

Electron transfer from diphenyl and triphenyl amines to excited coumarin dyes

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Abstract

Electron transfer (ET) from diphenylamine (DPA) and triphenylamine (TPA) to a series of excited coumarin dyes having differently substituted 7 amino groups have been investigated in acetonitrile solution. The bimolecular quenching constants (k_q) obtained from steady-state (SS) and time-resolved (TR) fluorescence measurements are the same within the experimental error. Direct evidence for the ET reactions have been obtained using picosecond transient absorption measurements by characterising the DPA cation radical. Experimentally determined k_q values are seen to correlate well with free energy changes (ΔG^0) for the ET reactions within the framework of Marcus ET theory. Under the present experimental conditions, where diffusion of the reactants is a prerequisite for the reaction to take place, the solvent reorganisation appears to play the main role in governing the ET dynamics. The contribution from intramolecular reorganisation appears to be negligible, though under non-diffusive conditions it is reported that the ET for the similar systems can occur much faster than the solvation dynamics through the participation of the intramolecular modes. Differences in the ET dynamics for diffusive and non-diffusive conditions have been discussed in the light of the possible structural differences of the encounter complexes formed under the two experimental conditions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Coumarin; Electron transfer; Diffusive

1. Introduction

Electron transfer (ET) is one of the most fundamental reaction in chemistry and biology [1–6]. Though the ET reactions between donors and acceptors with both of them in the ground state are usually not favourable, photoexcitation of either of them often makes the ET processes to occur with reasonable rates [7]. Such photoinduced ET (PET) processes have the advantage that they can be initiated almost instantaneously by the use of ultra short laser pulses and thus the kinetics of the ET reactions can be investigated in real time. Measurements of this kind have made it possible to understand many details of the ET dynamics and thus to test the theoretical predictions with the experimental observations [1–10].

Coumarin dyes are good electron acceptors [11–15]. In the last few years we have investigated on the ultrafast PET reactions from neat anilines to excited (S_1) coumarin dyes [11–15]. Using femtosecond fluorescence up-conversion measurements [11–15] it has been observed that in neat

anilines the PET reactions often occur with rates much faster than those predicted by the conventional ET theories [1–10]. In neat anilines, an excited acceptor is always within the encounter distance with a donor molecule and thus ET can occur effectively as an unimolecular process, without involving any diffusion of the reactants [11–15]. So far in our knowledge, there is no report on the PET reactions from anilines to the excited coumarin dyes in a diffusing medium except our one recent communication [16], where aniline and *N*-alkylanilines have been used as the electron donors. In the present work we have investigated the PET reactions from diphenylamine (DPA) and triphenylamine (TPA) to a series of excited coumarin dyes in acetonitrile (ACN), using both steady-state (SS) and time-resolved (TR) fluorescence quenching measurements. The experimentally determined quenching constants (k_q) have been correlated with the free energy changes (ΔG^0) of the ET reactions using Marcus ET theory. Picosecond transient absorption measurements have been carried out to obtain a direct evidence for the ET reactions in the present systems. The chemical structures of the acceptors and the donors used in this study are given in Fig. 1.

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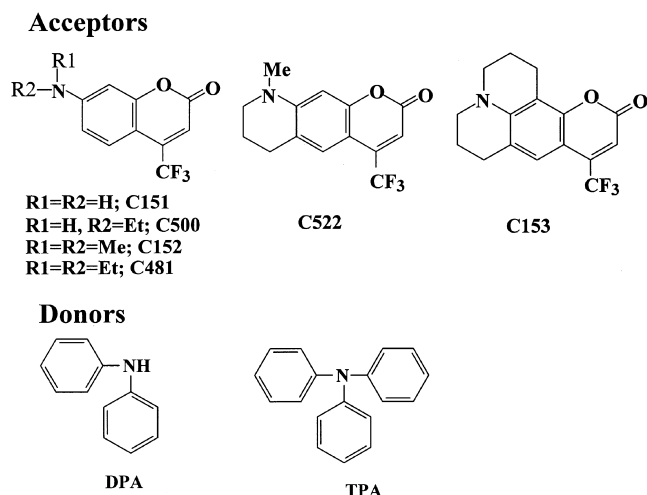


Fig. 1. Chemical structures of the donors (amines) and acceptors (coumarins) used in the present study.

2. Materials and methods

Laser grade coumarin dyes were obtained from Lambda Physik, Kodak or Exciton. Purest grade DPA and TPA were obtained from Qualigens Fine Chemicals, India and Fluka respectively. Acetonitrile was of spectroscopy grade from Spectrochem India and used as received.

Shimadzu UV–VIS spectrometer, model UV-160A, was used for ground state absorption measurements. Hitachi spectrofluorimeter, model F-4010, was used for SS fluorescence measurements. Time resolved fluorescence measurements were carried out using time-domain spectrofluorimeter from Edinburgh Instruments, UK, model 199. The instrument works on the principle of time correlated single photon counting [17]. The details of this instrument is described elsewhere [18]. The fluorescence decay curves were analysed as a monoexponential function (Eq. (1)), with chi-square (χ^2) values close to unity [17].

$$I(t) = B \exp\left(\frac{-t}{\tau}\right) \quad (1)$$

where τ is the fluorescence lifetime and B is the pre-exponential factor.

Transient absorption measurements were carried out using a picosecond laser flash photolysis set up. The details of this instrument is described elsewhere [16,19]. Briefly, the third harmonic output (355 nm, 5 mJ, 35 ps) of an active-passively mode-locked Nd-YAG laser (Continuum, USA, model 501-C-10) was used for the excitation of the samples. The transients were detected as their time-resolved absorption spectra using a white light continuum (~ 400 – 900 nm) produced by focusing the residual fundamental (1064 nm) of the Nd-YAG laser onto a 10 cm long quartz cell containing 50:50 (v/v) H_2O – D_2O mixture as the monitoring light source. The time delay between the pump and probe pulses was varied using a 1 m long delay rail at the probe end.

3. Results and discussion

3.1. Fluorescence quenching studies

SS fluorescence of the coumarin dyes in ACN are efficiently quenched by DPA and TPA. For all the present coumarin–amine systems, there is no change in the shape of the fluorescence spectra, even with the highest concentration of the amines used ($\sim 0.1 \text{ mol dm}^{-3}$). Thus no exciplex formation is indicated. Similarly no change in the long wavelength absorption band of the coumarin dyes were observed even with the highest concentration of the amines, indicating no ground state complex formation. Typical SS fluorescence quenching results are shown in Fig. 2 for C522–DPA system in ACN. Results on the ground state absorption spectra for the same system is also shown in the inset of Fig. 2.

From TR fluorescence measurements it is seen that the fluorescence lifetimes (τ) of the coumarins dyes in ACN are substantially reduced in presence of DPA and TPA. It is seen that both SS and TR quenching follow the Stern–Volmer (SV) linear relationship [20].

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \quad (2)$$

where I_0 and I are the fluorescence intensities in the absence and presence of the quenchers ($Q \equiv$ amines), τ_0 and τ are the fluorescence lifetimes of the coumarins in the absence and the presence of the quenchers and k_q is the bimolecular quenching constant. The k_q values obtained from the slopes of the SV plots obtained from SS and TR measurements are listed in Table 1. It is seen from this table that for a particular coumarin–amine system, the k_q values obtained from SS and TR measurements are the same within the experimental error.

Oxidation potential of the amines $E(\text{D}/\text{D}^+)$ [21] and the reduction potential of the coumarins $E(\text{A}/\text{A}^-)$ [11–15] in ACN are listed in Table 2. Comparing Tables 1 and 2 it is

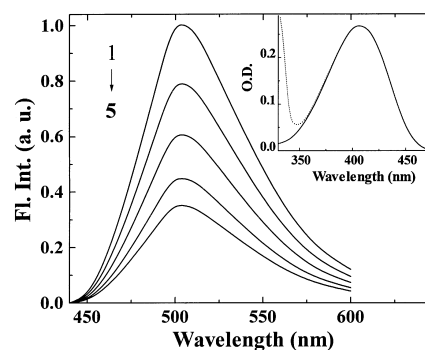


Fig. 2. Steady-state fluorescence quenching of C522 by DPA in ACN. The DPA concentrations are (1) 0.0; (2) 4.76×10^{-3} ; (3) 16.7×10^{-3} ; (4) 28.6×10^{-3} and (5) $39.4 \times 10^{-3} \text{ mol dm}^{-3}$. Inset: Ground state absorption spectra of C522 in ACN in absence (—) and in presence (···) of 0.1 mol dm^{-3} of DPA.

Table 1
Bimolecular quenching constant (k_q) of the coumarin–amine systems in ACN

Donor	Acceptor	τ_0 (ns) ^a	ΔG^0 (eV)	k_q ($10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	
				SS	TR
DPA	C151	5.18	−0.688	12.5	12.2
	C500	5.28	−0.515	11.8	11.5
	C152	1.96	−0.401	11.0	10.5
	C481	0.71	−0.359	10.3	10.0
	C522	5.48	−0.313	9.0	8.5
	C153	5.54	−0.201	5.6	5.7
TPA	C151		−0.604	12.6	13.0
	C500		−0.434	10.4	11.0
	C152		−0.320	10.5	10.7
	C481		−0.282	11.2	11.5
	C522		−0.234	6.9	7.0
	C153		−0.124	2.7	2.8

^a Fluorescence lifetime of the coumarin dyes in ACN solutions in the absence of quenchers.

seen that, the k_q values gradually increase as the $E(A/A^-)$ of the coumarins becomes less negative. Similarly for a coumarin dye the k_q value is more with DPA having less positive $E(D/D^+)$ value than with TPA. These observations indicate that the ET type of interaction between the amines and the excited coumarin dyes is responsible for the observed fluorescence quenching. An alternative singlet–singlet energy transfer mechanism for fluorescence quenching is easily ruled out because the S_1 state energies (E_{00}) of the amines are much higher than those of the coumarins (cf. Table 2). A mechanism involving the hydrogen bonding interaction between the excited coumarins and the ground state amines was also excluded on the basis of the following arguments: (i) If the amino group hydrogen of the amines were to form hydrogen bonds with the coumarins, then TPA should not have given any quenching. (ii) If the amines were acting as the hydrogen bond acceptors, except C151 and C500 all other coumarins should not have shown any quenching interaction.

Table 2
Redox potentials (vs SCE) and E_{00} energies of the acceptors and donors in ACN

Acceptor		Donor			
Compound	E_{00} (eV) ^a	$E(A/A^-)$ (V)	Compound	E_{00} (eV) ^a	$E(D/D^+)$ (V)
C151	2.98	−1.565	DPA	3.86	0.78 ^b
C500	2.85	−1.607	TPA	3.65	0.87
C152	2.76	−1.626			
C481	2.75	−1.660			
C522	2.70	−1.653			
C153	2.62	−1.685			

^a E_{00} energies were estimated from the intersecting wavelengths of the normalised emission and excitation spectra.

^b $E(D/D^+)$ for DPA was considered about 0.14 V more positive compared to the reported value (0.64 V [21]) to obtain better correlation among the DPA and TPA results.

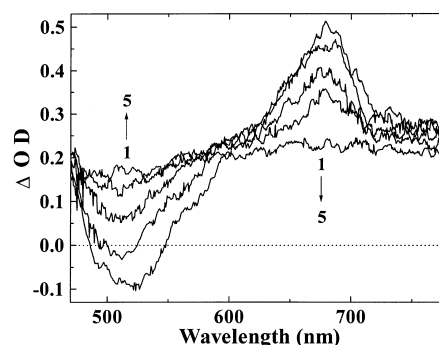


Fig. 3. Picosecond time-resolved transient absorption spectra for the C481–DPA system in ACN. The DPA concentration used was 1 mol dm^{-3} . The time delay between the pump and probe pulses are (1) 0; (2) 33; (3) 132; (4) 198 and (5) 528 ps.

3.2. Picosecond transient absorption studies

To have a direct evidence for the ET interaction in the present systems we carried out the picosecond transient absorption studies using 35 ps, 355 nm laser light excitation. The picosecond transient absorption measurements were carried out for all the coumarin–DPA systems in ACN. Since almost all the coumarin dyes (except C152 and C481) are strongly fluorescent in ACN [22,23], the contributions from the stimulated emissions in the transient absorption spectra are always very large. Thus, to minimise the effect of stimulated emissions in the transient absorption spectra, we had to use about 1 mol dm^{-3} of DPA. For coumarin–TPA systems, transient absorption measurements were not possible due to strong singlet–singlet ($S_1 \rightarrow S_n$) absorption of TPA in the 400–800 nm region with 355 nm laser excitation¹. For DPA, however, no $S_1 \rightarrow S_n$ absorption was observed in the 400–800 nm region by carrying out the blank experiments with 355 nm excitation.

Typical picosecond time-resolved transient absorption spectra as obtained for C481–DPA system in ACN are shown in Fig. 3. Immediately after the excitation pulse, an absorption band appears at around 670 nm region. This absorption band is attributed to that of the DPA cation radical [24,25]. The negative absorption signals observed in the 480–550 nm region at the early time scales are attributed to the stimulated emission, because the fluorescence spectra of C481 appears in this wavelength region. A broad absorption signal above 720 nm is also seen in the transient spectra and is probably due to the coumarin anion radicals². To the best

¹ Carrying out blank experiment with TPA in ACN following 355 nm laser excitation, there was a strong transient absorption band in the 400–800 nm region with absorption peak around 685 nm. Following the time-dependant variation in the absorption signal at 685 nm, the life time of the transient was estimated as 1.9 ns. This is very similar to the singlet state life time of TPA in ACN (1.91 ns) as estimated by time-dependant fluorescence measurement in this work.

² Absorption spectra of the coumarin anion radicals have been obtained in the pulse radiolytic reduction of the dyes in isopropanol–acetone–water mixture and also in pure isopropanol. These results will be published separately.

Table 3

Lifetimes of the ion-pair states (τ_{IP}) and the free energy change for CR reaction for different coumarin–DPA systems in ACN solution

Coumarins	C151	C500	C152	C481	C522	C153
τ_{IP} (ps)	400±50	500±50	430±50	450±50	410±50	450±50
ΔG^0 (CR) (eV)	-2.402	-2.447	-2.465	-2.497	-2.490	-2.522

of our knowledge, the absorption spectra of the coumarin anion radicals are not reported in the literature. The results obtained in the picosecond transient absorption studies for all other coumarin–DPA systems in ACN are qualitatively similar to those observed for C481–DPA system.

As seen from Fig. 3, both the signals for the DPA cation (670 nm), the stimulated emission (480–550 nm) and the broad absorption signal beyond 720 nm gradually reduces as the delay between the pump and probe pulses is increased. Similar observations are also made for the other coumarin–DPA systems. Assuming that the transient absorption signals at the 670 nm region is due to the DPA cation radical in the ion-pair states ($A^- \cdots D^+$) produced by ET from amines (D) to coumarins (A), the lifetime of the ion-pair states (τ_{IP}) were estimated following the decay of 670 nm absorption signals. The τ_{IP} values thus obtained for different coumarin–DPA systems in ACN are listed in Table 3 and are seen to be of the similar time scale, cf. about 400–500 ps. The results in the picosecond transient absorption measurements for the coumarin–DPA systems provide a direct evidence for the ET reaction between the excited coumarin dyes and the ground state of the DPA molecules. Though for the coumarin–TPA systems the picosecond transient absorption measurements could not be carried out, drawing an analogy with the coumarin–DPA systems, it is inferred that in the former systems also the ET is the mechanism responsible for the fluorescence quenching of the coumarin dyes.

3.3. Correlations of the quenching constants with Marcus ET theory

Feasibility of PET from a ground state donor (D=amines) to an excited state acceptor (A=coumarins) is dictated by the standard free energy change, ΔG^0 , of the ET reaction. The ΔG^0 for a PET reaction in a polar solvent like ACN can be expressed as

$$\Delta G^0 = E(D/D^+) - E(A/A^-) - E_{00} - \frac{e^2}{\epsilon r} \quad (3)$$

where e is the charge of an electron, ϵ is the dielectric constant of the solvent and r is the separation between the donor and acceptor at the encounter [7]. Since an exact estimation of r is not possible, we assumed it to be equal to the sum of the radii of the donors and acceptors. The sizes of the donors and acceptors were estimated using Edward's volume addition method [26], assuming the molecules are the effective spheres. The ΔG^0 values thus estimated for different coumarin–amine pairs are listed in Table 1.

Electron transfer under a diffusive condition, as in the present case, can be presented by Scheme 1 [1–7], where the excited acceptor (A^*) and the ground state donor (D) first diffuse together to form an encounter complex ($A^* \cdots D$). Reorganisations in the encounter complex causes the reactants to cross the transition state (TS) for ET, to produce the ion-pair state ($A^- \cdots D^+$). The parameters, k_d and k_{-d} are the diffusion controlled rate constants for formation and dissociation of ($A^* \cdots D$), k_{et} and k_{-et} are the forward and reverse ET rate constants and k_p is the sum of all the rate constants causing the disappearance of the ($A^- \cdots D^+$) state. The important process included in k_p would be the charge recombination (k_{CR}) in the ion-pair state to produce back the ground states of the acceptor and donor (A+D). In polar solvents like ACN the ion dissociation (k_{ID}) to give the solvent separated ions ($A^- + D^+$) may also contribute to some extent in the overall k_p .

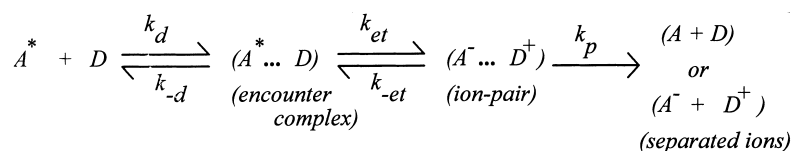
From energetic considerations, the reverse ET (k_{-et}) is usually an unlikely process [1–7]. Thus it can be assumed that $k_p \gg k_{-et}$. Based on this assumption and applying the SS conditions in Scheme 1, one can derive [1–7] the expression for k_q as

$$k_q = \frac{k_d}{1 + (k_d/Kk_{et})} \quad (4)$$

where $K (=k_d/k_{-d})$ is the diffusional equilibrium constant for the encounter complex formation and can be expressed as [27,28]

$$K = \frac{4\pi N r_{DA}^2 \delta r}{1000} \exp\left(-\frac{w_c}{RT}\right) \quad (5)$$

In Eq. (5), N is Avogadro's number, r_{DA} is the separation between donor and acceptor in the encounter complex, r_{DA} and $(r_{DA} + \delta r)$ are the centre to centre distances over which the ET can take place and w_c is work required to bring the donor and acceptor to the encounter distance. For neutral molecules diffusing freely in solution w_c is assumed to be zero. In general a value of about 2 Å is considered for δr



Scheme 1.

in the ET reactions [27,28]. Thus following Eq. (5), an approximate estimate for K is made to be about $1 \text{ mol}^{-1} \text{ dm}^3$ for two neutral reactants diffusing freely in solution.

The activation controlled ET rate constant (k_{et}) can be expressed in its simplified form as

$$k_{\text{et}} = \nu \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (6)$$

where ν is the frequency factor and ΔG^* is the free energy of activation for the ET process. The value of ν can range from 10^{12} to 10^{14} s^{-1} depending on the systems [29,30]. While a variety of forms have been proposed for ΔG^* , the quadratic relation (Eq. (7)) derived by Marcus [1–10] have extensively been used for a variety of ET reactions.

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \quad (7)$$

where ΔG^0 is the free energy change for the ET reaction and λ is the total reorganisation energy, given as

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{s}} \quad (8)$$

where λ_{in} is the contribution arising due to the intramolecular bond length and bond angle changes in the donor and acceptor during ET and the λ_{s} is the contribution arising due to the solvent reorganisation. From the consideration of the non-equilibrium polarisation of the medium and employing the dielectric continuum model for the solvent, Marcus derived [1–6] the following expression for λ_{s} .

$$\lambda_{\text{s}} = (e^2) \left\{ \frac{1}{2r_{\text{D}}} + \frac{1}{2r_{\text{A}}} - \frac{1}{2r_{\text{DA}}} \right\} \left\{ \frac{1}{n^2} - \frac{1}{\epsilon} \right\} \quad (9)$$

where r_{D} and r_{A} are the radius of the donor and acceptor, respectively, r_{DA} is the separation between the donor and acceptor in the encounter complex, n is the refractive index and ϵ is the dielectric constant of the solvent. Average values of r_{D} ($=3.05 \text{ \AA}$) and r_{A} ($=3.68 \text{ \AA}$) were estimated using the sizes of the donors and acceptors as obtained using Edward's volume addition method [26]. Similarly r_{DA} ($=6.73 \text{ \AA}$) is considered to be equal to the sum of the average r_{D} and r_{A} values. We used the average values of r_{D} , r_{A} and r_{DA} for the calculation of λ_{s} , because, a small difference in the radii of the donors and acceptors do not make any significant variations in the estimated λ_{s} values. The λ_{s} for the present systems was thus estimated to be about 1.1 eV using Eq. (9).

Using Eqs. (4), (6) and (7), the bimolecular quenching constants (k_{q}) were calculated for different ΔG^0 values. The equilibrium constant K for the encounter complex formation was assumed to be $1 \text{ mol}^{-1} \text{ dm}^3$ for the present systems. Different combinations of k_{d} , ν and λ values were tried to get a good correlation between the calculated and the experimental k_{q} values. The best correlation thus obtained with $k_{\text{d}}=1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\nu=5 \times 10^{12} \text{ s}^{-1}$ and $\lambda=1.0 \text{ eV}$, as shown in Fig. 4, where the circles are the experimental points and the continuous curve is the calculated k_{q} values for different ΔG^0 . From Fig. 4 it is indicated that the k_{q}

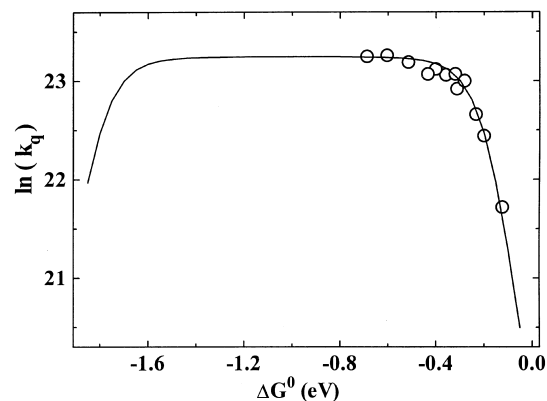


Fig. 4. Plot of $\ln(k_{\text{q}})$ vs. ΔG^0 for the different coumarin-amine systems in ACN. Experimental points are represented by circles and the calculated k_{q} values using Marcus ET theory are presented by the continuous curve.

value initially increases steeply as ΔG^0 gradually becomes more negative and then ultimately it levels off at the diffusion controlled limit at highly negative ΔG^0 values. Thus, it is indicated that all the coumarin-amine systems investigated in the present work seems to fall in the normal Marcus region. Further, the nature of correlation we observe in Fig. 4 indicates that the present systems under diffusive conditions behave exactly in the similar way as are generally seen in most of the ET reactions under similar condition [7,16,29–35].

An interesting point to be noted here is that the λ value of 1.0 eV, as obtained from the correlation in Fig. 4, is quite similar to the λ_{s} value calculated using Eq. (9). Since the estimations of r_{D} , r_{A} and r_{DA} are quite approximate, such an agreement between the two values is quite satisfactory. Present results thus indicate that the solvent contribution is the only reorganisation required for the ET under the diffusive conditions. The contribution from the intramolecular reorganisation seems to be very negligible.

3.4. Comparison of ET rates under diffusive and non-diffusive conditions

In our earlier studies in the femtosecond PET reactions in neat anilines [11–15], where the diffusion of the reactants are not required, it was observed that the ET occurs much faster than the solvent reorganisation rates. Such results could not be explained using conventional ET theories [1–6]. On the contrary, under diffusive conditions, as the present results indicate, the observed rates are well correlated using Marcus outer sphere ET theory [1–6]. Present systems under diffusive condition thus seems to behave very normally, similar to the observation made by many authors under similar experimental conditions [7,16,29–35].

In the conventional ET theories, the solvent and the intramolecular modes are considered in a coupled manner and thus the reaction is viewed simply as a one-dimensional mechanistic model. Since such a simplified model cannot

explain the results for the coumarins in neat anilines (non-diffusive conditions) [11–15], one had to consider a two-dimensional ET (2DET) model [36], where the intramolecular and the solvent modes are assumed to participate in a non-coupled manner. In this 2DET model, the reorganisations along the intramolecular modes can occur much faster than the solvent modes causing the ET to occur faster than the solvation process. Comparing the results in neat anilines [11–15], with the present results under diffusive conditions, it is evident that there must be a fundamental difference in the ET mechanism under the two experimental conditions.

When a ground state donor and an excited state acceptor diffuse towards each other in a solution, each of the reactants are expected to move with their respective solvation shells (cf. D_{sol} and A_{sol}^*). It is thus expected that the encounter complex will be formed with a layer of solvent between the donor and the acceptor ($D/S/A^*$). Similarly the ion-pair state produced following ET must also have a solvent layer between the two ions ($D^+/S/A^-$), i.e. the solvent separated ion-pair (SSIP) [20,37]. Under non-diffusive conditions, as in the case of coumarins in neat anilines, the donor and acceptor must be in physical contact (D/A) prior to the photoexcitation. Thus, the encounter complex (D/A^*) under this condition is structurally different than in the diffusive condition. The ion-pair state produced following ET in a non-diffusive condition (D^+/A^-) is thus the contact ion-pair (CIP) rather than the SSIP [20,37]. Scheme 2 shows the conceptual presentation of these two situations.

Intervention of solvents between D and A^* in the encounter complex under the diffusive conditions, makes the ET reactions highly sensible to the solvent reorganisations but less sensible to the intramolecular reorganisations. Under non-diffusive conditions, the situation becomes just opposite and the ET reactions are mostly controlled by the intramolecular reorganisations of the reactants. Further from Scheme 2, it is expected that under diffusive condition, the mixing of the reactant state ($D/S/A^*$) with the product state ($D^+/S/A^-$) will be much weaker than that between (D/A^*) and (D^+/A^-) states under non-diffusive conditions. The net result will thus be slower ET dynamics in the former than in the latter conditions. Though for the coumarin–DPA/TPA systems this point could not be verified due to the lack of ET data under non-diffusive conditions, for coumarin–*N*-alkylaniline

systems, this have been shown to be so in our earlier communication [16].

Recently Iwai et al. [38] have also observed some similar results in the fluorescence quenching dynamics of cyanoanthracenes by *N,N*-dimethyl aniline (DMAN) in solutions. It has been shown that in the lower concentration range of the quenchers ($<0.15 \text{ mol dm}^{-3}$), where the diffusion of the reactants is a prerequisite for the reaction to take place, the quenching dynamics are nicely explained using the conventional Marcus ET theory. At higher amine concentrations, where the static quenching (non-diffusive condition) is expected to contribute to a good extent, the fluorescence decays are always seen to have an ultrafast component. As Iwai et al. [38] observed, this ultrafast component of the ET dynamics cannot be accounted on the basis of the conventional Marcus ET theory and thus requires a separate mechanistic model. These authors assumed the involvement of a charge transfer (CT) interaction between the cyanoanthracenes and the amine to explain the ultrafast component in the quenching dynamics [38]. For the coumarins in neat anilines [11–15], however, no indications for such CT interactions were observed, though the quenching dynamics showed the ultrafast nature of the ET processes, which could not be explained using conventional Marcus ET theory. Since in the present study we used a reasonably lower concentration range of the quenchers ($<0.1 \text{ mol dm}^{-3}$), the diffusion of the reactants are the prerequisite for the ET to take place and under this condition the Marcus ET theory is seen to correlate the experimental results quite successfully.

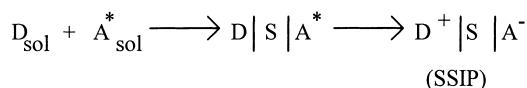
3.5. Charge recombination rates in the ion-pair states of the coumarin–DPA systems

At this point it is interesting to consider the lifetime of the ion-pair states (τ_{IP}) for the coumarin–DPA systems as estimated from the picosecond transient absorption measurements. From Table 3 it is indicated that the τ_{IP} values for all the coumarin–DPA systems are almost in the same range. Considering the charge recombination (CR) as the major decay channel for the ion-pair state, the similarities in the τ_{IP} values for all the coumarin–DPA systems can qualitatively be accounted from the following consideration. The free energy change for the CR process [$\Delta G^0(\text{CR})$] in the ion-pair state can be estimated [1–7] following Eq. (10).

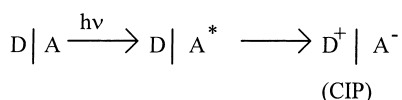
$$\Delta G^0(\text{CR}) = E(A/A^-) - E(D/D^+) - \frac{e^2}{\epsilon r} \quad (10)$$

Thus, for the different coumarin–DPA systems the $\Delta G^0(\text{CR})$ calculated are listed in Table 3. It is seen that the $\Delta G^0(\text{CR})$ for all the coumarin–DPA systems are almost in the similar range, i.e. within -2.402 to -2.522 eV . The small differences in the $\Delta G^0(\text{CR})$ values for the different coumarin–DPA systems (cf. Table 3) hardly make any differences in the CR rates, which can be expressed as [1–6]

Diffusive condition:



Non-diffusive condition:



Scheme 2.

$$k(\text{CR}) = \nu \exp \left[\frac{-[\Delta G^0(\text{CR}) + \lambda]^2}{4\lambda RT} \right] \quad (11)$$

Further, with the time resolution of our picosecond set up (~ 50 ps), it is difficult to differentiate the small changes in the CR rates. Thus, the τ_{IP} values estimated in the present picosecond transient absorption measurements appear to be in the same range of 400–500 ps.

4. Conclusions

Fluorescence of the 4-CF₃-coumarins having differently substituted seven amino groups are quenched by DPA and TPA in acetonitrile solutions. The quenching mechanism have been attributed to ET from the ground state amines to S₁ coumarin dyes. The k_{q} as estimated from fluorescence quenching measurements are well correlated with ΔG^0 within the framework of Marcus ET theory. The solvent reorganisation appears to play the main role in governing the ET dynamics under the diffusive conditions. The contribution from the intramolecular reorganisation appears to be negligible under the present experimental conditions, though under non-diffusive conditions the intramolecular reorganisation is reported [11–15] to play the dominant role to make the ET process to occur faster than the solvation dynamics. Direct evidence for ET reactions in the present systems have been obtained using picosecond transient absorption studies. The ion-pair states produced following ET reactions in acetonitrile are quite short lived and having lifetimes in the same range of 400–500 ps. The similarities in the lifetimes of the ion-pair states for different coumarin–amine systems have been attributed to the similarities in the free energy changes for the charge recombination reactions, $\Delta G^0(\text{CR})$.

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