Picosecond dynamics of twisted internal charge transfer phenomena. The role of the solvent

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To probe the role of the solvent in intramolecular charge transfer processes, and in particular, the origin of the well-known dual fluorescence phenomena of p-dimethylamino benzonitrile (DMABM), picosecond laser studies in mixed polar/nonpolar solutions were undertaken. The anomalous long wavelength emission is attributed to a complex formed between excited DMABN and butanol with a rate constant of $(9.7 \pm 1.5) \times 10^8$ $M^{-1} s^{-1}$. The dominant stabilization of the twisted intramolecular charge transfer state is therefore concluded to be due to a short range specific interaction with a polar solvent molecule. A secondary solvent effect arises from a further stabilization of the complex by long range polarization interactions with solvent molecules. Evidence on the existence of ground state complexes between DMABN and butanol are also presented. Excitation of these ground state complexes leads to the rapid formation of the excited state complexes in 30 ps, which we have interpreted to be the time required for the complex to relax intramolecularly, presumably a rotational motion along the C–N bond of DMABN, to achieve the final twisted charge transfer geometry.

I. INTRODUCTION

The differences between gas phase and solution phase chemistry are largely determined by the nature of the solute–solvent interactions. In the weak interaction limit, simple collisions between solutes and solvent molecules can alter the reaction dynamics. For example, the photodissociation of iodine molecule[1,2] in the gas phase is much more efficient than in the liquid phase. This is because the recombination of photodissociated iodine atoms is greatly enhanced in the liquid phase by interacting with solvent molecules which interfere with the escape of the fragments (usually referred to as the "cage effect"[3]). When the solute and solvent molecules are charged or polar species, the strong solute–solvent interaction between them can not only affect the reaction rates but also change the reaction pathways, therefore the overall chemistry. The intermolecular excited-state charge-transfer processes between anthracene and N,N-dimethylaniline (DMA) serves as a good example.[4] In the absence of strong solute–solvent interactions (e.g., in the nonpolar solvents) the dominant energy relaxation channel for excited anthracene is the formation of exciplex with DMA. However, in the presence of strong polar solvents such as acetonitrile, a new energy relaxation channel, direct electron transfer to form an ion-radical pair, becomes dominant. In this case, the long-range polarization interaction between solvent molecules (acetonitrile) and ion-radical pairs strongly stabilizes the latter and makes the e^- transfer step energetically favorable.[4(a)] When the solute–solvent interaction becomes sufficiently strong, the local specific interaction can occur and lead directly to the complex formation, i.e., the solute and solvent molecules essentially "react" with each other.[37–39] In this paper, we will demonstrate the dominant effect of this strong solute–solvent interaction on the intramolecular charge transfer process in a photoexcited p-dimethylamino benzonitrile (DMABN) molecule, which we will show is the origin of the well-known dual fluorescence phenomenon.[17,26]

The dual fluorescences phenomena of DMABN and related molecules is a subject that has received intensive studies in the past.[5–27] In nonpolar solvents, excitation of the DMABN molecule results in a single fluorescence band centered around 340 nm. However, in polar solvents a new, Stokes-shifted fluorescence appears, which is associated with a large dipole moment of ~ 16 D.[17] To explain the origin of this new emission band, a number of mechanisms have been proposed.[5–19] These include the initial proposal of solvent induced level reversal of S_2 and S_1 by Lippert et al.,[5] the excimer formation by McGlynn et al.,[6–8] the excited state proton transfer by Kosower et al.,[9,10] the complex formation with solvent by Chandross et al.,[11,39] and the twisted internal charge transfer (TICT) by Grabowski et al.[12–17] The results accumulated over the past several years indicate that both the bond twisting (between the amino group and the benzene ring) and solvation play important roles in causing the charge redistribution.[17–19,26]
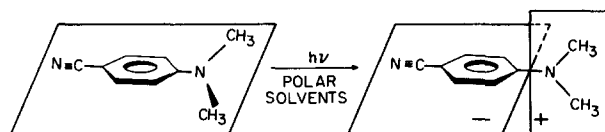
In spite of the numerous studies on the subject, the relationship between the two fluorescence bands was, surprisingly, not fully understood until recently. By using picosecond fluorescence spectroscopy we[26] have directly demonstrated the parent-daughter relationship between the short wavelength emission band and the long wavelength emission band. We have shown that the two emitting species reach equilibrium very rapidly (~ 20 ps) with an equilibrium constant ≥ 30 in propanol solution.[26] The interconversion rate between the two species depends on the viscosity of the solvent, as will be discussed at a later point in this paper. The picosecond kinetic measurements in demonstrating both a viscosity dependence and the presence of two distinct species therefore supports the hypothesis of the TICT mechanism.[12–19]

This mechanism suggests that the intramolecular charge transfer of DMABN molecule is induced by rotation around the C–N bond between the amino group and the benzene ring. The short wavelength emitting species, identified with the planar form of DMABN, and the long wavelength emitting species, the perpendicular form, are in equilibrium. Although the TICT mechanism is currently the favored model and supported by many experimental data and theoretical calculations,[12-19] it does not provide insight into the exact role of solvent molecules in the intramolecular charge transfer process. Energetically, we know solvation must be important based on the facts that the dual fluorescence phenomenon was not observed in the hydrocarbon solvents, and furthermore in polar solvents the CT emission maximum Stokes shifts as the solvent polarity increases. The key issues that have to be answered are: (1) By what mechanism do the solvent molecules stabilize the intramolecular charge transfer process? Is it mainly the long range polarization interaction or is it the local solute–solvent interaction. (2) If the local interaction is the dominant mechanism, then it is important to describe the local configuration, i.e., the required number of solvent molecules, and the functional form of the interaction potential. For example, in the case of electron solvation it was found that several alcohol molecules are required to form a solvated electron[28,29] and the local interaction can be approximately represented by a square well potential.[30,31]

To address these questions, we used "dipole dilution" to probe and control the local environment around a solute molecule. In this method, the number density of the solvent dipoles surrounding the solute molecules is reduced successively by diluting with nonpolar molecules, the effects of this dilution on the yield and formation dynamics of the intramolecular CT complex are then studied. Previously, Chandross et al.[11] studied the steady-state fluorescence spectra of DMABN in mixed methylcyclohexane/propionitrile solutions and suggested that specific interaction between DMABN and polar solvent molecules could lead to the formation of $1:n$ stochiometric complex, which is responsible for the long wavelength emission. No quantitative information was available in that study. We have carried out a detailed study on the picosecond dynamics of photoexcited DMABN molecule in mixed butanol/hexadecane solutions. Our results reported here present a coherent picture on the TICT phenomenon and support the earlier suggestion made by Chandross et al.

II. EXPERIMENTAL

A mode-locked Nd^{+3}-phosphate glass oscillator generated a pulse train from which a single TEM_{00}, 4–8 ps pulse was extracted and amplified to an energy of ~15 mJ. The amplified 1054 nm pulse was then frequency doubled to 527 nm and frequency quadrupled to 264 nm. In this work, this 264 nm pulse was used to excite the DMABN molecule. The observed pulse broadening at 264 nm compared with that at 527 nm has been included in the signal convolution procedure.

The fluorescence signal from the sample was collected

and focused into an Imacon streak camera which was coupled to an OMA and interfaced to a Digital MinC computer. FWHM of the resolution function of the streak camera-OMA system was five channels which corresponds to about 5 ps on the fastest time scale. The streak speed was calibrated with an etalon. Linearity of the intensity response was checked in every experiment and the curvature introduced by the streak camera-OMA response function was corrected for each shot. The wavelength of the fluorescence signal was selected by a combination of interference and cutoff filters.

The p-(dimethylamino)benzonitrile compound was purchased from Aldrich and was purified by vacuum sublimation twice. The purity was checked by NMR, absorption, and fluorescence spectra. We observed no absorption in the 330–360 nm region where an impurity had been previously observed.[25] n-Butanol was from Aldrich (99 + %, gold label) and was purified by fractional distillation, then dried with Linde type 4A molecular sieve. Hexadecane (Aldrich, 99%) was dried with Linde Type 4A molecular sieve. All chemicals were stored in the dark, in a refrigerator, and over P_2O_5. The sample solutions were deoxygenated by repetitive freeze-pump-and-thaw cycles before use. All the experiments were done at $20 \pm 1\,°C$.

III. RESULTS AND DISCUSSION

A. In pure alcohol solutions

The DMABN/alcohol solutions (2.5×10^{-4} M) were excited with a single 264 nm ps laser pulse. The "normal" short wavelength emission and the stokes shifted CT emission were then monitored at 350 and 470 nm, respectively, by a streak camera. In both propanol and butanol solutions, the short wavelength fluorescence decay can be clearly resolved into two exponential components. The fast component decays with a lifetime of 19 ± 3 ps in propanol solution and 30 ± 5 ps in butanol solution, which are equal to the risetimes of the CT fluorescence in the corresponding solutions. The slow decay component at 350 nm has the same lifetime as the decay of the CT emission, being 2.3 ± 0.2 ns in propanol solution and 2.2 ± 0.2 ns in butanol solution. The results in butanol solution are shown in Fig. 1.

These data clearly demonstrate that in pure alcohol solutions an equilibrium between the two emitting species is rapidly established after excitation. This equilibrium can be described by

$$S^* \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CT^* \qquad (1)$$
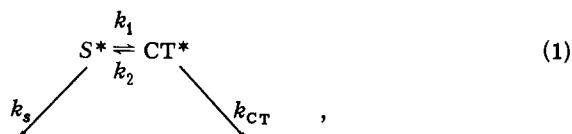
where S^* and CT^* represent the states responsible for the short wavelength and long wavelength emissions, respectively, k_s and k_{CT} represent the radiative and nonradiative decay rates for S^* and CT^*, respectively, exclusive of the interconversion rates. As shown in Fig. 1, an excellent fit was obtained between the experimental data and the theoretical curves calculated from the coupled differential equations based on the above
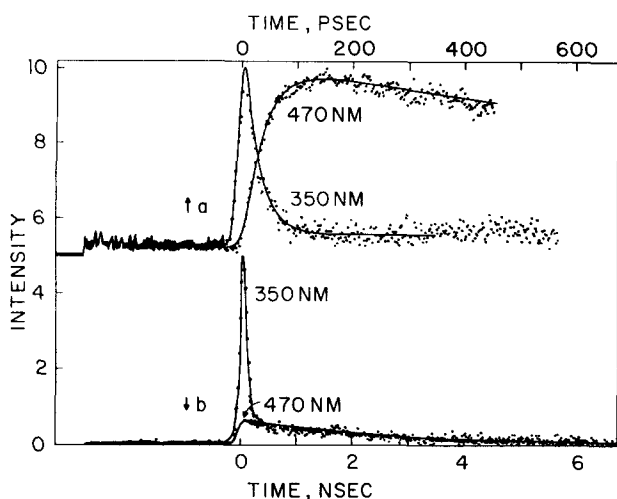
FIG. 1. Fluorescence decay curve monitored at 350 nm and rise curve monitored at 470 nm of 2.5×10^{-4} M DMABN/butanol solution excited at 264 nm. Arrows indicate the associated time scales. (a) On the fast streak speed 0.06 ns/mm; (b) on the slow streak speed 0.6 ns/mm.

equilibrium relationship. Although the dual fluorescence phenomenon of DMABN molecule has been extensively studied for years, this is the first direct experimental evidence that clearly demonstrates the equilibrium relationship of the two bands. This confirms the assumption explicitly made in the previous oxygen quenching works.[16,17] Based on our data, the equilibrium constant can be estimated to be ≥ 30 for propanol solution[26] and ≥ 25 for butanol solution. The forward reaction rates, about 19 ps for propanol and 30 ps for butanol, are interpreted to be a measure of the conformational relaxation times required for the solute molecule and solvent to achieve the nonplanar charge transfer geometry. The viscosity dependence of the transformation rate, which decreases as the solvent viscosity increases, is consistent with the interpretation that molecular motions (bond twisting and solvent reorganization) are involved.

B. In mixed butanol/hexadecane solutions

To study the role of solvent molecules in the intramolecular CT process of excited DMABN molecule and hopefully to gain a better understanding of the coupling between the twisting motion and solvent relaxation, the dynamics of the CT transfer process in mixed solvents were investigated. The basic idea is to control the local number density of the polar solvent molecules without greatly altering the viscosity of the solution. The effect of the change in local dipole density on the dynamics and yield of the CT process could then yield information on the role of the polar solvent molecules. A convenient way to adjust the local dipole density is by diluting the polar solvent molecules with nonpolar molecules. We have chosen to study the mixed solvent system butanol/hexadecane because of their similar viscosities 3.0 and 3.3 cp at 20 °C, respectively.

1. Picosecond dynamics

The evolution of the photoexcited DMABN molecule from the initial planar structure to the final perpendicu-

lar structure was followed by monitoring both the singlet fluorescence decay at 350 nm and the CT fluorescence rise at 470 nm as the butanol solution is successively diluted by the nonpolar hexadecane molecules. In Fig. 2, the fluorescence rise curves of the CT state at several butanol concentrations are shown. In pure butanol solution, the rise curve can be fitted by a single exponential with formation time of 30 ps. When the solution is diluted by hexadecane, two components appear in the rise curves. The magnitude of the fast component decreases as the butanol concentration decreases; but its rise time 30 ps, stays the same within the experimental uncertainty. On the other hand, the rate of the slow formation component increases *linearly* with the butanol concentration. Since the excited DMABN concentration is much less than the butanol concentration, the observed reaction can be treated as a pseudo-first-order process. The plot of this pseudo-first-order constant vs butanol concentration yields a straight line (Fig. 3). The pseudo-first-order rate constant, being equal to the product of the bimolecular rate constant and the butanol concentration, the slope of the line $(9.7 \pm 1.5 \times 10^8$ M^{-1} s$^{-1})$ yields the bimolecular rate constant for the reaction of excited DMABN with butanol. It should be noted that this rate constant is smaller than that for a diffusion controlled reaction and thus its value gives the intrinsic rate constant between the reacting moieties.

The decay kinetics of the "normal" blue emission at 350 nm has also been analyzed. Several examples of the decay curves at different butanol concentrations are shown in Fig. 4. Two decay components can be clearly resolved. The fast component has a decay time of 30 ps, independent of the butanol concentrations, and its magnitude decreases as the butanol concentration is diluted. The slow component decays with the same rate as the rise of the slow component monitored at 470 nm, and the rate increases linearly with the butanol concentrations. We therefore see that results obtained from
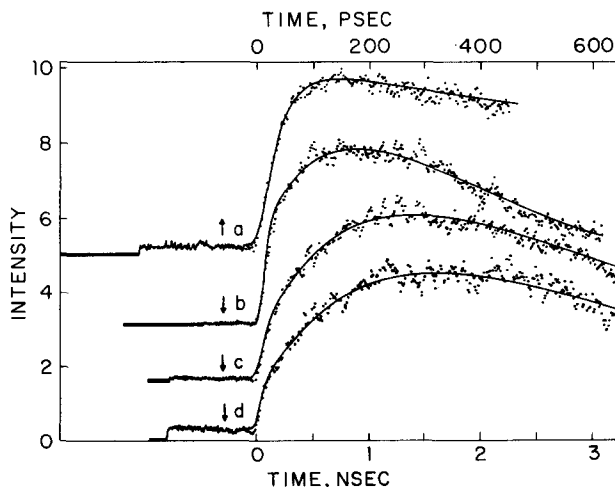

FIG. 2. Fluorescence rise curves monitored at 470 nm of 2.5×10^{-4} M DMABN in mixed butanol/hexadecane solutions excited at 264 nm. Arrows indicate the associated timescales. (a) pure butanol; (b) [butanol] = 1.82 M; (c) [butanol] = 0.81 M; (d) [butanol] = 0.42 M.
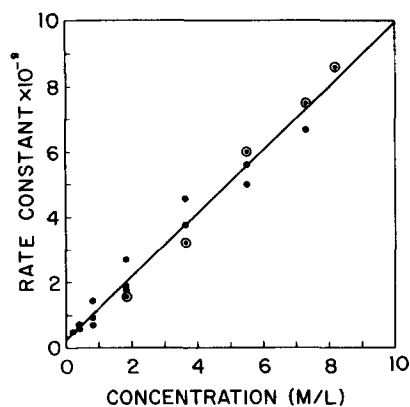
FIG. 3. The plot of the first order rate constant of the slow component as a function of the butanol concentration. Solid circles, •, are from the rise curves. Open circles, ⊚, are from the decay curves.

FIG. 5. The ratio of the concentration of the ground state complexes to the total concentration of free DMABN and complexes plotted against the butanol concentration. Solid curves are calculated from Eq. (4) with $K1 = 0.3$ and $K2 = 0.1$.

the decay kinetics at 350 nm are the same as the formation kinetics obtained at 470 nm.

In Fig. 5, we have plotted the ratio of the population of the DMABN* molecule that leads to the fast formation of the CT state to that of the total DMABN* molecules. It is evident that the ratio increases with the butanol concentration nonlinearly. The quantitative analysis of this data will be discussed later in this paper.

It is appropriate at this point to mention several important experimental considerations. Control experiments were done where the fluorescence signals were monitored through a polarizer set at 54°, with respect to the polarization of the excitation pulse, in order to assure that fluorescence depolarization has no significant effect on the data. In the data analysis, transient effects at early time, i.e., nonexponential contributions,[1,32] were also considered in the calculation and found to be unimportant within our experimental precision. The absence of transient effects is expected for
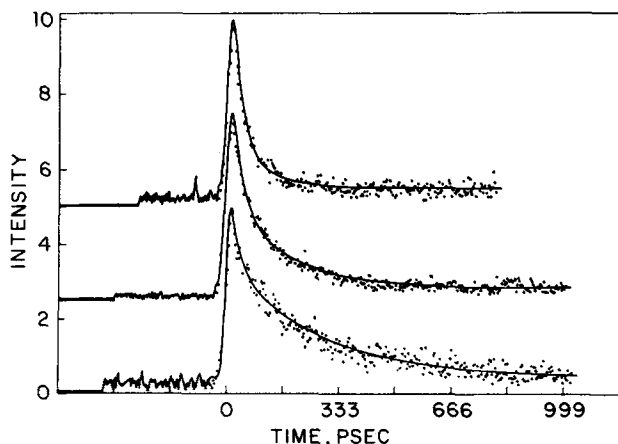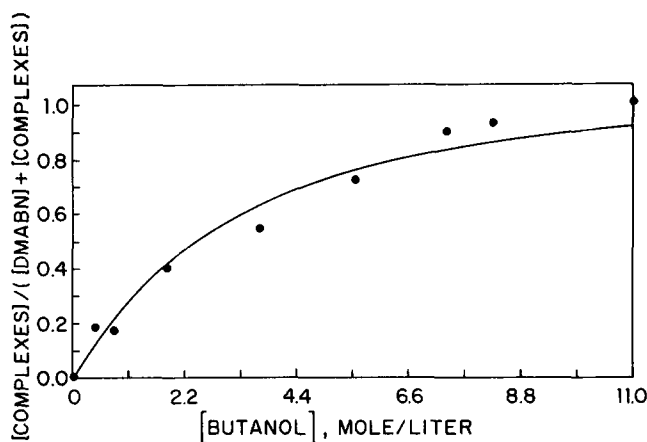

FIG. 4. Fluorescence decay curves monitored at 350 nm of 2.5×10^{-4} M DMABN in mixed butanol/hexadecane solutions excited at 264 nm. Arrows indicate the associated timescales. (a) [butanol] = 8.2 M; (b) [butanol] = 5.5 M; (c) [butanol] = 3.6 M.

systems in which the reaction rate between the reacting moieties is slow compared with their relative diffusive motions as is the case for the system described in this paper. Theoretical curves shown in Figs. 2 and 4 were therefore, calculated without consideration of transient effects.

To interpret these interesting results, we focus on three key observations, namely, (1) the appearance of a fast and a slow kinetic process upon the dilution of butanol solutions, (2) the dynamics of the fast process is independent of the dilution while the rate of the slow process shows a linear dependence on the butanol concentration, and (3) the relative importance of the two processes is affected by the dilution, the fast process dominates at high butanol concentration.

The origin of the fast process (i.e., the 30 ps rise observed for all butanol concentrations), we believe, is due to the excitation of the complexes already formed in the ground state between DMABN and butanol molecules. This 30 ps rise is faster and larger than can be accounted for by a diffusion controlled process for the lower butanol concentrations. The formation of the ground state complexes is really not surprising in light of the large dipole moment 7 D of the ground state DMABN molecule.[17] According to our interpretation, the measured 30 ps risetime for the fast process is then mainly due to the intramolecular bond twisting motion along the C–N bond of the excited DMABN-butanol complex. This intramolecular twisting motion can be impeded by the frictional force of the solvent molecules, thus accounting for the observed viscosity dependence.

As the rapid rise component (30 ps) reflects the population of ground state complexes, the slow component of the rise reflects those excited DMABN molecules which either do not have neighboring butanol molecules or do not have the proper arrangement of butanol molecules for reaction to occur. Even at the higher alcohol concentrations, for which there are several alcohol molecules, on the average, surrounding a ground state DMABN molecule, a slow component is observed. It is

not until the appropriate configuration is achieved, as given by the slower time component, that the rapid 30 ps reaction can occur. The key feature in the stabilization of the twisted intramolecular charge transfer structure appears to be the prior formation of a complex between excited DMABN and some butanol molecule or molecules.

With regard to the observed linear dependence of the slower kinetic component on butanol concentration, we note that this result does not necessarily imply that the reaction of DMABN* is with one butanol molecule or for that matter, with any particular butanol oligomer, albeit dimer, trimer, etc. The linearity of the reaction rate is obtained by plotting the total butanol concentration as given in Fig. 3, without consideration of the aggregation of the alcohol, which we do not know in any case. For the aforementioned description of the reaction of DMABN* with one butanol moiety to be correct, would require the concentration of the reacting butanol moiety (monomer, dimer, etc.) to scale linearly with the total butanol concentration over a considerable concentration range. This linear scaling is not known to be the case, nor anticipated, at high alcohol concentrations. A description that is compatible with the observed linearity is one in which the reaction of the excited DMABN molecule with butanol, producing a complex is insensitive to whether the butanol molecule is a monomer or part of some molecular aggregate (dimer, etc.). The details of the ground state complex, i.e., whether it is a 1:1 or 1:n complex, does not seem to be crucial to the dynamics of TICT formation. Support for this is obtained by noting that the same 30 ps risetime is found for all of the butanol solutions, 0.19 M– 11 M (neat butanol), despite our expectation that the relative populations of butanol monomer, dimers, etc., would change significantly over this wide concentration range.

Our proposed mechanism can be briefly summarized in the figure shown below, noting that the single butanol entity shown in the figure can be monomeric or part of some higher aggregate.
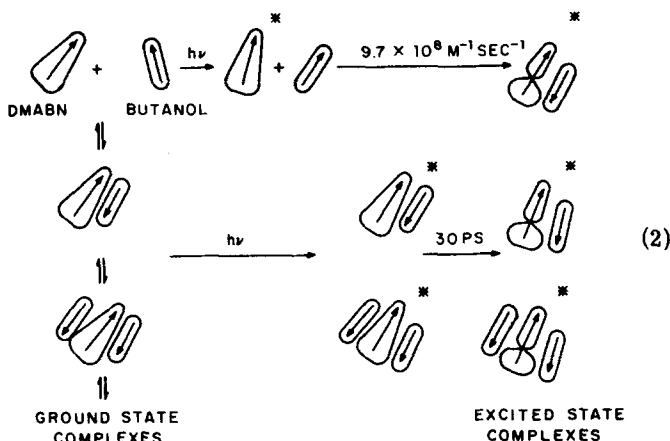
Since the magnitude of the fast component is a measure of all the ground state complexes and the slow component reflects the amount of the free DMABN molecule, their relative ratio as a function of butanol concentration (as shown in Fig. 5) should provide us quantitative
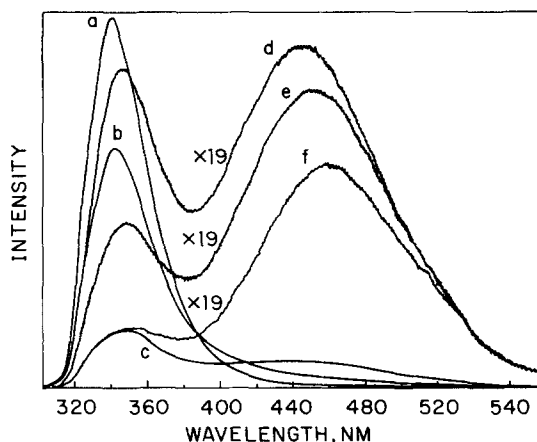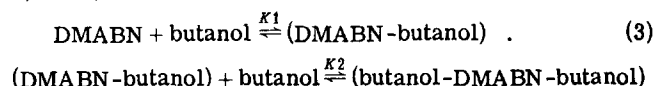

FIG. 6. Uncorrected fluorescence spectra of 2.5×10^{-4} M DMABN in mixed butanol/hexadecane solutions excited at 264 nm. (a) pure hexadecane; (b) [butanol] = 0.39 M; (c) [butanol] = 1.65 M; (d) [butanol] = 3.43 M; (e) [butanol] = 5.46 M; (f) pure butanol.

information on the ground state equilibrium. As the first approximation, let us assume that the ground state equilibrium mainly involves 1:n complexes for n up to 2, i.e.,

$$\text{DMABN} + \text{butanol} \overset{K1}{\rightleftharpoons} (\text{DMABN-butanol}) . \qquad (3)$$

$$(\text{DMABN-butanol}) + \text{butanol} \overset{K2}{\rightleftharpoons} (\text{butanol-DMABN-butanol})$$

The above relationship can be simplified by the fact that the butanol concentration is much higher than the concentration of either the free DMABN molecule or the DMABN-butanol complex. The ratio of the concentration of the ground state complexes to the total concentration of the DMABN molecules plus the complexes can then be derived as follows:

$$\frac{[\text{complexes}]}{[\text{DMABN}] + [\text{complexes}]} = \frac{K1^*K2^*[B]^2 + K1^*[B]}{K1^*K2^*[B]^2 + K1^*[B] + 1} , \qquad (4)$$

where $[B]$ represents the butanol concentration without regard to aggregation. The value of this ratio as a function of the butanol concentration has been measured from the picosecond kinetic data as shown in Fig. 5. We can therefore derive the values of $K1 = 0.3$ and $K2 = 0.1$ by fitting Eq. (4) to the experimental data. These values must be viewed, however, as fitting parameters at this time, since the distribution of butanol oligomers is not known. For purposes of comparison, we note that the equilibrium constants obtained from a number of studies of hydrogen bonded complexes yield values which are typically larger than those reported here.[41] The analyses were similar in that the aggregation of the alcohol was neglected.

2. Steady state absorption and fluorescence spectra

In the previous section we have proposed a mechanism for the dual fluorescences of photoexcited DMABN molecule on the basis of picosecond kinetic data. It is desirable to know if this mechanism can help us understand the results of steady state absorption and fluorescence spectra.

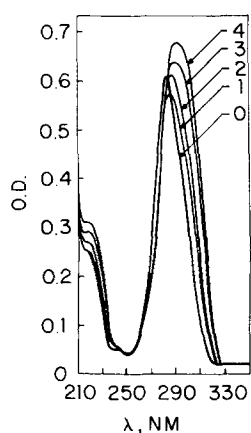The fluorescence spectra of 2.5×10^{-4} M DMABN in

FIG. 7. Absorption spectra of 2.5 $\times 10^{-4}$ M DMABN in mixed butanol/hexadecane solutions. (0) pure hexadecane; (1) [butanol] = 1.0 M; (2) [butanol] = 3.64 M; (3) [butanol] = 7.3 M; (4) pure butanol.

mixed solutions of butanol/hexadecane are shown in Fig. 6. As the butanol concentration increases the intensity of the blue emission decreases and its maximum red shifts. At the expense of the blue emission, the intensity of the long wavelength CT emission increases and its maximum also shifts to the red. No isobestic point was observed. These features can be qualitatively understood in terms of our proposed mechanism. The dependence of the fluorescence spectra on the butanol concentration corresponds to the quenching of the blue emission by the butanol molecules and the concurrent formation of the long wavelength CT emission. The absence of an isosbestic point is the result of the long range polarization interaction between the excited DMABN−butanol complex and the solvent dielectric, which shifts the emission maximum of the complex to the red as the macroscopic dielectric constant of the solvent increases. The dependence of the emission maximum of a polar excited state on the solvent polarity has been extensively studied and is a convenient way to estimate the dipole moment of the excited state.[33,34] In our case, the addition of the butanol molecules to the nonpolar hexadecane solution certainly increases the overall dielectric constant of the solution. Since the emitting dipolar complex corresponds to an intramolecular CT state with dipole moment (16 D) much larger than that of the ground state (7 D), it is preferentially stabilized by the polar solvent through the polarization interaction. This stabilization lowers the transition energy and shifts the emission maximum to the red. The complicated fluorescence spectra of photoexcited DMABN molecule in mixed solvents is therefore a reflection of the coupling of both the local interaction between the DMABN and the butanol and the long range polarization interaction between the complex and butanol solvent.

In our proposed mechanism [Eq. (2)] we suggested the formation of ground state complexes between DMABN and butanol on the basis of our kinetic measurements. One would expect that the formation of ground state complexes would change the absorption spectrum of DMABN upon the addition of butanol molecules, due to the strong interaction between the DMABN and butanol in the complex. The steady-state absorption spectra of DMABN in mixed solvents are shown in Fig. 7. The absorption maximum shifts to the longer

wavelength from the nonpolar hexadecane solution to the polar butanol solution. Such an effect, attributed to solvent polarization, is typical of an absorption band corresponding to the transition from a state with a small dipole moment to a state with a large one.[35,36] However, the more interesting observations are that the transition strength of the absorption band drops initially and then increases again as the band maximum Stokes shifts. At the same time the FWHM of the band also increases. This change of transition strength and bandwidth upon the addition of butanol are consistent with our proposed mechanism that in the ground state the free DMABN molecules are in equilibrium with complexes formed between the DMABN and butanol molecules. These complexes may have slightly different absorption maxima and oscillator strengths compared to the free DMABN molecules. The interaction between butanol and DMABN molecule may also induce structural change in the DMABN chromophore and thus changes its absorption strength and bandwidth. Similar behavior has been observed for other systems involving ground state equilibration with electrostatic complexes (e.g., hydrogen-bonded complexes[40]).

IV. CONCLUSIONS

Our results on the photophysics of excited DMABN molecule in polar solvents can be summarized in the following: (1) We have demonstrated the parent-daughter relationship between the short wavelength emitting state and the long wavelength emitting charge transfer state. Upon excitation, they reach equilibrium very rapidly in about 30 ps for butanol solvent and 19 ps for propanol solvent. The difference in the rise times is in part due to the viscosity dependence of the chromophore twisting process. (2) The observation of a rapid rise component in the TICT emission (30 ps) in all the mixed butanol/hexadecane solutions indicate the presence of ground state DMABN−butanol complexes, and is interpreted as the time required to achieve the twisted charge transfer geometry by rotation of the dimethylamino group about the C−N bond. The slow component in the rise of the TICT emission is found to vary linearly with butanol concentration, yielding a reaction rate constant of 9.7 $\pm 1.5 \times 10^{8}$ M^{-1} s^{-1}, that is slower than diffusion controlled. It is suggested that the kinetics of the reaction of excited DMABN with butanol is insensitive to the state of butanol aggregation, i.e., whether the butanol is a monomer, dimer, or part of a higher aggregate. A key step in the subsequent stabilization of the twisted intramolecular charge transfer structure appears to be the formation of a complex between excited DMABN and butanol. The twisted structure is further stabilized by interacting with the solvent dielectric through the long range polarization interaction. This is reflected by the continuing shift of its emission maximum to the red as the butanol concentration is increased. The fluorescence spectra of DMABN molecule in mixed solvents can be understood on the basis of both the local and long range interactions. We thus note that the observed kinetics, steady state absorption and fluorescence spectra of the dual emission properties of DMABN can be explained by the mechanism proposed in this paper.

ACKNOWLEDGMENTS

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