \mu^{*2}) - m_1/m_2(\mu^{*2} - \mu^2))$$

1.2 Method II

The value of excited state dipole moment was also calculated using Richardt-Dimroth equation, as suggested by Aaron et al. [22]. The excited state dipole moment of several substituted coumarins was calculated by means of microscopic solvent polarity parameter, E_T^N (Method II). Correlation of solvatochromic Stokes shift was superior to the one obtained by using bulk solvent polarity functions. Also the error in estimation of Onsagar cavity radius "a" has been minimized since a ratio of two Onsagar radii is involved.

The excited state dipole moment is determined by:

$$v_a - v_f = 11,307.6((\delta\mu/\delta\mu_B)^2 * (a_B/a)^2)E_T^N + \text{const.} \quad (9)$$

where, E_T^N is the solvent polarity parameter proposed by Reichardt [23], which is based on the absorption wavenumber of a standard betaine dye in the solvent. Its value for different solvents is given in Table 1. $\delta\mu_B = 9$ D and $a_B = 6.2$ Å are the dipole moment changes on excitation and Onsagar cavity radius respectively of betaine dye, whereas $\delta\mu$ and "a" are corresponding quantities for the molecules of interest. The change in dipole moment $\delta\mu$ is evaluatedusing the plot of ($v_a - v_f$) Stokes shift verses E_T^N, then value of excited state

Table 1 Observed values of v_a (cm⁻¹) and v_f (cm⁻¹) of all the coumarin studied in different solvents along with the calculated values of solvent parameters $F_1(\varepsilon, n)$,$F_2(\varepsilon, n)$ & E_T^N.

Compound	Parameter $\times 10^{-2}$ (cm⁻¹)	Solvents						
		A	B	C	D	E	F	G
1a	v_a	263	265	259	258	257	259	254
	v_f	242	227	229	230	218	221	210
1b	v_a	247	245	239	240	237	237	231
	v_f	209	200	200	204	192	193	187
	$F_1(\varepsilon, n)$	0.04	0.04	0.62	0.37	0.81	0.55	0.89
	$F_2(\varepsilon, n)$	0.29	0.31	0.61	0.49	0.65	0.79	0.75
	E_T^N	0.006	0.164	0.321	0.259	0.654	0.386	0.775

A = cyclohexane, B= dioxane, C = dichloromethane, D = chloroform, E = EtOH, F = DMF, G = formamide

		A1	B1	C1	D1	E1	F1	G1
1c	v_a	227	226	231	227	224	235	227
	v_f	206	205	213	206	203	231	207
	$F_1(\varepsilon, n)$	0.82	0.86	0.49	0.87	0.84	0.00	0.78
	$F_2(\varepsilon, n)$	0.65	0.65	0.50	0.67	0.74	0.26	0.65
	E_T^N	0.654	0.762	0.228	0.460	0.444	0.012	0.617

A1 = EtOH, B1 = MeOH, C1 = ethyl acetate, D1 = acetonitrile, E1 = DMSO, F1 = n-hexane, G1 = propane-2-ol

1a = C-480 coumarin,1b = C-540A coumarin,1c = C-337 coumarin.

Table 2 Calculated values of μ and μ^* along with cavity radius (a) for all the compounds studied.

Compound	a (Å)	μ (D)	μ^* (D)	μ^* (D)$^\wedge$
1a	3.80	1.36	4.17	3.34
1b	3.90	4.92	6.40	6.09
1c	3.71	1.83	4.93	4.85

Values of excited state dipole moment calculated using Reichardt-Dimrothequation [23].
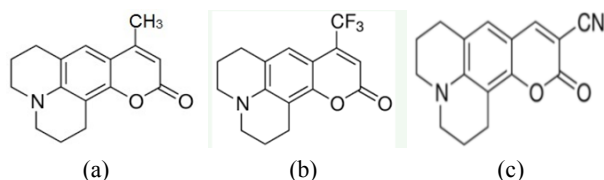

(a)　　　　　　(b)　　　　　　(c)

Fig. 1 (a) C-480 coumarin; (b) C-540A coumarin and (c) C-337 coumarin.

dipole moment is estimated by using the value of ground state dipole moment calculated from Method I.

2. Experiments

C-480 and C-540A coumarins, of laser grade purity, were obtained from Sigma Chemical Co. and used without further purification. All the solvents used were of AR grade. They were found to be transparent and non-fluorescent in the range of excitation and fluorescence emission. Absorption spectra were recorded using a Shimadzu 260 UV-Vis spectrophotometer in a 1cm path length cuvette. Fluorescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer equipped with a 200 W xenon arc lamp as the excitation source and an IP21 photomultiplier as detector. Dye concentration was kept low at about 10^{-6} M to avoid self quenching or inner-filter effects. Recorded fluorescence emission wavelengths were accurately estimated to within ±2 nm and absorption wavelengths to within ±1 nm.

The experimental data for C-337 coumarin were taken as it is from Ref. [9].

The molecular structures of C-480, C-540A and C-337 coumarins are given in Fig. 1

3. Results and Discussion

We have divided our study into two parts: solvent effect and substituent effect.

3.1 Solvent Effect

The observed values of v_a and v_f in various polar and nonpolar solvents are listed in Table 1. The calculated value of the solvent parameter F_1 (ε, n), F_2 (ε, n) and E_T^N are also given in Table 1.

It is observed from Table 1 that with increase in the polarity of the solvent the fluorescence and absorption band maxima undergo bathochromic shifts indicating $\Pi \to \Pi^*$ transitions. Using the values of v_a and v_f and Eqs. (1)-(9) (Method I and Method II) obtained from theoretical consideration, the excited and ground state dipole moments are calculated.

The slopes m_1, m_2 and m_3 are obtained by plotting the Stokes shift ($v_a - v_f$) verses F_1 (ε, n) and E_T^N also $1/2(v_a + v_f)$ verses $F_2(\varepsilon, n)$. The plots were drawn using least square fit method and are shown in Figs. 2-5 for all the three coumarins. Although some points deviates from linearity which could occur due to many different reasons such as excimer formation, intermolecular hydrogen bonding, the difference between the effective and bulk solvent polarity values or some other specific solute-solvent interactions.

The values of μ^* and μ obtained from the plots and the relations are given in Table 2. It can be seen in Table 2 that the value of $\mu^* > \mu$ in all the cases, i.e., the dipole moment of the molecule increases on excitation. A plausible explanation for the increase lies in the ICT process. Charge transfer accompanying excitation to the lowest excited singlet state usually results in the excited molecule having greater dipole moment than the ground state molecule. Although the values of μ^* obtained from Methods I and II are different but the trend in values is very much clear.

The value of angle φ calculated from Eq. (9) is very small nearly equal to zero, indicating that the ground

**Comparative Study of Excited State Dipole Moment of Coumarin Laser Dyes:
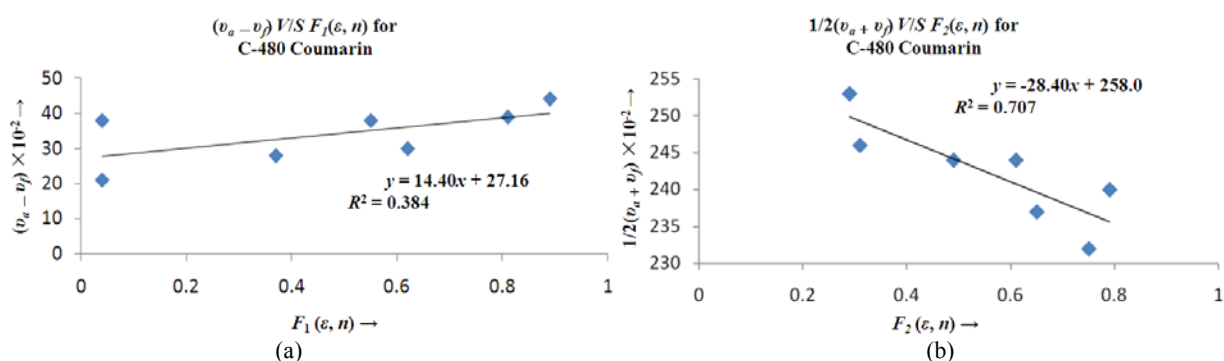Solvent and Substituent Effect**

Fig. 2 The plots of (a) $(v_a - v_f)$ *V/S* $F_1(\varepsilon, n)$ and (b) $1/2(v_a + v_f)$ *V/S* $F_2(\varepsilon, n)$ using least square fit method for C-480 coumarin.
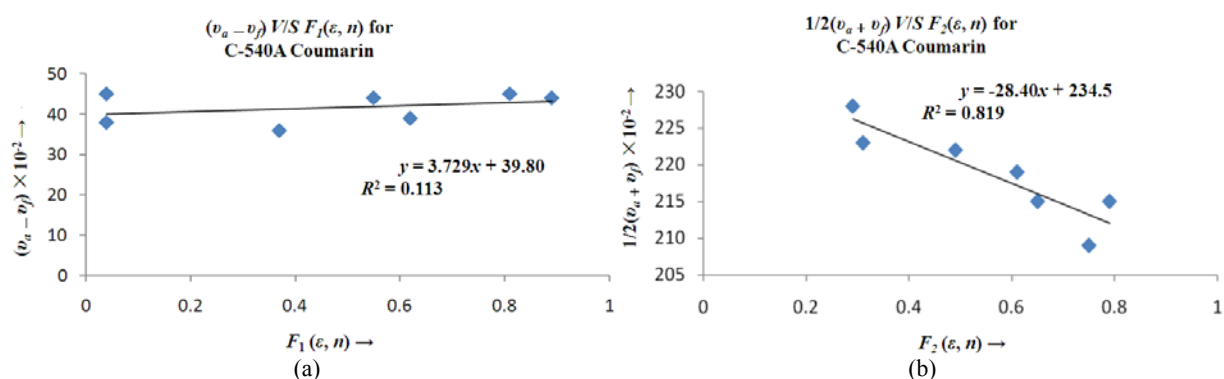

Fig. 3 Theplots of (a) $(v_a - v_f)$ *V/S* $F_1(\varepsilon, n)$ and (b) $1/2(v_a + v_f)$ *V/S* $F_2(\varepsilon, n)$ using least square fit method for C-540A coumarin.
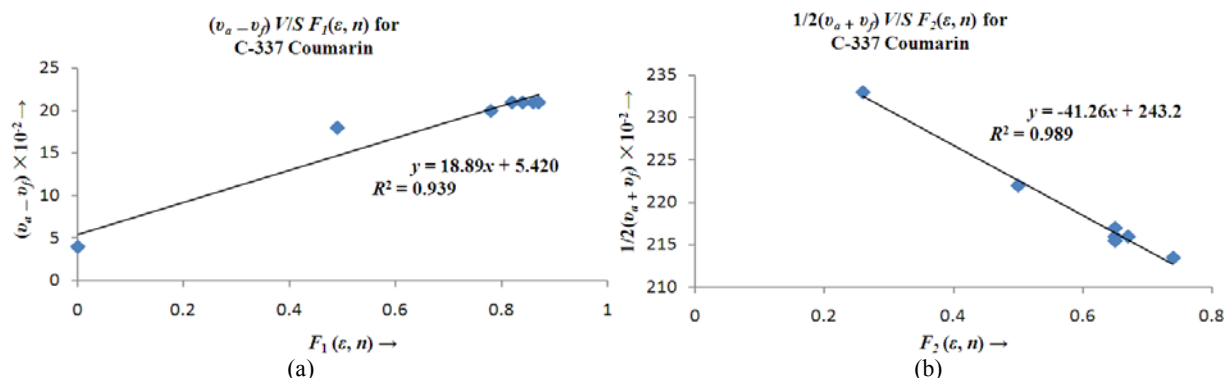

Fig. 4 Theplots of (a) $(v_a - v_f)$ *V/S* $F_1(\varepsilon, n)$ and (b) $1/2(v_a + v_f)$ *V/S* $F_2(\varepsilon, n)$ using least square fit method for C-337 coumarin.

and excited state dipole moment are almost parallel to each other, i.e., there is no change in the orientation of dipole moment in excited state for all the coumarin studied.

3.2 Substituent Effect

Substituent groups could be of various types: (1) electron donating groups, e.g., $-NH_2$, $-N(CH_3)$, $-NH(C_2H_5)$, $-SH$; (2) electron withdrawing groups, e.g., $-CF_3$, $-CHO$, $-C\equiv N$; (3) groups like $-CH_3$ which neither donate nor accept electrons.

The substituent leads to a redistribution of charge in the ground as well as the excited state. Some times more efficient conjugation takes place due to intramolecular charge transfer in the excited state. The effect was demonstrated in terms of the calculated values of excited state dipole moment.

3.2.1 Effect of Electron Donating Substituent

As electron donating substituent has a pair of unshared electron which is expected to reside in molecular orbitals which are largely localized. But when this group form a part of another molecule as

substituent as in the present case, then the charge on the group get substantially delocalized through out the system. Hence when the electronic transition takes place in the substituted molecule, the participating energy level is the delocalized energy level π_d and not the ground state enegy level π (Fig. 6). Absorption and fluorescence in these substituted molecule then takes place $\pi_d \rightarrow \pi^*$. As the energy gap between the highest occupied and the lowest unoccupied π^* orbital of these substituted molecules is considerably less than that of the highest occupied and the lowest unoccupied π^* orbital of the unsubstituted molecule. Thus the substitution causes a bathochromic shift in the values of absorption maxima and emission maxima. Also the excited state of the substituted molecule is seem to be more polar than the unsubstituted molecule

3.2.2 Effect of Electron Withdrawing Substituent

-CF$_3$ and -C $\equiv$N groups are electron withdrawing substituents, these groups provide a vacant electron acceptor orbital π_a^* which is lower in energy compared to π^* (Fig. 6) The net effect is that the energy gap between $\pi \rightarrow \pi_a^*$ is lesser than $\pi \rightarrow \pi^*$. The values of absorption maxima and emission maxima observed indicates it really so. The excited state of 1b and 1c is more polar than 1a as seen from the calculated value of μ^*.

The observed values of v_a and v_f for 4-CF$_3$ substituted coumarin 1b are lower than the corresponding values for a 4-CH$_3$ substituted coumarin 1a. It may be noted that the -CH$_3$ group neither donates nor accepts electrons and has virtually no effect on v_a and v_f. The observation in Table 1 shows that this is really so.

Now if we compare the values of v_a and v_f for 4-CF$_3$ and 3-C$\equiv$N substituent in coumarin 1b and 1c, which is a comparison of both electron withdrawing substituent.

As seen from the Table 1 in the case of ethanol solvent, the values of v_a are in following order: v_a for 1a > v_a for 1b > v_a for 1c, which indicates that the effect of 3-$\equiv$N substituent is more on the coumarin than 4-CF$_3$ substituent.
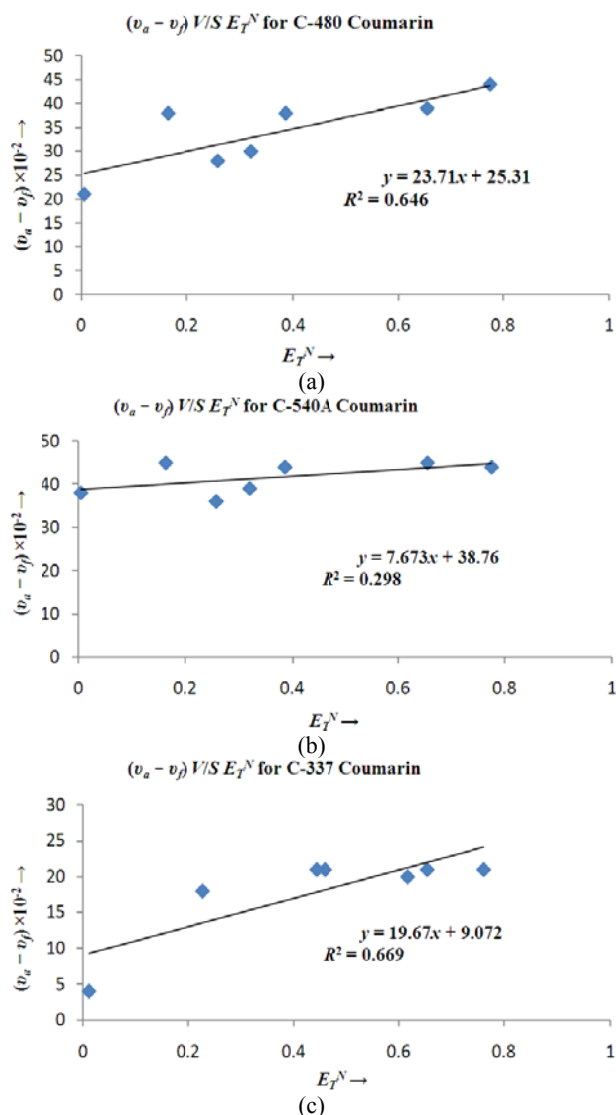

Fig. 5 The plots of $(v_a - v_f)$ V/S E_T^N using least square fit method for (a) C-480; (b) C-540A and (c) C-337 coumarins.
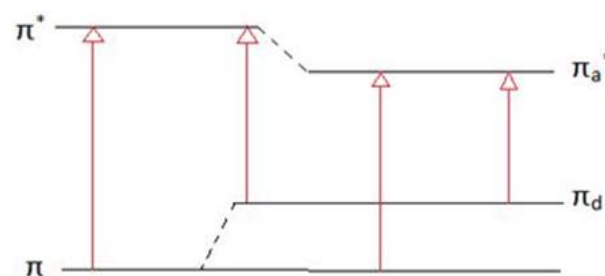

Fig. 6 Shifting of energy levels due to electron donating and electron withdrawing substituent.

The value of dipole moment μ^* and μ in the case of 1c is lesser than 1b whereas if we see it in terms of ratio μ^*/μ which is more for coumarin 1c compared to 1b, this is explained because in 1c coumarin, there is an

extra nitrogen atom having lone pair of electron at position 3. An electron from this pair gets promoted to a vacant π orbital of the aromatic ring during absorption process. This intramolecular charge transfer results in the excited molecule having a greater dipole moment than ground state molecule as observed in the present case. So the extent of intramolecular charge transfer and its effective location would be different and may account for substantially different values of μ^* and μ in both cases.

4. Conclusions

The present investigation of photophysical behavior of C-480, C-540A and C-337 coumarins indicates that on replacing -CH$_3$ group by a -CF$_3$ group at position 4, the longest absorption as well as the fluorescence peak shift to longer wavelength (bathochromic shift). The effect of 3-C≡N group is more prominent than 4-CF$_3$ group in coumarins. For all the coumarins, the emission as well as absorption maxima shifts to lower energy with increasing solvents polarity. There is an increase in the dipole moment for all the coumarins studied.

The small angle between μ^* and μ indicates that there is no change in the direction for excited state dipole moment from ground state for all the coumarins studied.

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