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Environmental and Magnetic Field Effects on Exciplex and Twisted Charge Transfer Emission

Kankan Bhattacharyya* and Mihir Chowdhury*

Physical Chemistry Department, Indian Association for the Cultivation of Science, Jdavpur, Calcutta 700032, India

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Contents

I. Introduction

Exactly 4 decades ago Mulliken[1] introduced the concept of charge transfer (CT) transitions. This refers to direct excitation into a state involving complete transfer of an electron from a donor to an acceptor. Apart from direct excitation, the CT state can also be produced by electron transfer between donor and acceptor when either of them are excited. Weller[2] first showed that complexes are formed between the excited acceptor (or donor) and the unexcited donor (or acceptor), even though no complex formation could be detected in the ground state. These CT complexes are known as exciplexes. They are highly reactive due to their radical and polar character. The exciplex-mediated photoinduced CT phenomena play an important role in a wide area of photochemistry and photobiology, including photosynthesis, light harvesting, and energy-storage processes.[3] The dynamics of the radical pair and solvation of the polar CT state has generated a lot of interest in recent years. In the fortuitous case of luminescent CT states, CT emission can be used as a probe to study their dynamics. In the present article we will focus our attention on two aspects of CT emission, namely effect of magnetic field and of environment.

Sections II and III deal with donor–acceptor (D–A) excited-state complexes where the donor and the acceptor are *distinctly* different molecules or part of the same molecule but separated by saturated carbon chains. Basic concepts on statics and dynamics of D–A complexes are dealt with in section II while section III summarizes the work done on different systems. Since the role of exciplexes in condensed media is pretty well known and has been reviewed from time to time,[3] only a brief overview of exciplex emission in condensed phase is given in section III.A. The more recent topic of CT emission under solvent-free, isolated conditions in supersonic jet is reviewed in section III.B. The major emphasis of section II and III is, however, on how an external magnetic field affects spin-forbidden nonradiative transitions in radical pairs and hence exciplex emission. Since the magnetic effect depends on spin dynamics as well as on diffusion dynamics of the radical

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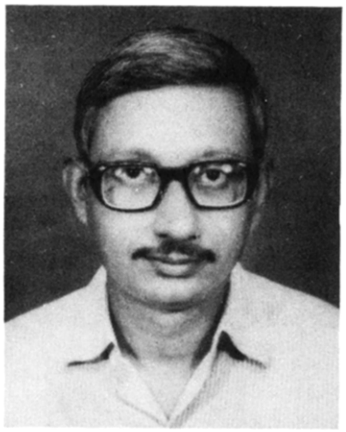

Kankan Bhattacharyya was born in 1954. He received his M.Sc. degree in Chemistry in 1976 from Calcutta University, Calcutta, India.′ From 1978 to 1984 he worked with Professor Mihir Chowdhury on laser spectroscopy at the Indian Association for the Cultivation of Science (IACS) to receive his Ph.D. degree in 1984. Subsequently, he worked with Dr. P. K. Das as a postdoctoral associate at the Radiation Laboratory, University of Notre Dame, from 1984 to 1986. In 1986 he joined Professor K. B. Eisenthal's group at the Chemistry Department, Columbia University, and studied liquid surfaces using nonlinear laser technique before joining the faculty of the Physical Chemistry Department, IACS, in 1987. His research interests include picosecond spectroscopy of organic molecules, organized assemblies, dynamic solvent effects, and nonlinear laser spectroscopy.

Mihir Chowdhury was born in 1937. He received his M.Sc. degree in 1957 and Ph.D. degree in Chemistry in 1961 from the Calcutta University, Calcutta, India, for his works on charge transfer spectroscopy with Professor S. Basu. He was a postdoctoral associate at Pennsylvania State University from 1961 to 1962 with Professor L. Goodman. From 1962 to 1964 he worked with Professor D. S. McClure at the University of Chicago. He joined Presidency College, Calcutta, as a professor in 1966. In 1976 he became Professor and Head of the Physical Chemistry Department, Indian Association for the Cultivation of Science (IACS). His research interests include high-resolution laser spectroscopy of organic molecules in supersonic jets, magnetic field effects on molecular luminescence, time-resolved studies of emission in fluid solutions and in rare earth single crystals, two-photon absorption of organic molecules and rare earth single crystals, circular dichroism of single crystals, and theoretical spectroscopy.

ion pair, and the diffusion depends on the medium, environment has a marked influence on the magnetic effects. This aspect will be discussed in sections II.B.3, II.B.4, and III.C.

In section IV another interesting CT process, namely the twisted–intramolecular CT (TICT) process,[4] will be reviewed. In this case the donor and the acceptor moiety are joined by a chemical bond and the electron transfer is accompanied by a twist about this bond.

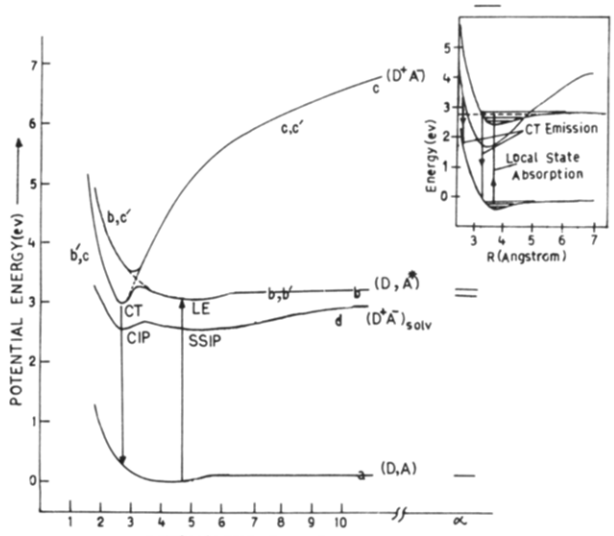

Figure 1. Schematic diagram for the potential energy of charge-transfer complexes, as a function of intermolecular separation: curves a–c, in the vapor phase or nonpolar solvent, (d) in polar solvent. The zero-order LE (curve b) and CT (curve c) states interact at the crossing point, giving rise to first-order curves b′ (lower) and c′ (upper). The insert shows a possible alternative way of curve crossing and activated transfer from the LE to CT state.

The dynamics of this process are remarkably sensitive to the environment. The TICT process in a host of media ranging from homogeneous solution to supersonic jet and a number of organized assemblies will be discussed in this section.

II. Exciplex Emission: Basic Concepts

A. Potential Energy (PE) Curves for the Exciplex Systems

1. PE Curves in the Vapor Phase

When both the electron donor (D) and the acceptor (A) are in the ground state the donor–acceptor (D–A) complex possesses no stabilization energy except the very small resonance energy due to the ionic structure D^+A^-. The potential energy (PE) curve for the D–A pair in the ground state as a function of donor–acceptor distance (R), is shown in Figure 1a. Stability of the complex in the ground state, as indicated by the very shallow minimum,[1] is often too small to be detected in fluid media. However, van der Waals complexes involving the D–A pair are easily formed in the case of ultracold molecules in supersonic jets. Such complexes will be discussed in detail in section III.B.

Figure 1b corresponds to the zero-order neutral, locally excited (LE) state of the exciplex, D,A*, where A* represents the lowest singlet excited state of A. In this case of a large R, the curve is more or less similar to 1a except that it is shifted from the ground-state curve by the energy of the photon absorbed. The minimum in the curve 1b, however, is much deeper due to considerable binding energy between the donor and the acceptor in the excited state, essentially resulting from exciton and charge transfer resonances due to close proximity of a charge transfer (CT) and a number of locally excited (LE) states.[5–9]

The PE curve corresponding to the zero-order CT state (D^+A^-) is shown by curve 1c. When the separation is large, the energy difference between the ground and the CT state is $I - A$, where I is the ionization potential of the donor and A the electron affinity of the acceptor. Typically, I's of the aromatic compounds are of the order of 7–10 eV, and A's are of the order of 0–1 eV.[10] Thus at infinite separation the CT state is at least 6 eV above the ground state, and the CT state is above the LE state in order of energy. This renders generation of the free-radical ions D^+ and A^- from D,A* nearly impossible in the vapor phase for normal UV excitation. At smaller intermolecular separation, the zero-order state (D^+A^-) gains stability partly due to covalent interaction between the radical pairs and partly due to the attractive electrostatic potential between oppositely charged ions. For a typical distance of about 3 Å, the gain in energy due to the latter cause alone will be about 4.8 eV if one neglects mutual polarization of the two charged ions. Thus, at smaller intermolecular separation, the energy of the CT state may be greater than, nearly equal to, or less than that of the neutral LE state. In the first case, only luminescence from the neutral LE state is possible and the luminescence is almost like the donor luminescence.[11,12] In the second case, strong resonance is expected, leading to a change in the character of luminescence. In the last case, the luminescence emerges from the CT state. In view of the strong Coulombic interaction between D^+ and A^-, the separation corresponding to the minimum in the CT curve is expected to be less than that for the ground state. Thus, a vertically downward transition from the upper CT state ends up on the repulsive part of the ground-state potential where the energies vary strongly with distance; this makes the exciplex transitions red-shifted, broad, and structureless—even in situations where the temperature is very low, as in a jet, or when the solid complex is cooled down to liquid helium temperature.

The zero-order curves b and c should cross in the last case. If there is no symmetry restriction for interaction between the zero-order states CT and LE, new first-order curves like b′ and c′ will result. Depending on where the crossing point is, the curve b′ may exhibit two minima separated by an energy barrier, one corresponding to the CT state and the other to the LE state. Thus two luminescences, one corresponding to the CT state and the other to the LE state, are expected if the temperature of the system is low enough to prevent complete transition from one state to the other over (or through) the potential barrier. It is possible that other coordinates also differ for the LE and CT structures; i.e., they are conformers. At the crossing point, the system initially in the LE state either, in the adiabatic case, continues along b′ and crosses over to the CT state with unit probability or, in the diabatic case, returns to the LE state and the probability of crossover is less than unity. It may be pointed out here that the barrier height may not be same for all vibronically excited A* states[11,12] and the effective barrier height depends on the complex dynamics involving relaxation of various modes.

For triplet states of A, curves similar to the singlet curve b are expected at the triplet excitation energy. The energy of the triplet, $^3A^*$, being smaller than the singlet, $^1A^*$, the nearly degenerate $^{1,3}(D^+A^-)$ states are relatively more likely to be higher in energy compared to the triplet ^{3}LE state. Although there is a possibility of interaction between the $^3(D^+A^-)$ and the ^{3}LE state leading to a stabilization of the ^{3}LE state, curve crossing and dual triplet luminescences hardly occur in the vapor state. The exciton interaction, under dipole–dipole approximation,[13] is proportional to the product of the oscillator strengths of D and A. Since the oscillator strength is small in the triplet case, stabilization of triplet exciplexes due to exciton interaction is small. The observation of emission from the triplet exciplex is further difficult because of spin forbiddenness. Nevertheless, examples of phosphorescence in rigid media from a triplet CT complex have been reported.[14]

For D,A systems linked by flexible chains, it is necessary to add the strain energy to get the PE curves, but this is difficult to calculate. In addition, there may be a through-bond interaction between the D and the A, even though the linking chain consists of saturated carbon atoms. One limiting case is when the donor and the acceptor are directly joined by a single bond. In such cases the mutual overlap of the donor and the acceptor orbitals depends markedly on D–A separation distance and the torsion or twist about the D–A bond. The energy, dipole moment, and other properties of such complexes vary in a highly interesting way with the twist angle.[4] The minimum of energy occurs at different twist angles for the ground, CT, and neutral excited states. This will be discussed in more detail in section IV, in connection with twisted intramolecular charge transfer.

2. PE Curves in Solutions: Effect of Solvation

In solutions, the solvation energy due to solute–solvent interaction needs to be added to the curves 1a–c. The differential solvation of the LE and the CT states due to the difference in their dipole moments brings about large change in energy ordering of the states and curve crossing. The energy of the LE and the CT states in a solution can be obtained from the experimentally determined electrode potential as explained by Rehm and Weller[16] or using the different theoretical models of the dielectric properties of the media. In the simplest case, assuming both D^+ and A^- are spherical ions of radii r_D and r_A, respectively, the solvation energy is given by[15]

$$-\frac{e^2}{2}\left(\frac{1}{r_D}+\frac{1}{r_A}\right)\left(1-\frac{1}{\epsilon}\right) \qquad (1)$$

In a medium of dielectric constant $\epsilon = 10$, for $r_D = r_A = 3$ Å, this comes out to be about 4.3 eV. Thus, even for large D–A separation, E_{CT} may be lower than E_{LE}. Figure 1d gives the PE curve of the CT state in a polar solvent. Evidently curve d in polar medium is much more shallow compared to that in vapor or nonpolar solvent. The difference in energies of the exciplex at large separation and at the distance, R_{SSIP}, corresponding to the solvent-shared ion pair (SSIP), is given by $e^2/\epsilon R_{SSIP}$, which decreases as the polarity (i.e. ϵ) increases. In polar solvent there are usually two minima corresponding to the solvent-shared ion pair (SSIP) and the contact ion pair (CIP), respectively.[17] The two minima of the curve are separated by an energy barrier, because in going from the SSIP to the CIP the solvent has to be squeezed out (Figure 2). The barrier heights are difficult to obtain either theoretically or experi-

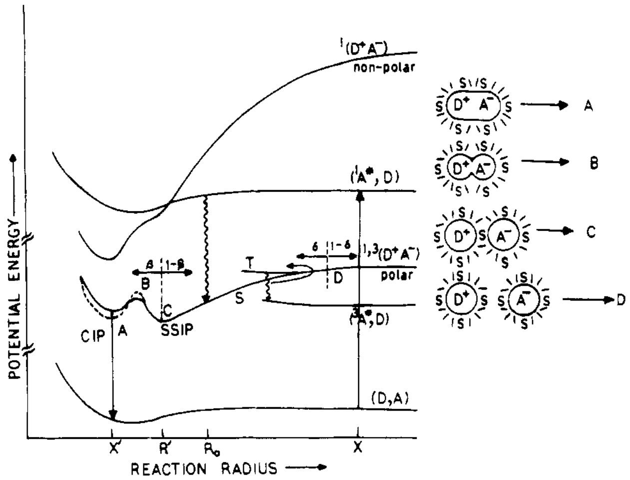

Figure 2. Schematic PE curves for CT complexes in solvents as a function of intermolecular separation. The vertical scale for the CT curve in polar solvents is magnified to indicate more clearly CIP (A), transition state (B), SSIP (C), and relatively free ion pair (D). Possible structures of the solvated ion pair corresponding to A, B, C, and D are shown. The triplet states and the leak to the triplet manifold from the singlet manifold are also indicated. β represents the fraction of SSIP's forming CIP and δ represents the fraction of the ion pairs that return from diffusional excursion from the imaginary boundary at D.

mentally. These are expected to be dependent not only on the dielectric constant of the medium but also on specific interactions, such as H-bonding ability of the solvent molecules. Thus, isodielectric protic and nonprotic solvents may behave differently.[18] Further, in mixed solvents due to dielectric enrichment the "local" composition in the immediate neighborhood of the ion pair might be different from that in the bulk.[19-20,297] In the Kirkwood–Onsager continuum model, solvent stabilization of the CIP is

$$\frac{\mu^2}{\rho^3}\frac{\epsilon - 1}{2\epsilon + 1}$$

where ρ is the radius of an equivalent spherical cavity and μ the dipole moment of the CIP.[6] μ can be determined from the plot of emission frequency of the CIP against

$$\frac{2(\epsilon - 1)}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

(See refs 7, 21–22.) The energy expression for CIP also contains the electrostatic part e^2/R_{CIP} and the covalent exchange part ΔE_{ex}. The energy difference between the CIP and SSIP is given by

$$E_{\text{CIP}} - E_{\text{SSIP}} = \frac{e^2}{2}\left(\frac{1}{r_{\text{D}}} + \frac{1}{r_{\text{A}}}\right)\left(1 - \frac{1}{\epsilon}\right) + \frac{e^2}{\epsilon R_{\text{SSIP}}} - \frac{\mu^2}{\rho^3}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \Delta E_{\text{ex}} - \frac{e^2}{R_{\text{CIP}}} \quad (2)$$

If we assume $\Delta E_{\text{ex}} = 0$, it is easy to verify that SSIP is more stable than CIP at $\epsilon > 7$. Thus, at high polarity the equilibrium between SSIP and CIP lies in favor of SSIP. Since SSIP gives rise to free ions while CIP is responsible for CT emission, ion yield increases and CT emission decreases with a rise in polarity of the medium.[3a,15,23-25]

B. Dynamics in Exciplexes

The transition of the system from one point of a potential energy curve to another point of another potential energy curve may be considered in three steps: (a) diffusion-controlled horizontal movement along the initial curve (Figure 2) from the intermolecular separation X up to the intermolecular separation R_o, followed by (b) vertical transition to the final curve at R_o, followed by (c) gradient-controlled diffusional movement along the final curve from the point R_o to the point X'. Any of the steps could be the rate-determining factor. In section II.B.1 we consider the quantum mechanical and the classical approach to the transition probability between two electronic states. In section II.B.2, the classical approach toward transition is applied to the electron-transfer process. Section II.B.3 deals with spin development in a radical pair, while section II.B.4 discusses in an integrated way combination of diffusional motion and spin-dependent recombination.

1. Nonradiative Transitions between Electronic States

The nonradiative (NR) transitions between two electronic states refer to transitions which occur without absorption or emission of radiation. An excited molecule can come down nonradiatively to its lower excited states or to the ground state in a number of ways. This includes internal conversion (IC), intersystem crossing (ISC), isomerization, electron transfer, and other photochemical reactions. In this section we will briefly recall some general features of IC and ISC. Electron-transfer process will be discussed in section II.B.2. TICT, an interesting NR process involving CT and isomerization, will be taken up in section IV.

1.1. Golden Rule Rate for IC and ISC. The usual starting point of quantum mechanical approaches to nonradiative transitions from an electronic state i to another f is the Fermi "golden rule", according to which the transition rate, k_{if}, is proportional to the square of the matrix element between the two states, V_{if} $(=\langle\Psi_{\text{f}}|V|\Psi_{\text{i}}\rangle)$, where V is the appropriate perturbation causing the transition.[26-38] For internal conversion (i.e. NR transitions between states of the same spin multiplicity), V is the nuclear kinetic energy operator. For intersystem crossing (ISC), i.e. transitions between states of different spin multiplicity, spin–orbit coupling (**L·S**) or hyperfine coupling (**I·S**) is the major perturbation. With a number of approximations it can be shown that the NR rate k_{if} decreases exponentially with an increase in the energy gap (ΔE_{if}) between the two states.[26-32] This is the well-known energy gap law for IC and ISC. The energy gap law plays an important role in the solvent-mediated electron-transfer process, crossover from the LE to CT state, and decay from the TICT state.

1.2. Semiclassical Treatment. An alternative explanation of the NR transition is based on the semiclassical treatment of Landau and Zenner. In this model the probability of transition between the two PE curves is related to the energy difference, ΔE_{if}, the difference in slopes of the two curves, and the velocity of the system near at the crossing point.[3a,28c,33-38] Physically slope, $(\mathrm{d}E / \mathrm{d}r)$ of the curve gives force on the nuclei. Only the quantities near the crossing point are important because in both the classical and quantum case at high vibrational quantum number the residence and overlap probability is high far from the mean position.

2. Electron-Transfer Processes

The first step in the formation of the exciplex involves electron transfer (ET). Thus the experimentally determined rate of formation of an exciplex provides excellent testing grounds for the various theoretical models of electron transfer.[231c,238] In the vapor phase or in nonpolar solvents, the two potential energy curves (PECs) of Figure 1, b and c, cross, and the ET may be expected to occur at a fixed intermolecular separation (R_o) corresponding to the crossing point. In polar solvents, however, the PECs b and c of Figure 1 do not cross, and hence one cannot define a particular intermolecular separation where the ET occurs. Nevertheless, at any intermolecular separation the CT and LE surfaces may cross when plotted against coordinates of internal modes of D or A or external modes involving solvent reorganization. The barriers to ET due to solvent and internal mode reorganization have been considered classically by Marcus.[35-38] The frequency of ET at any intermolecular separation R, is given by

$$\nu_{et} = \langle \bar{k} \rangle \frac{kT^2}{h} \exp\left(\frac{(\lambda + \Delta G)^2}{4\lambda kT} \right) \qquad (3)$$

where λ is a composite reorganization energy term and ΔG, the overall free energy change in the electron transfer process. The transmission coefficient $\langle \bar{k} \rangle$ depends on the diabatic and adiabatic nature of the process.[33] An important feature of the Marcus' theory is that as the free energy difference ΔG increases, the rate of electron transfer initially increases, reaches a maximum at $\Delta G = -\lambda$, and then decreases for very large ΔG. The so called "Marcus-inverted" region, where ν_{et} decreases with increase in ΔG, is akin to the energy gap law for NR transitions. Such "inverted" behaviors have been reported for electron transfer in rigid systems, and for radical ion recombination.[39] However, in the case of bimolecular quenching or charge separation, the ET rate shows only a steep rise around the zero-energy gap to the diffusion-limited value, and no decrease of the ET rate on further increase of ΔG could be observed.[40,16] Several tentative explanations for such nonexistence of the inverted region have been proposed. The parallelism of thermal and optical electron transfer phenomena, i.e. the similarity between the CT-band intensity vs frequency plot and the ν_{et} vs $-\Delta G$ plot, has recently been analyzed by Marcus.[35e]

The question of how the ν_{et} depends on R_o is an intricate one. Several attempts have been made to determine the average R_o in polar solvents experimentally from the quenching rate of D* fluorescence by electron-accepting quenchers. All the techniques of finding R_o show that, in polar and/or viscous solvents, the average electron transfer distance R_o may be large and increases with the polarity of the medium.[41] The value of R_o also increases with reduction in the oxidation potential of the quenchers.[42] Various explanations of such large-range electron transfer in polar media have been proposed.[41,42]

3. Intersystem Crossing and Magnetic Field Effects

During the intersystem crossing (ISC) from the singlet manifold to the triplet manifold the electronic spin angular momentum changes. To conserve total angular momentum the orbital angular momentum of the electron must change. The Hamiltonian which brings about this is the spin–orbit coupling, H_{so}, given by $\sum_i \lambda_i \mathbf{l}_i \cdot \mathbf{s}_i$, and this is the perturbation responsible for ISC. Since it is a one-electron Hamiltonian, it can only connect zero-order initial and final states which differ by an orbital occupancy of one orbital. The interaction matrix element V_{if} $(= \langle \psi_i | H_{so} | \psi_f \rangle)$ is roughly proportional to the overlap of the two orbitals occupied by the electron and inversely to the energy difference in the initial singlet and the final triplet state. This term plays a very important role in intramolecular S → T transitions for both LE and CT states of the exciplex (CIP).[43] If the separation between the donor and the acceptor is large, e.g., for a transition from ^{1}SSRIP to ^{3}SSRIP, contribution of this term diminishes. Further, if the orbital occupancies of ^{1}SSRIP and the ^{3}SSRIP are same, it is not possible to compensate the spin angular momentum change by a corresponding orbital angular momentum change. However, the spin–orbit coupling within each radical may still play an indirect role by influencing the g value of each radical as discussed below.

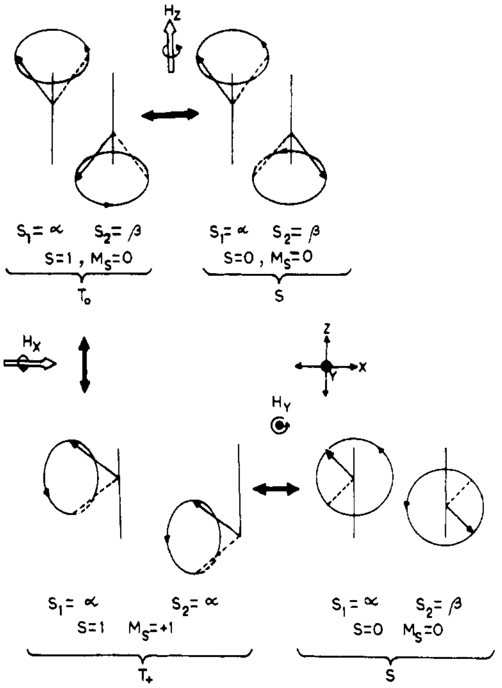

Figure 3. Vector diagram for singlet ↔ triplet interconversion by a magnetic field, assuming the field is applied along one of the laboratory axes and the two spin vectors (α, β defined with respect to the Z direction) lying in the XZ plane before the application of the field (T_- behaves similarly as T_+).

If the g value of the two radicals are different, the compensatory change in angular momentum may be provided by the laboratory apparatus, namely an external magnetic field. This topic has been reviewed a number of times,[44] most comprehensively by Steiner.[44s,t] The relevant term in the Hamiltonian which induces an ISC process in an RP is $g\beta\mathbf{H}\cdot 2\mathbf{S}$. Its effect may be diagramatically illustrated. In Figure 3, the relationship of the two spin moments in the singlet (S) and three triplet (T_0,T_{+1},T_{-1}) states are represented. If the coupling between the two spin vectors are negligible (i.e., $J \approx 0$ in the exchange term $J\mathbf{s}_1 \cdot \mathbf{s}_2$ of the Hamiltonian), as is true for separations of two radicals greater then 10 Å, the two vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ will precess independently around the applied field with frequencies given by $g_1\beta H$ and $g_2\beta H$, respectively. If the two g values are different, the relative spin orientation corresponding to S will evolve into a spin orientation corresponding to T_0. This will cause reversible transitions between the S and T_0 state. In presence of a large magnetic field, transition from or to $T_\pm$ states are only possible via spin relaxation to the T_0 state. If, say, $\Delta g \approx 0.001$, then a field on the order of 10 kG can cause a transition in about 10 ns, which is within the lifetime of many radical pairs.[44p] Although the coherent spin evolution between S and T_0 is a reversible process, there may be a faster transition from ^{3}CT curves to lower energy (D,^{3}A*) states, making the leakage from the ^{1}CT curve virtually an irreversible one. Out of the initially formed radical pairs at R_0, some will form CIP and produce exciplex luminescence, while others will diffuse out to the zone where S,T curves are degenerate. Some of the latter group of ion pairs will produce free ions, uncorrelated in spin, while the rest will return from the diffusional excursion and recombine to produce CIP and exciplex luminescence. Due to the Δg effect, an application of magnetic field should increase the leaking hole in the ^{1}CT surface and thus cause a decrease in exciplex luminescence. Such decrease of CT luminescence, however, can only take place at very high fields and has been reported for transient absorption studies of radical pairs.[44p]

The third possible way to compensate the spin-angular momentum change is by flip-flop adjustment of the nuclear spin momentum.[44] The hyperfine interaction term of $\mathbf{A}_{ni}\mathbf{I}_n\cdot\mathbf{S}_i$ is similar to the Zeeman term $H\cdot S_i$. Although any change of electron spin needs to be accompanied by a simultaneous nuclear spin change, the relative change in $\mathbf{I}$ is small in a large molecule with many magnetic nuclei and may be treated as constant, at least for the sake of the qualitative argument that follows. $I\cdot S$, unlike $H\cdot S$, will have three components $\mathbf{I}_z\mathbf{S}_z$, $\mathbf{I}_x\mathbf{S}_x$, and $\mathbf{I}_y\mathbf{S}_y$ with respect to the laboratory axes. This will cause not only S $\leftrightarrow$ T_0 transition but also S $\leftrightarrow$ $T_\pm$ transitions, for the vectors now can precess around X and Y axes as well. The number of channels for S $\leftrightarrow$ T transition will thus be three due to the internal magnetic field of nuclei. If, however, an external field is applied on the top of the internal nuclear field, there will be competition between the two. It can be shown that for a two-level (A,B) system, the rate of transition, k_{AB} is proportional to $\langle A|H'|B\rangle^2/\Delta E$, where the matrix element represents the coupling of the two states and ΔE the energy gap. If the Zeeman splitting is greater than the hyperfine interaction, the S $\leftrightarrow$ $T_\pm$ evolution will be increasingly suppressed due to the energy difference between them. This reduction in the number of channels from three to one on application of field, which makes the ZI greater than the HFI, means that the leaking hole in the ^{1}CT surface will diminish in size, and qualitatively this will produce an increase in CT luminescence intensity on increasing the external field from zero to a value greater than the hyperfine interaction. Thus on increasing the field, the exciplex luminescence increases in intensity but reaches a saturation at a field even as low as 100 G. At very low and high fields, the field dependence may show nonmonotonic behavior. If the separation between the two radicals $D^{\bullet+}A^{\bullet-}$ is such that the exchange integral J is not zero, the S and $T_{0,\pm}$ states will be nondegenerate at $H = 0$. A very small field can cause S and T_- (or T_+) to coincide in energy.[45] This increases the ISC leak in the ^{1}SSIP surface and hence decreases the exciplex luminescence. Further increase of field decreases ISC and hence increases exciplex luminescence. Thus exciplex luminescence intensity will go through a minimum at low fields. Again, a field much greater than the saturation value may decrease the intensity for reasons explained in the previous paragraph.

At high field, analytical expressions of spin evolution have been obtained,[44a–o] but for low fields, quantitative treatment of the spin evolution becomes a difficult problem when the number of magnetic nuclei are many and nonequivalent. For most chemically relevant molecules only numerical solutions are possible.[44a–o] For the $Py^{\bullet-}/DMA^{\bullet+}$ case there is almost a linear increase of triplet population with time at short intervals and then it becomes steady after a few small-amplitude oscillations. A recent review discusses the methodology for spin-polarization calculation.[46] The integration of the spin-evolution process with diffusional motion and chemical reaction is discussed in the next section.

4. Spin-Dependent Recombination and Separation of Radical Ion Pairs

The radical ion pairs formed as a result of electron transfer undergo both spatial diffusion and spin evolution during which their space and spin coordinates change with time. There is a finite probability that during random diffusion the radical pair reencounter and recombine. The reaction rate at the time of reencounter depends on the spin state of the radical pair. Thus the radical ion pair can undergo three processes, namely, recombination, diffusion, and spin evolution. The rates of these three processes are mutually dependent on each other. The most appropriate way to handle this type of interdependent motion is through stochastic Liouville equations (SLE). The different theoretical approaches to spin polarization and RP recombination and their relationship to SLE have been summarized by Steiner et al. in two recent reviews.[44s,t] Briefly, the complete physical information on an ensemble of RPs is contained in the spin-density matrix $\rho(r,O,t)$. If the orientational relaxation is fast and the medium is isotropic, the SLE for $\rho(r,t)$ can be written as

$$\dot{\rho}(r,t) = -\frac{i}{\hbar}[H,\rho(r,t)] + L(r)\rho(r,t) - K\rho(r,t) \qquad (4)$$

The first term represents spin evolution for appropriate distance dependent exchange interaction, $J(r,t)$) and the last term describes recombination. The second term takes into account the spatial diffusion. For a spherically symmetric, three-dimensional system, L is given by

$$\mathbf{D}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\frac{\partial}{\partial r} + \frac{1}{kT}\frac{\partial V(r)}{\partial r}\right)\right]$$

where $V(r)$ is the potential energy of interaction between the particles and D is the bulk diffusion coefficient.

In principle, the SLE approach represents accurately isotropic continuous diffusion in an arbitrary potential and takes full account of the interdependence of various dynamical terms. The complete analytic solution of SLE is, however, difficult especially due to the lack of detailed knowledge about $V(r)$. However, approximate solutions can be arrived at by suitable choice of the initial and boundary conditions commensurate with the experimental situation. Time-independent[48] and time-dependent[49] solutions have been obtained numerically and analytically[48b,c] using a finite-difference technique. Werner et al. calculated a recombination yield for unlinked radical ion pairs.[50] Schulten and Bittl have made an elegant analysis of flexibly-linked D–A pairs.[51] Recently, Staerk et al.[52] have provided diagrammatic illustration of the results.

An alternative strategy is the re-encounter method.[53–58] In this method, one assumes existence of a clearly demarcated reaction zone inside which all the reactions take place and outside which no reaction occurs except the scavenging processes. Explicit space dependence of the quantum mechanical operators is considered inside the reaction zone only. It is assumed that there is no space dependence outside the reaction zone. Because of recombination during encounter, the singlet population decreases but the triplet population remains unchanged. As a result the S–T correlation is lost at least partly at each encounter. The singlet and the triplet population evolve coherently only in between the encounters. The total number of encounters can be calculated assuming continuous diffusion and free spin evolution inbetween encounters. The probability of re-encounter is obtained by Noyes' method.[53] The result is summed encounterwise, such as over all radical pairs experiencing first encounter at all times, second encounter at all times, etc. Thus, the final result is not time-dependent and no temporal information is available in this procedure of calculation, but it gives the total yield in a compact form. For example, for very high field when spin evolution takes place only between S and T_0 states, it has been shown[57,58] that the total recombination yield for triplet-born RP is given by $(^1/_2)\Lambda\delta$, where Λ is the spin free reactivity and $\delta = a(\omega_n/D)^{1/2}$, where a is the contact radius, ω_n is the frequency of spin evolution and depends on ZI and HFI, and D is the mutual diffusion coefficient of the two diffusing radicals. It has been demonstrated that the net effect of exchange interaction is to reduce ω_n slightly. The advantage of this approach is that it can give rise to conceptually simple analytic solutions[59] and the effect of various aspects of the diffusion process can be analyzed. The inherent disadvantage is that the general r dependence of the operators cannot be treated exactly, but recently Pederson has taken care of this to some extent.[47]

III. Effect of Environment on Exciplex Emission: Examples

A. Factors Affecting Exciplex Emission in Liquid Solutions

1. Solvent Polarity

As explained in section II.A.2 in homogeneous media, the dipole moment of the exciplex may be calculated from the slope of the plot of CT emission frequencies against

$$\frac{2(\epsilon - 1)}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

In heterogeneous mixed solvents, one has to consider specific effects in addition.[102b] Mataga found that in many cases the slope varies with polarity. This has been interpreted as due to solvent-induced change in the degree of charge transfer and hence dipole moment of the CIP.[7,102d] It may be pointed out that while the contact ion pair interpretation of exciplex has been vindicated by chemiluminescence experiments[103] and solvent effect studies, chemical reactivity of exciplexes is not always consistent with complete charge separation.[104] Exciplexes with dipole moment considerably less than that corresponding to complete charge transfer are more usually obtained.[6,17,3a–m,21]

As already pointed out, quantum yield and lifetime of CT luminescence vary quite sharply with solvent polarity mainly because of the ionic dissociation of the CIP.[77] After electron transfer and production of an SSIP at a particular intermolecular separation, a fraction of the SSIP's recombine while the rest dissociates into free ions (Figure 2). With increase in the polarity of the medium the CT luminescence yield decreases and the ion yield increases sharply,[21–23,78] even in a linked system.[79] This is because of the stabilization of the free ion pair relative to the CIP with increase in medium polarity. Mataga[25] used the empirical relation

$$\log\left(\frac{1}{\phi} - 1\right) = \frac{p}{\epsilon} + f \tag{5}$$

where ϕ is the ionic dissociation yield, ϵ the static dielectric constant, and p and f are constants. The equation has been justified[7] on the basis of Onsagar's ion-recombination model[80] and Horiuchi–Polany's expression for activation energy.[81] Using an analytic solution[82] of the Smoluchowski equation and ϵ-dependent Onsagar radius, Nath et al.[18] deduced an expression for the emission yield, ϕ_f, assuming that the distance at which the ion pair is formed to be independent of the polarity of the medium. Several experiments, however, indicate that the latter increases with polarity of the medium.[41]

Several authors addressed the issue whether the contact ion pair (CIP) or the solvent-shared ion pair (SSIP) is formed directly from the D* and A on electron transfer. If the process involves formation of CIP followed by formation of SSIP and finally ionic dissociation, the rate of decay of the CIP should correspond to the rise time of formation of the ions. Mataga, however, observed that for intermolecular system the rise time of formation of free ions is somewhat shorter than the fluorescence decay of the exciplex.[78b] One group of workers attributed this to direct formation of some SSIP's without the intervention of the CIP.[41,21–23,78] Others suggested that the unrelaxed CT state, rather than the relaxed fluorescent state, may be the precursor for radical ions.[86] The relative magnitude of ion formation by dissociation of CIP and by direct electron transfer in collision complex varies from case to case.[78b,83] In some cases the relaxed fluorescent state is supposed to be the precursor for ions.[87] Whether a CIP is formed directly or indirectly from the precursor SSIP depends on several factors such as dielectric constant of the medium, ΔG of the reaction, charges of the species, and ground-state distance distribution.[88,23]

The dynamics and thermodynamics of CIPs are further complicated by specific interactions (such as hydrogen bonding).[84] In alcohols, the solvation of the exciplex competes with strong association of the solvent. Due to this the gain in stability caused by solvation is not considerable.[85] Studies with isodielectric mixtures of aprotic and protic solvents indicate that lifetimes are longer in protic solvent mixtures than in aprotic solvent mixtures. This indicates that the barrier height between CIP and SSIP is larger in protic than in aprotic solvents.[18]

2. Conformational Effects

Verhoeven and co-workers studied photophysical properties of the D_1–D_2–A system, linked by saturated hydrocarbon bridges with various degrees of flexibility.[92] Electrostatic forces strongly modify the conformational dynamics occurring after the initial charge transfer especially in solvents of low dielectric constant. For a flexible bridge system this allows the occurrence of multiple exciplex emission from widely different conformations ranging from fully extended to fully folded. The folded species having a lower dipole moment is preferred in nonpolar medium while charge separation increases in polar medium by migration of the positive hole to the second donor. It is suggested that the through-bond interaction considerably extends the distance of not only initial charge separation but also of radiative recombination.

Inai et al.[93] studied D,A pairs covalently linked with an α-helix chain of synthetic semirigid helical polypeptides and compared the results with corresponding simple peptides. The separation distance and orientation of D (=DMA, dimethylaniline) and A (=naphthyl) groups were varied by inserting different numbers (m) of alanyl $[(NHCH(CH_3)CO)_m]$ units. The estimated center-to-center and edge-to-edge distances are about 8 and 5.5 Å, respectively, for both $m = 0$ and $m = 2$, while for $m = 1$, the corresponding distances are about 1.5 times larger. No exciplex emission could be observed for the $m = 1$ case, indicating that the electron transfer occurs through space. The favored orientation of D,A groups is head-to-tail in $m = 0$, but head-to-head in $m = 2$. The naphthyl fluorescence quenching efficiency was found to be insensitive to orientation. However, exciplex fluorescence intensity is greater for the face-to-face orientation ($m = 2$) than for the head-to-tail ($m = 0$) one. Similarly, it has been found that the meso form of the Tp_2O (Tp = tripticenyl) derivative, with one napthalene group in one Tp unit and a tertiary amine group on another Tp unit, does not exhibit exciplex luminescence, but the raecemic form does.[94] In fact, in this case the exciplex luminescence is used for finding the energy barrier through which one form is converted into another.

The exciplex fluorescence from poly-*N*-vinylcarbazole (PVCz) doped with acceptors like dimethylterephthalate has been well-studied. From the studies on a small model compound Hoyle[100a] inferred the presence of an exciplex and two kinds of exterplex in solution, one corresponding to the sandwich and the other to the partial overlap configuration of two carbazole moieties as in isotactic and syndiatactic PVCz, respectively. Time-resolved studies in solution[100b] and film[100c] support this conclusion. In film, the relatively slow formation of relaxed fluorescent CIP from nonrelaxed excited ion-pair state competes with thermal dissociation into free carriers.

The conformation of the exciplex may not be the same as that of the ground-state EDA complex. In glassy media both EDA fluorescence and exciplex fluorescence with characteristically different lifetimes have been observed by Lim et al. for tricyanobenzene (TCNB)–ether complexes.[91a] It seems that the conformation in glassy medium is not same as that in fluid medium, as assumed by Mataga and Murata to explain the large decrease in radiative decay rate of a TCNB/benzene complex in glassy media.[91b] For freely diffusing radical pairs, conformational multiplicity is difficult to detect, although such possibility exists, e.g. for azines.[91c]

3. Exterplex

Usually the donor–acceptor interaction takes place in a 1:1 ratio, but exciplexes containing more than two species are well-known. These play an important role in photochemical reactions[105–109] and in the primary step in photosynthesis.[110–113] Termolecular complexes or exterplexes have been reported even for inorganic systems.[115] Electron hopping between two identical donors may be responsible for resonance stabilization of exterplexes. The exterplexes are formed usually in solvents of high polarity and are evidenced by a red-shift of the emission maximum as well as a quenching of the exciplex emission. They are more easily formed when the donor–acceptor groups are linked.[92,106,113] For instance, *N*,*N*-dimethyl-3-(1-naphthyl)propylamine forms ternary complexes with pyridine, dioxane, triethylamine, DMF, etc. In some cases the acceptor may be linked with two donor moieties.[21] Using time-resolved methods Itoh and co-workers studied triplet exciplex formed by 1,3-dinaphthylpropane as acceptor and 1,4-dicyanobenzene as donor in dioxane medium.[109] They suggested that the trimethylene chain locks the molecule in a favorable conformation. When the emission spectrum of the exterplex is not much different from that of the exciplex, evidence for a 1:2 complex is obtained from the Stern–Volmer quenching plots as observed for quenching of the anthracene–DMA exciplex emission by excess DMA.[113] Dutta et al.[114] reported formation of fluorescent exterplex between 1,6-diphenylhexatriene/1,4-diphenylbutadiene and DMA in polar medium. The 1:2 stoichiometry was established from nonlinear dependence of intensities of acceptor and exciplex emission on DMA concentration.

Nonfluorescent complexes are also formed through the interaction of the exciplex with a molecule other than the donor or the acceptor. Analysis of the rise and decay curves of the pyrene–DMA exciplex in perfluorohexane (PFH) indicates a charge-transfer interaction between the polar exciplexes and PFH.[116] Similarly, dynamical studies and other evidences point to hydrogen-bonded exciplexes.[18,117,118] Electrostatic interactions between added salt and exciplex can also modify the luminescence and ionic dissociation behavior. The process of ion-pair formation from exciplex in electron-accepting solvents has also been presumed to involve an exterplex.

4. Organized Assemblies

The exciplex fluorescence has been studied in various organized media, e.g. micelles,[89,90] macrocycles,[95,96] liquid crystals,[97] cyclodextrins,[98] lipids,[99] and surfaces.[101]

4.1. Micelles. Micelles provide an interesting situation where both polar and nonpolar phases are present in dynamic equilibrium. Due to their dipolar or multipolar character, D,A pairs prefer to stay at the interfacial regions. Since one of the mediums for micelles or reversed micelles is invariably water, a medium of high ϵ, D,A pairs dissociate into RIP's on electron transfer. Although these RIP's have been extensively studied by transient absorption spectroscopy, concentrations of CIPs are so low that CT emission could hardly be observed. One way to observe the CT emission in micellar medium is to choose D,A pairs with zero dipole moment, where the extent of charge transfer in the CIP is small. Thus, exciplex luminescence could be obtained from complexes of octafluoronaphthalene with anthracene, pyrene, etc., in micellar medium.[90a] If either the donor or acceptor is ionic, the situation might be different. Exciplex emission between anthracene and counterions of CTAX (cetyltrimethylammonium, X = F, Cl, Br, I) micelles were observed by Wolff et al.[89] above 250 K. The existence of exciplexes below the macroscopic melting point indicates that even at low temperatures the ions have enough mobility to form exciplexes. In micelles emissions from D,A pairs joined by flexible links increase considerably.

4.2. Macrocycles. Macrocycles are interesting light-driven ionic molecular devices which on irradiation release or take up ionic species.[95] Fages et al.[96] have studied the interesting linked system of macrobicyclic anthracenocryptands (A_{nn}) in which an anthracene ring bridges an 18-N_2O_4 macrocycle. Both monomer and solvent-sensitive exciplex fluorescence were observed, indicating intramolecular exciplex formation between N lone pairs and the anthracene ring. In the case of A_{22}, the exciplex emission is suppressed in protic solvent. Apparently a H-bond between methanol and the N lone pair prevents exciplex formation by favoring an out–out conformation. Specific cations and protons are also active in suppressing anthracene–N lone pair interaction by forming bond with the 18-N_2O_4 macrocycle.

4.3. Liquid Crystals. The excimer and exciplex luminescence in liquid crystals have been studied by several groups[97] and have been reviewed recently by Weiss.[97a] Liquid crystals permit the diffusional mobility required for exciplex formation and also provide the orientational rigidity needed for polarization measurements. When the donor or the acceptor group is covalently linked to a cholesteric molecule, the ordering effect becomes pronounced.[97b] Steady-state and time-resolved studies (ordinary or circularly polarized emission) as a function of temperature revealed the presence of multiple conformers.[97a] Cholesteric order strongly influences the folding dynamics of such systems.[97c]

4.4. Cyclodextrins (CDx). Cyclodextrins are water-soluble cyclic polymers of α-amylose.[298] In the β-CDx cavity both intermolecular[98a,b] and intramolecular[98c] exciplex formation have been reported. Since the wavelength of the exciplex emission is highly sensitive to polarity of the medium, the polarity of the CDx cavity can be inferred from the exciplex emission inside β-CDx. It is observed that the polarity inside the cavity is similar to that of dioxane, as expected from the structure of CDx.

4.5. Solid Surfaces. Exciplex emission is also reported on solid surfaces.[101] The exciplex emission wavelength is insensitive to the pore size of silica and suggests a low polarity environment, apparently provided by the unimolecular layer of the electron donor–acceptor (EDA) complex. The sensitivity of the yield of exciplex emission to the pore size has been attributed to the restriction imposed on attaining the favorable orientation due to surface irregularity.

5. Competition with Chemical Reactions

Nonluminescent exciplexes are frequently postulated as intermediates in chemical reactions.[3a,3c,44t] Direct evidence about an exciplex intermediate is, however, obtained only if the exciplex is luminescent.[3a,c,j] We will discuss a few recent examples where the CT luminescence and reaction yield are studied parallely to prove the intermediacy of CIP in chemical reaction.

Ci and Whitten studied oxidative fragmentation of amino alcohol using luminescent exciplexes with 1-amino 2-alcohols as donors and dicyano aromatics as acceptors.[87] Both exciplex fluorescence and photofragmentation rates are observed to be closely correlated in the intermolecular reaction and both attenuate when the solvent polarity is increased. This has been explained by assuming a luminescent CIP exciplex as the reactive intermediate. The rates of both radiative decay and photofragmentation are supposed to be small compared to the back-electron-transfer process and thus instead of one growing at the expense of the other, both are identically affected by a change in the back-electron-transfer rate. When the donor and the acceptor are joined by short chains, an enhancement of fluorescence and photofragmentation efficiencies compared to the intermolecular case, is observed, but the two rates are now anticorrelated with respect to a change in solvent polarity or base strength. It is suggested that, in the intramolecular case, the two rates, being much larger than the back-electron-transfer rate, compete with each other. A similar conclusion regarding the intermediacy of a fluorescent CIP exciplex in the photoreduction of phenazine, acridine, and anthracene in presence of DMA has been arrived at by Usacheva et al.[122] from the parallelism of the quenchings of exciplex fluorescence and the photoreduction by butyl methacrylate, a selective exciplex fluorescence quencher. Aloisi and Elisci[123] simultaneously studied yields of exciplex fluorescence and intramolecular cis–trans photoisomerization of five *trans*-*n*-styrylphenanthrene isomers (n = 1, 2, 3, 4, 9) using several amines [tributylamine (TBA), diethylaniline (DEA), and bromodimethylaniline (Br-DMA)] as donors in hexane solvent. Some of them are slightly fluorescent and slightly reactive complexes, while some others are highly reactive, but practically nonfluorescent. In between these two extremes there are systems that are moderately reactive and fluorescent. The heavy atom in the quencher amine (Br-DMA) has been found to quench fluorescence and simultaneously enhance isomerization yield, indicating that isomerization is preceeded by intersystem crossing in the exciplex. However, in a heavy atom containing solvent where the ISC takes place by a direct route, exciplexes were found not to enhance the quantum yield of photoreaction.[123] The thermodynamic and kinetic parameters for the system are obtained from pulse-fluorimetric studies.[123b]

6. High Pressure and Supercritical Fluids

Application of very high pressure changes viscosity of the medium at constant temperature. This affects both the equilibrium and kinetic parameters of exciplex formation and decay and has been discussed by Drickamer and others.[121a,b]

Recently Brennecke et al. studied exciplex formation in supercritical fluids.[121c] The latter refers to fluids near critical temperature and as such slight changes in pressure and temperature cause the property of the medium to change considerably. Formation of the naphthalene–triethylamine (TEA) exciplex has been found to be affected significantly in supercritical fluid CO_2. At 35 °C, near the critical point of CO_2 (31 °C and 73.9 bar), the ratio of exciplex to normal fluorescence increased dramatically with increase in pressures, but such pressure dependence is not observed at 50 °C, which is just 19 °C above the critical temperature. The observation has been interpreted in terms of change in activation volume and solvent clustering around the polar ($\mu \approx 11$ D) exciplex (electrostriction). The exciplex formation process can be represented as

$$A^* + Q \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} (AQ^*)_{TS} \rightarrow (AQ^*)$$

The pressure dependence of k_3 is given by

$$\frac{d\,(\ln k_3)}{dP} = -\frac{\Delta V^*}{RT}$$

where ΔV^* is the activation volume ($\Delta V^* = \bar{\nu}_{TS} - \bar{\nu}_A - \bar{\nu}_B$). Apart from the normal equation of state contribution to ΔV^*, there should be an additional contribution due to the electrostriction by the exciplex, which can be expressed as

$$V_2 = -\frac{\mu^2}{r^3}\left(\frac{\partial}{\partial P}\frac{(\epsilon - 1)}{(2\epsilon + 1)}\right) \qquad (6)$$

where ϵ is the dielectric constant and r the radius of the cavity. The electrostriction is overwhelming and causes the activation volume to be large and negative. Thus $d\,(\ln k_3)/dP$ has a large positive value.

7. Effect of Electric Field

An applied external electric field not only can orient the dipoles but should also influence the ionic dissociation process.[44a–l] The electric field studies are difficult and very few are on exciplex fluorescence. It has been shown that prompt fluorescence amplitude (from chlorophyll) of nonoriented photosynthetic reaction centers is increased by an applied electric field.[44a–l] For an exciplex formed in polyvinylcarbazole film doped with acceptors, the exciplex decay rate is increased by application of a field presumably due to electric-field-assisted thermal dissociation into free ions.[100c] In the case of phthalocyanines the excited singlet state with considerable CT character subsequently dissociates to form an ion pair. An electric field assists the ion-pair formation and quenches the fluorescence by lowering the Coulombic barrier.[90b]

B. CT Emission in Supersonic Jet

Exciplex emission in the vapor phase offers a means to study the CT state free from any complications due to interaction with solvent molecules. Although luminescent rare gas exciplexes have been extensively studied because of their importance in excimer lasers, the low vapor pressure of organic molecules below their decomposition temperatures and consequently low probability of exciplex formation prevented extensive gas-phase exciplex luminescence studies. The organic gas phase CT luminescence was reported by several groups around 1978.[60] However, spectral broadening and congestion made unambiguous conclusions rather difficult. A supersonic jet provides a cold beam of isolated molecules and is ideal for the purpose of providing information about the statics and dynamics of PES. Jet cooling prevents NR decays including chemical reactions and thus allows emission from the exciplex to be intensified. In several cases CT emission has been observed in jet but not in solution.[11,74] In case of jet-cooled molecular mixtures, the components are bound in the ground state by a van der Waals interaction and it is possible to pump the system directly to the CT state or to the LE state,[61–65] the latter being more common. The first observation of jet fluorescence of a CT complex was reported by Levy,[61] which was followed by reports of exciplex fluorescence by Itoh[63,66] and Prochrow.[67]

The appropriate potential energy curves (PEC's) for the discussion of jet fluorescence are curves a–c of Figure 1. Actual potential energy surface (PES) calculations by the "exchange perturbation" method with semiempirical correction for the change of polarizability in the excited state have been carried out for systems having perylene/anthracene as donors and benzene derivatives as acceptors.[12] As expected, complexes with donors of low ionization potential have the CT state as the lowest state and give CT fluorescence, and those with donors of high ionization potential have the lowest minima corresponding to the LE state and give LE fluorescence. In some cases double minima with a small barrier can be obtained in the PES. Dual luminescences originating from the LE and CT states have been observed for a number of systems.[11,63,64,68–74] Although the bands are too broad to derive structural information, it is frequently assumed that the LE and CT luminescences originate from two different isomeric conformations. The relative ratio of LE and CT luminescences depends sensitively on the relative rates of various dynamical processes, such as intramolecular vibrational relaxation (IVR) and barrier crossing, the latter being dependent on the density of states near the crossing point. Even in a closely analogous molecule, the dual luminescence may reduce to single luminescence, due to slight change in relative rates of competing processes. Thus, only broad CT luminescence has been observed for quite a few molecules[11,65,68a] while only perturbed structured LE fluorescence has been observed for others.[11,69–74] Attempts have been made to rationalize the observed ratios of CT to LE luminescences.[74b] Proton transfer has been suggested to be a specific deactivation channel for some conformers of complexes of primary and secondary amines.[68]

The interesting question whether the two conformers, attributable to the CT and LE luminescences, have the corresponding ground-state conformers as their precursor, or whether there is a dynamic excited state transformation from one conformer to another, has been addressed to by several workers. The answer depends quite markedly on the system concerned. Itoh et al. concluded that the van der Waals complex of 6-MCNN [(methylcyano)naphthalene] and TEA transformed to the exciplex on excitation of vibronic bands of the complex, but no exciplex formation was detected on excitation in the origin band of the complex.[73] It is believed that excess vibrational energy in the LE state helps the system to crossover to the CT state. In case of 4-MCNN and TEA, however, they conclude that two ground-state van der Waals complexes of different geometrical structures, on excitation, provide two different LE luminescences but the same CT fluorescence, the transformation to the CT state being helped by excess vibronic energy.[73] For the fluorene/9-ethylfluorene–hexadiene (Fl/9-ethyl Fl-HD) system, Ito and Hayashi observed a double exponential decay for exciplex fluorescence with decay times of 3–6 and 30–60 ns, which they attributed to structurally unrelaxed and relaxed exciplexes, respectively.[72] Moreover, they noticed a remarkable increase in exciplex fluorescence accompanied by a spectral red-shift with increasing diene pressure, from which they concluded that more than one cluster size was present. They proposed a rather complex mechanism involving transformation between LE and CT conformers in the excited vibronic state and vibrational relaxation in each conformer. Anner and Haas, on the other hand, reported two geometrically different ground-state van der Waals complexes between perylene and ammonia, one giving predominantly LE luminescence and the other more CT luminescence.[74] Although exciplex fluorescence could not be detected for the perylene–1-chlorobutane/1-chloropentane (Prl-1-Clb/1-Clp) system, Motyoka et al. concluded that there exists multiple conformers in the ground state and that activated barrier crossing occurs between conformers in the excited state.[71] In the complexes of anthracene–DMA and perylene–monomethylaniline, the fluorescence excitation spectrum may be rationalized by assuming two isomeric forms with different fluorescence spectra and different time-evolution of the excited state. The barrier between the two forms is supposed to be large enough to prevent isomerization in the excited state for limited-energy excitation.[70] In case of anthracene complexes with diethyl ether (DEE) or anisole, substitution of at the 9,10-positions with a CH_3 group results in the appearance of structured excitation and emission bands, while substitution in the 2-position leads only to minor changes in the fluorescence characteristics. These results have been interpreted in terms of an orbital orientation model involving localized electron transfer.[69] Substitution effects have similarly been studied for the 1-CNN/TEA system. It is found that intra- and intermolecular vibrational energy redistribution is more efficient for the 4-methyl derivatives of 1-CNN.[73]

The mode specificity of exciplex formation under supersonic beam conditions was originally demonstrated for the 1-CNN–TEA system, where large changes in exciplex fluorescence yield were observed upon excitation of the low-frequency intermolecular mode coupled to intramolecular modes.[64] Recent studies of the anthracene–DEA exciplex system have also clearly demonstrated that reaction pathways do not depend only on the total amount of excitation energy but also on the particular low-frequency mode that was excited.[75] A rather unexpected observation has been reported for the 2-CNN–DMB (2,3-dimethyl-2-butene) exciplex, where the excitation at 722 cm^{-1} above the 0–0 band actually causes a decrease of CT/LE emission ratio relative to the 0–0 excitation.[11] Apparently, potential energy surfaces for each intramolecular vibronic mode are not parallel to each other. Indeed, from a model calculation Prochrow concludes that mode specificity is not a general phenomenon, but depends on special relationship of various surfaces and rates in specific cases.[12]

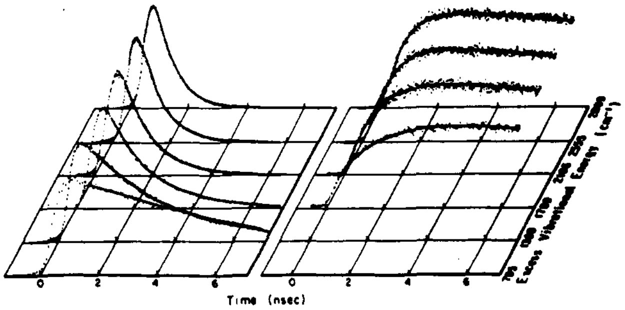

Figure 4. Observed time-resolved fluorescence intensities for the decay of the initially excited anthryl type state and the formation of the exciplex as a function of excess vibrational energy (from ref 62; copyright 1984 American Institute of Physics).

CT jet luminescence from chained D/A systems have been studied by Zewail and co-workers with $D(CH_2)_3A$, where D = DMA and A = anthracene, and the conclusions are more or less similar to those for unchained van der Waals complexes of D and A.[62] Time-resolved CT and LE fluorescence measurement (Figure 4) as a function of specific vibrational energy above the zero-point level of the S_1 state led to the following conclusions: (i) Intramolecular vibrational relaxation is much faster than reaction at all excess energies studied and hence no mode specificity could be observed. (ii) The energy threshold for product formation is approximately 900 cm^{-1} (2.6 kcal/mol), which may be considered as the barrier height for the CT product formation from the LE state. (iii) The CT state has a stabilization of $\Delta H = -9.2$ kcal/mol with extensive charge transfer—similar to what is observed in nonpolar solution. (iv) Four torsions were identified as critical to the reaction dynamics which could be modeled according to a multidimensional reaction coordinate using a RRKM scheme. (v) The dynamics is faster (540 ps) in jet than in solution (ca. 1.4 ns), apparently caused by interference by solvent in the chain-folding motion. The conclusions, rich in details, illustrate the power of time-resolved jet spectroscopy, but these need to be generalized by more extensive studies on similar systems. A general pattern is yet to emerge from all the detailed jet spectroscopic works on specific systems.

C. Magnetic Field Effect (MFE) on Exciplex Luminescence

1. Experimental Techniques

The exciplex luminescence may be produced by chemical/electrochemical reaction,[124] by high-energy synchrotron radiation (producing oppositely charged ions),[154] or near-UV excitation. If the magnetic field effect is large, as in the case of some linked systems, no special techniques for studying emissions are required, it is enough to connect an X–Y chart recorder directly to the DC signal of the photomultiplier.[52] In many cases, however, the MFE constitutes less than 2% of the total luminescence. In such cases the signal-to-noise ratio is increased by using a sinusoidally varying magnetic field produced in a Helmholtz coil and phase-locking the luminescence detector with it.[125,153] Instead of modulating the whole field, a small modulating field may be superimposed on a static field. This allows one to perform derivative spectroscopy.[52,126,127] Very small changes in chemiluminescence have been measured in this way, and the mechanism of chemiluminescent reactions, such as luminol oxidation, has been unravelled.[127b] Since the phase-sensitive detection measures only the fundamental Fourier component of the signal waveform, care must be exercised with quantitative measurements, for the exciplex fluorescence intensity does not vary linearly with field. A light chopper method with slowly scanning magnetic field is preferred for very accurate quantitative measurements.[52] RYDMR techniques, where a microwave field is used for causing transitions between triplet sublevels and thereby influence the fluorescence intensity, can provide additional information.[128]

The optical method for studying radical–ion pair (RIP) is intrinsically capable of providing high time-resolution. Time-resolved magnetic field effect can be obtained by standard time-correlated single-photon-counting technique if the MFE is appreciable.[129–137,160] In order to increase the reliability several checks are required.[129,134,136] Time-resolved RYDMR measurement is also a powerful technique and involves capturing the fluorescence decay curves repeatedly in the presence and in the absence of a microwave radiation resonant with the applied magnetic field and finding the difference between their averages.[130]

It is pertinent to point out that elegant methods have been developed to monitor processes which compete with RIP recombination resulting in exciplex fluorescence. The molecular triplet formation (i.e. $^3A + D$) has been studied by both delayed fluorescence[139] and transient absorption,[140] while the radical ion yield has been followed by photoconductivity[141] as well as transient absorption.[142] A two-step laser excitation technique has also been used.[143] Resonance techniques are capable of providing detailed information on the spin state and nature of radicals.[44u,s]

2. MFE: Steady-State Exciplex Emission

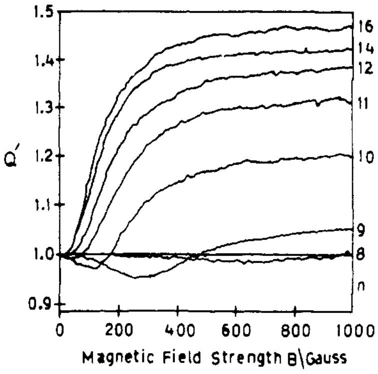

Figure 5. Exciplex luminescence intensity of Py–$(CH_2)_n$–DMA plotted against magnetic field for various n (from ref 158; copyright 1985 Elsevier). The shape of the free ion pair curve is similar to $n = 16$, but the magnitude is much smaller.

2.1. Unlinked System. The reasons for the magnetic field dependence of luminescence intensity have been discussed in section II.B.3 and II.B.4. The shape of the luminescence intensity vs magnetic field curve depends on whether the donor and the acceptor is linked or not. In case of unlinked systems, the general shape of the curve is illustrated in Figure 5. It is consistent with the $J = 0$ case discussed in section II.B.4, as is expected for freely diffusing pairs. One useful parameter in such cases is $B_{1/2}$ or the field at which the MFE reaches half the saturation value. Since the saturation occurs when the level degeneracies are completely removed, the $B_{1/2}$ depends, in general, on the spread of the levels. Common causes for the spread are hyperfine interaction (HFI), uncertainty broadening, dipolar-interaction-induced zero-field splitting. In most cases the $B_{1/2}$ (extrapolated to zero concentration of donor) has been correlated with the average hyperfine interaction present in the two radicals[144,145] either obtained experimentally from ESR measurements or calculated theoretically.[146,147] When the observed $B_{1/2}$ is greater than the HFI,[114,17] other explanations need to be invoked. For example, if the donor/acceptor concentration is increased, $B_{1/2}$ has been found to increase.[17,148,149,150] Similarly, exterplexes of the type D_2A have $B_{1/2}$ higher than the calculated value.[114] On the basis of the observation in transient absorption studies that the $B_{1/2}$ for a short-lived radical pair (RP) is greater than that for a long-lived RP, it was proposed that uncertainty broadening occurs due to shortening of residence time caused by rapid electron exchanges between D and D^+ at high concentrations. The influence of the hopping rate on the spin-evolution rate has been analyzed theoretically by Schulten et al.[51,144,166] If, however, instead of adding the same donor D to the mixture, another donor D′ with the same hyperfine constant (HFC) as the donor D was added, the increase in $B_{1/2}$ was identical, although the hopping rate is expected to be lower in the mixed-donor case than in the single-donor case.[153] Lifetime variation by addition of quenchers did not change $B_{1/2}$.[169] It has been suggested that additional unbound or bound donors present in the immediate environment of the exciplex influence the average hyperfine coupling of the exciplex.[153,169] Tanimoto et al. noted that even linked systems behaved in an analogous way with respect to increase in concentration of free donors and suggested structural changes in the exciplex as an additional cause.[154] $B_{1/2}$ for the RIP formed from quinone-depleted chlorophyll, is greater than that expected from hyperfine parameters. This has been ascribed to a dipolar interaction between radicals which causes a zero-field splitting in the triplet state and leads to a complicated spin-evolution process.[44a–i,155] Similarly, apart from electron hopping between two DMA units, anisotropic dipolar interaction could be another reason for higher $B_{1/2}$ for the 1:2 complex between diphenylhexatriene (DPH) and DMA.[114]

Frequently MFE increases sharply with field initially and at a slower pace subsequently. The initial sharp increase is commonly ascribed to the HFI mechanism and the slow increase to relaxation mechanism. Okazaki et al.[156] studied MFE on luminescence from the X-generated Py^+/Py^- system as a function of temperature, medium viscosity, and quencher concentration with a view to determine the relative contributions of the two mechanisms. For decane (a low-viscosity medium) as well as ethylene–propylene rubber (a nearly rigid medium), the relaxation mechanism has little contribution and the magnetic field dependence is sharp, whereas for squalene (a viscous fluid) the relaxation mechanism contribution is significant and the fluorescence continues to increase even at 300 mT. Quencher reduces the slow-rise part (relaxation mechanism contribution) in squalene medium. The observed data were interpreted in terms of relative value of $(\bar{T}_g T_R)^{1/2}$ and $(\gamma H_{loc})^{-1}$, where T_g is the average recombination time, T_R the viscosity-dependent rotational correlation time, γ the gyromagnetic ratio, and H_{loc} the randomly modulated field perpendicular to the applied field direction which induces the spin–lattice relaxation.

The ϕ vs H curve is rather flat in the low-field region.[126] This is consistent with the $J = 0$ theoretical calculation.[52] Indeed, in some cases under higher resolution the magnetic field dependent reaction yield (MARY) spectrum of free D,A pairs reveals a small negative slope.[126] The low-field minima in the ϕ vs H curve was also obtained previously in the case of recombination of pulse-radiolytically produced ions from C_6F_6 and was ascribed to interference between different S-T_i channels.[44a–o,151]

2.2. Linked System. A fairly marked difference between linked and unlinked systems in the dependence of luminescence yield on magnetic field H has been observed.[52] The first and the most extensive studies have been made by Weller et al.[157,158] with the system Py–$(CH_2)_n$–DMA (Figure 5). They have found that the exciplex fluorescence yield is extremely sensitive to the number of methylene links. For $n \leq 6$, the fluorescence yield is high and nearly independent of H. This has been ascribed to interference with spin evolution by a large exchange interaction, J. For $6 \leq n \leq 12$, the fluorescence yield decreases with n and exhibits a minimum before increasing to a saturation value. This minimum gets less and less pronounced with increasing n. Also, the field at which this minimum is obtained decreases with increasing n. The minimum in the experimental curves is obtained due to T_-/S level crossing. The field at which this minimum is obtained may be related to the exchange interaction J by the relation $B_{min} = 2J_{eff}$, where J_{eff} is the J corresponding to the average end-to-end distance. The longer the chain length, the smaller the value of J and consequently, the smaller the B_{min} and the greater the spin evolution. Finally, for $n \geq 12$, the RIP's behave as if they were free, which is manifested by the disappearance of the inflexion point. The last observation that long-chained systems behave like unlinked systems has been confirmed by Basu et al.[160] from studies on a polystyrene polymer ($\bar{M}_n = 4770$) containing pyrene as one end group and DMA as the other.

It has been observed that a decrease in temperature and increase in solvent viscosity shift B_{min} and $B_{1/2}$ to lower values, but the dielectric constant variation with isoviscous media has practically no effect.[52,159] Theoretically, it has been demonstrated that the effect of slowing down the motion is equivalent to a shift in the probability distribution of J, $\omega(J)$, and consequently J_{eff}, toward lower J.[52,51] This explains the changes of the curve observed on lowering the temperature. Consistent with this concept, polyether chain $-(CH_2\text{-}OCH_2)_m-$ with inherently higher flexibility than an alkane chain (as apparently from pyrene lifetime measurement) has a $B_{1/2}$ higher than that of an alkane chain.[52]

The shape of the ϕ vs B curves has been utilized to obtain information on interaction in polymers which are not so well-defined. The exciplex fluorescence from copolymers of phenanthrene and DMA has been studied by Tanimoto et al.[164] The curves are similar to $J = 0$, from which it was concluded that exciplexes are formed between non-nearest neighbor phenanthrene and DMA moieties. The possibility of the electron hopping from one unit to another in this system was pointed out by Steiner and Ulrich.[44s] In a linked system it is possible to maintain high local concentration of DMA around the pyrene and yet effectively stop DMA-to-DMA hopping. The $B_{1/2}$ in such cases is found to be the same as the low concentration-limiting value for the unlinked system.[160]

3. MFE: Time-Resolved Exciplex Emission

The temporal dependence of MFE has helped to unravel the intricate details of spin evolution. Fairly extensive studies have been carried out on triplet RP's and RIP's generated by flash photolysis or pulse radiolysis. Brocklehurst[161] obtained RIP's by the latter technique and time-resolved the emission from the recombination product. Nolting et al.[148,162] performed flash-photolytic studies on triplet RIP's and found that the MFE has an initial latency of about 10 ns, which is followed by a growth period of about 30 ns in acetonitrile and 60 ns in methanol. Similar observations regarding the spin-evolution process were made by Nath et al.[163] and Basu et al.,[136,137] who carried out time-resolved studies on exciplex luminescence of freely diffusing pairs. They found that, in both Py–DMA and cyanophenanthrene (CNP)–anethole systems, the magnetic-field-modulated luminescence $\Delta\phi$ reached a maximum in about tens of nanoseconds and then decayed, while $\Delta\phi/\phi$ reached saturation in about 60 ns. The curves were fitted by coupling Hong and Noolandi's analytic solution[82] of Smoluchowski's diffusion equation with the simplified assumption that spin evolution is linear up to a limiting time and then remains steady. From a comparison of the calculated and experimental curves, it was found that the spin evolution takes 12 ns to saturate out.[136,137] In a bid to separate the luminescences from different species and formed by different routes, Lavrik et al.[135a] made a detailed study of Py/DEA exciplex luminescence in methanol as a function of time delay, wavelength of luminescence, and pyrene concentration. At times shorter than 50 ns the field effect was positive but very small, and this was ascribed to interference from nonmagnetosensitive excimer fluorescences. At very long times, greater than 10 μs, the MFE is negative, which has been ascribed to re-formation of CIP formed by a T-annihilation process. A maximum positive MFE of 88% was observed for a delay of about 130 ns (for λ > 600 nm). At this time delay, they observed that concentration dependence, unlike steady-state concentration dependence, is nonmonotonic, the maximum being at 0.05 M DEA. The experimental results were schematically explained with the help of a model. Following the approach used by Schulten et al. for calculation of triplet yield,[166] they calculated the singlet yield at any time T from the equation

$$\phi_S(B,T) = \int_0^T \rho_S(T,B)\dot{n}(t)\,dt \qquad (7)$$

where $\dot{n}(t)$ is the spin-independent total recombination rate calculated for different hopping frequencies. The theoretical curve, however, showed only monotonic increase with concentration of DEA, and the magnitude of MFE was much less than what was observed for 130-ns time delay. The fit significantly improves as regards shape and magnitude, if the lower integration limit in the expression above is taken around 10 ns instead of 0 ns. This has been taken to mean that the RIP's are born at distances greater than the contact distance, which naturally increases the proportion of magnetosensitive delayed radical-recombination part of the luminescence at t = 130 ns.

For chemically linked RIP systems, Staerk et al.[159] and Tanimoto et al.[164] obtained decay curves in the presence and absence of magnetic field. Basu et al.[160] carried out similar experiments with large-chain Py-(polystyrene)-DMA ($\bar{M}_n$ = 4770) and compared the results with those of the free Py-DMA system. It is found that inspite of the fact that the lifetime of the polymer-linked exciplex is much longer than that of the unlinked exciplex, the magnetic effect is similar. This was ascribed to saturation of the spin evolution after about 10 ns. One advantage of the chosen polymer was that, the growth of the exciplex emission being slow, MFE could be studied directly on the growth process. It was observed that MFEs on the growth and decay processes were are nearly equal. This implied a reversible CIP-SSIP equilibrium.[160]

In case of linked systems, the decay of the exciplex is found to be magnetosensitive and multiexponential, in general. For Ph-$(CH_2)_n$-DMA Tanimoto et al.[154] ascribed the two decay times to the presence of two conformationally different exciplexes, one magnetic-field sensitive and the other insensitive; Staerk et al.,[52] on the other hand, ascribed the multiexponentiality of Py-$(CH_2)_n$-DMA to the complexity of the kinetics (e.g. distribution of lifetimes and spatial and spin evolution). Both Tanimoto and Staerk et al. found that the decay times are affected by temperature to a much smaller extent than the rise time. While Tanimoto interpreted it as due to smallness of the barrier height between RIP and CIP, Staerk et al. ascribed this to the inherent small T dependence of the ISC process.

There have been several reports on quantum beats in exciplex luminescence reminescent of the reversible coherent spin evolution between S and T_0 states. Klein and Voltz[165,129c] and Brocklehurst[161] observed small oscillations riding over the decay curve for pulse-radiolitically generated organic ions. Basu et al.[136,137] observed some rapid oscillations when the decay curve in the absence of field was substracted from the decay curve in the presence of field, but these were rightly interpreted as noises and ignored. Recently, Batchelor et al.[138] performed time-resolved RYDMR experiments with pyrene as donor and three isomeric dicyanobenzenes (DCNB's) as acceptors and observed some oscillations superposed on a broad signal which itself goes through a maximum with time. The magnitude and the shape of the RYDMR-vs-time curve depend on the isomer and the phase of the signal varies with time and with the strength of the applied field. A simple kinetic and spin-mixing model, which assumes instantaneous formation of the exciplex, fails to rationalize the short-term oscillation, although the other features like phase inversion, broad background signal, and conformer specificity could be reproduced. Model calculations with a finite spin-dependent recombination rate comparable to spin correlation and exciplex decay rates showed that the observed oscillation might originate from long-term S $\leftrightarrow$ T_0 quantum beat in the spin-evolution process.[138]

The time-dependence of MFE on recombination fluorescence of ion-pairs generated from aromatic hydrocarbons by high-energy synchrotron radiation has been studied by Brocklehurst, Klein, and others.[154,129] A number of cross-recombination processes such as T-T annihilation and singlet fission, interfere with the main one and reduce the MFE.[154a] Klein's[129] MFE results are consistent with T-T annihilation at long times and fission into triplets at short times. A rather complicated time-dependent MFE was observed by Brocklehurst et al.,[154a] which coupled with other evidences indicated splitting of a singlet into two triplets under high vacuum-UV excitation.

4. MFE: Solvent Effect

4.1. Effect of Polarity and Restrictions on Translational Diffusion. As already discussion, the MFE is basically an interplay of the hyperfine interaction (HFI) induced spin-rephasing dynamics and the diffusion dynamics involving the radical ion pairs. The diffusion provides the radical pair the time required for comparatively slow spin evolution in a domain of inter-radical distance where the exchange interaction is negligible. Thus the effect has a strong dependence on the re-encounter time and probability of re-encounter. Variation of the dielectric constant (ϵ) of the solvent is an efficient way to modulate these parameters for the RIP system. Exciplexes produce RP's where the potential energy surfaces are strongly influenced by the dielectric constant of the solvent.

The first observation of dependence of percentage MFE on dielectric constant of the medium in case of alcoholic solvents was made by Petrov et al.[167] They found that in the case of the Py-DEA exciplex system, the field effect is small at low and high dielectric constants and peaks at an intermediate ϵ of 26. This observation was corroborated by the studies of Nath et al.[18,168,169] and Basu et al.[17] on Py-DMA and CNP-AN exciplex systems. It was found that these systems exhibit a maximum (in the $\Delta\phi/\phi$ vs ϵ curve) at around ϵ = 28 and 40, respectively (Figure 6). But in nonalcoholic solvents, both of these systems have a maximum of around ϵ = 18, irrespective of the choice of components of the nonalcoholic solvent mixtures. Moreover, the absolute magnitude of the percent MFE ($\Delta\phi/\phi\%$) is much greater (about 9%) in nonalcoholic media compared to that in alcoholic media[18] (about 2%) although the exciplex luminescence yields and lifetimes are larger in alcoholic media.[18] The variation of exciplex luminescence ϕ and the normalized change of exciplex luminescence in the presence of magnetic field ($\Delta\phi/\phi$) with dielectric constant (ϵ) is shown in Figure 6. Very recently, Petrov et al.[20] has confirmed the above results of Nath and Basu, and additionally showed that the MFE of the Py/DMA system could be increased further

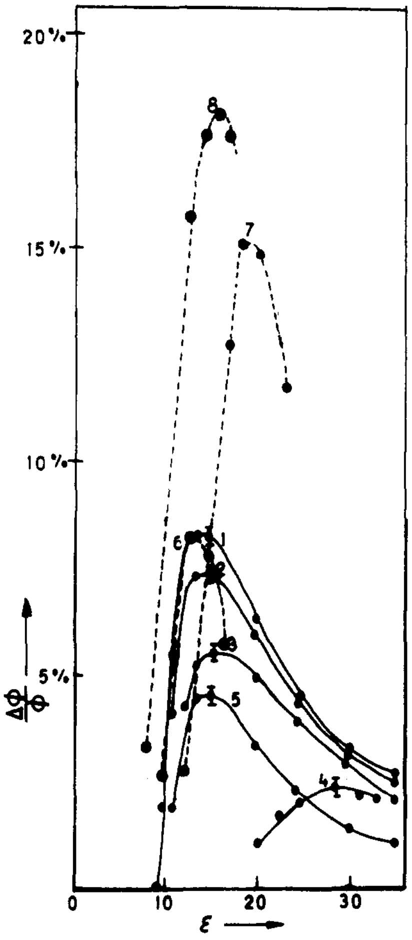

Figure 6. The percentage change in exciplex luminescence in a saturating field at different solvent composition. Curves 1–4 correspond to the Py–DMA exciplex in THF–DMF, ethyl acetate–DMF, ethyl acetate–acetonitrile, 1-propanol–methanol mixed solvents, respectively (from ref 18); curve 5 corresponds to CNP–An exciplex system in THF–DMF mixed solvents, and curves 6–8 represent $\Delta\phi/\phi$ in THF–DMF, dioxane–DMSO, and benzene–DMSO, respectively. Curves 6–8 are drawn after recalculating the average ϵ from mole % for the solvent mixtures from ref 20 (copyright 1992 American Chemical Society).

to about 18% by using a mixed solvent of bulk permittivity 16 in which one component is nonpolar (such as benzene or dioxane) and the other polar (such as DMSO) (Figure 6).

In order to have a qualitative picture of the magnetic field effect, one must consider the potential energy diagrams of the various uncharged ground and excited states and charged RIP states, which are shown schematically in Figure 2. The exciplex luminescence ϕ, is proportional to β, where β is the fraction of initially generated SSIP that crosses an activation barrier to form the luminescent CIP (or exciplex). On the other hand, the MFML ($\Delta\phi$) can be shown to be proportional to $(1 - \beta)\delta\beta$, where $1 - \beta$ is the fraction of the SSIP which diffuses outward and δ is the fraction of these escaping RIPs which recombine to form SSIP. Therefore, $\Delta\phi/\phi \propto (1 - \beta)\delta \simeq (1 - \phi)\delta$. For low dielectric media, $1 - \phi$, and hence $\Delta\phi/\phi$, is small. For high dielectric media, the potential energy curve is flat and hence δ is small. The $\Delta\phi/\phi$ therefore peaks at an intermediate ϵ.

If the RIP's are linked by a polymethylene chain (preventing diffusional excursion to large distances in high ϵ medium), the ϵ at which maximum MFE is obtained should be shifted to higher values. Indeed, it has been found that for Py–$(CH_2)_n$–DMA and Ph–$(CH_2)_n$–DMA systems there is a monotonic increase in $\Delta\phi_f/\phi_f$ with increasing ϵ.[159,164] If, however, the linking chain is very long as in the case of a regular polymer with donor–acceptor as end groups, the dielectric constant effect is similar to that of a freely diffusing pair.[160] There is, however, some interesting differences due to solvent effect on the polymer backbone itself. While for freely diffusing pairs the shape of the MFE vs ϵ curve for aprotic solvents is independent of the nature of the solvent molecules constituting the solvent mixture, in the case of a polymer-linked system, the curve is sensitive to the "good/bad" nature of the constituting solvents. The solvent-induced coiling of the backbone and the bulk permittivity compete with each other, affecting the MFE in a subtle way.[170]

Numerical calculation of the effect of viscosity and dielectric constant on the RIP system has been carried out by Schulten et al.[166c] Petrov et al.[167] formulated the problem analytically and showed that in alcohols, SSRIP → CRIP conversion involves an activation barrier on the order of 7 kT. Nath et al.[18] adopted a simplified approach where spatial and spin motions were decoupled; the Smoluchowski equation with a Coulomb potential was used for calculation of ϕ, while for calculation of $\Delta\phi$, a phenomenological leakage to the triplet surface was considered. The shape of the experimental ϕ vs ϵ and $\Delta\phi/\phi$ vs ϵ curves could be reproduced.

The behavior of alcohols in reducing MFE is fairly unique. The enhanced luminescence (ϕ) and longer lifetime in alcohols as compared to isodielectric mixtures of aprotic solvents indicate that alcohols are better cages. Effectively the alcohols form a relatively stronger hydrogen-bonded cage which limits the diffusional excursion and interferes with the spin-evolution process through exchange effects. However, an alternative explanation could be that, in alcoholic media, the hyperfine interactions are presumably reduced due to rapid hopping of hydrogen atoms. The radicals sense a fluctuating local magnetic field, which interferes with their spin evolutions. This possibility is suggested by the observation of a small change in $B_{1/2}$ on substituting CH_3OH with CH_3OD.[153] However, an alcohol effect has not been reported for ion yield measurements. It is therefore likely that the specific effect of alcohols observed in exciplex luminescence is connected with the modification of the PES by alcohols at short intermolecular distances.

Petrov et al.[20] has offered an interesting qualitative explanation of their observation that MFE in polar–nonpolar mixed aprotic solvent was much larger than that in a single solvent. They suggest that polar solvent molecules, though present in low concentration, preferentially form a sheath around the ions, reducing the exchange interaction between partners in close proximity and thus allowing spin evolution, while the low bulk permittivity ($\approx$16) does not allow the partners to stray away too far. This increases re-encounter and magnetosensitive-delayed recombination. Indeed, they could justify why MFE peak could be obtained at a bulk permittivity of 15.[20]

It has been demonstrated by Turro et al.[44p] that if a neutral RP is encaged in micelles, outward diffusion of the RP may be impeded at the boundaries leading to an increase of re-encounters and hence to an increase in MFE. The high viscosity inside the micelle might also augment the MFE process. However exciplex luminescence could not be studied in micellar environment as micelles, normally formed in water solution, have an open structure where water molecules have easy access, causing dissociation of RIP's. Dutta et al.[90] tried less polar exciplexes of octafluoronaphthalene and anthracene in uncharged Triton-X micelle and found the MFE to be only 0.3%. No micellar enhancement of MFE as normally observed for a neutral RP, could be observed in the case of exciplex luminescence.

The low-field feature of the MARY curve for triplet yield has been found to be solvent dependent. It has been observed that for Py–$(CH_2)_n$–DMA, the J resonance maxima $B_{\min}$ shifts to the lower value as one goes from acetonitrile to *n*-octyltetraoxyethylene and diethylene glycol.[129] This is consistent with theoretical ideas developed by Schulten et al.[51] and diagrammatically interpreted by Staerk et al.[52] (see section II.2.4).

4.2. Effect of Restrictions on Orientational Motion: Anisotropicity of MFE. The terms in the Hamiltonian which induce spin evolution are all, in principle, anisotropic. The MFE should therefore be dependent on the direction of the magnetic field with respect to the molecular axes. In fluid media, the rotational correlation time of the RP is on the order of several picoseconds, so that any anisotropic chemistry would not be observed. Boxer et al.[171,44a-l] observed anisotropicity in MFE in flash-photolytic study of quinone-depleted photosynthetic reaction centers where the radical pairs were held together at a fixed distance (<10 Å) such that translational diffusion effects could be disregarded. Rotational diffusion with time was brought down to the lifetime of the RP by suspending them in glycerol buffer. Anisotropic chemical reactivity in photosynthetic bacteria is more easily observed in spin-polarization studies.[172a] It has also been observed during polarized-light photolysis.[172b] Dutta et al.[114] was the first to observe anisotropicity in MFE on exciplex luminescence. They chose polyvinyl acetate in a THF/DMF mixture which provided a highly viscous medium of moderate polarity to the RIPs. Two experiments were carried out. In one, DPH molecules oriented parallelly and perpendicularly to the magnetic field were alternately selected by using suitably polarized exciting light. In another, unpolarized light was used for excitation but the emitting molecules oriented along and perpendicular to the field direction were selected by a polarizer in the emission path. A consistent difference of 0.5% between $(\Delta\phi/\phi)_{\parallel}$ and $(\Delta\phi/\phi)_{\perp}$ was obtained for both experimental arrangements. Obviously, the spin evolution and, consequently, the magnetic field modulated luminescence $(\Delta\phi/\phi)$ are dependent on the orientation of the DPH with respect to the direction of the magnetic field. Anisotropic dipolar coupling between $DPH^{\bullet-}$ and $DMA^{\bullet+}$, which is usually responsible for zero-field splitting was presumed to be responsible for the observed anisotropy.[114,44l,171]

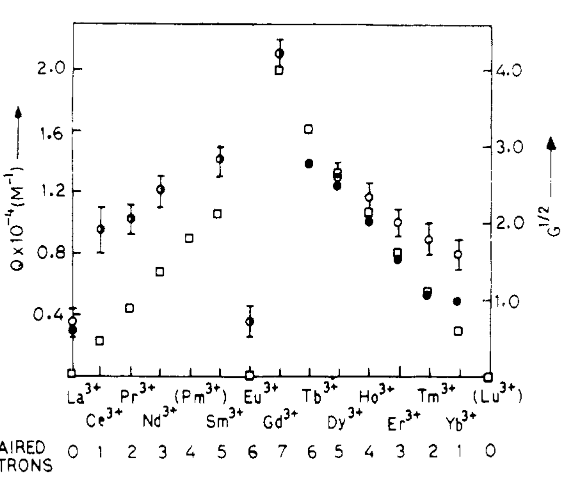

Figure 7. Plot of the quenching rate constants (Q) of the Py–DMA exciplex (○), CNP–An exciplex (●), and square root of de Gennes factor, $G^{1/2}$ (□) vs Ln^{+3} ions. Pm^{+3} and Lu^{+3} were unavailable for testing (from ref 175; copyright 1987 Elsevier).

5. MFE: Effect of Additives

The RIP spin evolution may be affected by the presence of other molecules, paramagnetic or diamagnetic, with which the RIP as a whole or one of its partners can exchange spin. The effect of paramagnetic Ln^{3+} and transition-metal ions on triplet RP's have been reported by Sakaguchi and Hayashi,[173] Turro et al.,[174] and Matsuo et al.,[173c] Shkrob et al.,[173d] Mints et al.,[173e] and Dutta et al.,[173f] for triplet RP in micellar systems. Paramagnetic ions were supposed to increase singlet ↔ triplet transitions by reopening the channels $S \leftrightarrow T_{\pm1}$ blocked by magnetic field through increased $T_{\pm1} \leftrightarrow T_0$ relaxation rate. Basu et al.[175,176] first investigated MFE on exciplex luminescence of Py/DMA and 9-CNP/*trans*-anethole in presence of various Ln–acetylacetonates. In both cases $\Delta\phi/\phi$ decreased linearly with Ln concentration and the slopes of the $\Delta\phi/\phi$ vs concentration curve were taken as a measure of the MFE-quenching efficiency of various rare-earth ions. It is found that the MFE-quenching efficiency parallels the number of unpaired f electrons in Ln^{3+} ion with a maximum at Gd^{3+} as shown in Figure 7. However, the behavior of Eu^{3+} is strikingly different. It is significant that despite wide differences in the medium, the charges of radicals, the structure of the lanthanide complexes, geneology of radicals, and method of studying MFE, all the studies lead to similar results, namely that quenching efficiency plotted against the atomic number shows a unimodal behavior characteristic of spin-only moment, and not the bimodal behavior characteristic of total moment. This correlation with the spin moment instead of the total moment of Ln^{3+} as expected for dipolar magnetic interaction is rather puzzling in view of strong coupling of L and S in rare earth ions. Basu et al.[175,176] pointed out that similar behavior was noticed in magnetic transition temperatures of solids and that this is what is expected on the basis of Heisenberg exchange interaction between the Ln^{3+} and the ^3RP. Following Elliot's explanation of the correlation between the spin moment and magnetic transition temperature in crystals,[177] Basu et al.[146,175,176] suggested that in the exchange Hamiltonian, $H_{ex} = \beta \mathbf{S}_1 \cdot \mathbf{S}_2$, the spins need to be projected onto J. Assuming $\mathbf{S}_1 \simeq (g-1)J$, where g is the Lande g factor, H_{ex} can be written as

$(g-1)\beta\bar{J}_1\cdot\bar{S}_2$. Assuming β to be constant along the Ln^{3+} series, H_{ex} becomes proportional to $(g-1)[J(J+1)]^{1/2}$ or the square root of the de Gennes factor G, which is known to play a pivotal role in determining magnetic transition temperatures in rare earths and alloys. The variation of $G^{1/2}$ along the Ln^{3+} series is shown in Figure 7, and all the interesting features of the observed curve including the dip at Eu^{3+} were qualitatively reproduced. Later on, Wang et al.[178] reached a similar conclusion via the exchange Hamiltonian commonly used in connection with lanthanide probes in ESR spectroscopy.[179] They, however, considered the relaxation times of Ln^{3+} ions in addition to the spin Hamiltonian. Tanimoto et al.[180] worked with chemically linked systems and observed a similar result, but thought that the observed correlation does not necessarily signify an exchange interaction between RIP and Ln^{3+}. The results can be equally well explained by magnetic dipolar interaction familiar in the theory of spin probes in ESR.[181] However, the magnetic dipolar interaction invoked by them is unable to explain some of the features of Figure 7, particularly the anomalous position of Eu^{3+}.

The spin exchange between D^+ and D has been discussed in section III.C.2 in connection with donor concentration effect on $B_{1/2}$. The effect of addition of stable radical on the Py/DMA system in ethanol has been studied by Petrov and Frankevich.[182a] The radical effects on MFE are believed to occur through a spin–lattice relaxation process.[182a] The MFE on electrogenerated chemiluminescence has been found to be sensitive to electrolyte concentration.[182b] Here the mechanism seems to be a Coulombic interaction between the salt and the ion pairs.

IV. Twisted Intramolecular Charge Transfer Process

A. Overview

Lippert first reported that while *p*-(dimethylamino)benzonitrile (DMABN) exhibits a single emission band at around 360 nm in nonpolar solvents, in polar solvents an additional emission band with very large Stokes' shift appears at around 450–500 nm.[183] Since then the dual-emission phenomenon of DMABN continues to fascinate and intrigue a vast number of workers.[4,184–209,260–267,278–294,300,301] Lippert originally proposed that there are two excited states, a highly polar (^1L_a) and a relatively nonpolar (^1L_b) state responsible for the long- and short-wavelength emission, respectively. In nonpolar solvents the "nonpolar" state (^1L_b) is lower in energy compared to the ^1L_a state. In polar solvent however the polar state (^1L_a) is stabilized more by solvation than the "nonpolar" state and becomes the lower energy state at sufficiently high polarity. The dual emission of DMABN is thus attributed to the reversal of the energy ordering of the two states. A more complete description of the dual-luminescence phenomena is provided by the concept of twisted intramolecular charge transfer (TICT) introduced by Grabowski et al.[4] According to this concept, upon electronic excitation DMABN initially forms a locally excited (LE) or "nonpolar" state with geometry and dipole moment (6 D) similar to those in the ground state (Figure 8). In polar media, subsequently an electron is transferred from the donor (dialkylamino) to the acceptor (cyanobenzene) and simultaneously the donor undergoes a twist. This twist makes the donor orbital orthogonal to the acceptor orbital, which ensures complete electron transfer. The resulting state is highly polar (μ = 16 D)[197,206–211] and is known as a TICT state. The main evidence in favor of this concept includes the large dipole moment of the TICT state,[206–211] observation of a cyanobenzene anion like species in picosecond transient absorption,[190,191] lack of TICT emission in structurally rigid, planar DMABN analogues, and the fact that when substitution by bulky groups at the ortho positions forces DMABN to be twisted in the ground state, TICT-like emission is observed without the requirement of the polar solvent.[4,187,197] This concept survived some early criticisms[205] and has been observed for a wide range of molecules.[184–230,254–285] The structures of TICT molecules discovered before 1986 is summarized by Rettig.[186] Recently, apart from molecules containing dialkylamino or arylamino groups,[268] TICT is reported for a host of other molecules such as amides,[225] aminosalicylate,[228] nitro aromatics,[210] diarylindenes,[258] sulfones,[199] aryldisilanes,[222,274] triphenylphosphines,[277] and biaryls.[208,209,227,240–251] Though dual emission is observed for many compounds,[4,213,221] in most cases the TICT state is found to be nonemissive, presumably due to rapid nonradiative decay from the TICT state. In the following sections we will discuss how the dynamics of the TICT process is affected in different media such as homogeneous solution, collision-free supersonic jet, and organized assemblies.

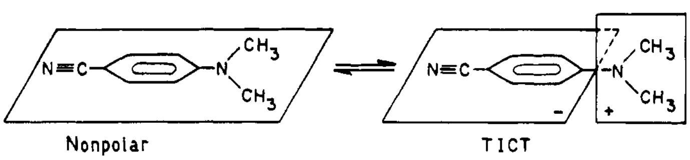

Figure 8. TICT processes in DMABN.

B. Solvent Effects on TICT Emission

1. Polarity versus Viscosity

The TICT process involves charge transfer as well as twisting. An increase of polarity is expected to stabilize the TICT state by solvation and hence should favor the TICT process. On the other hand, an increase in viscosity is likely to hinder the twisting motion. For DMABN, the rotating group (NMe_2) is quite small and hence the TICT process for DMABN does not involve significant displacement of solvent molecules. Thus solvent offers little friction to the twisting motion for DMABN and the TICT process in DMABN is found to be almost independent of viscosity upto moderate viscosity.[184,192–194] At very high viscosity, however, friction does play a role.[214,327–336] For molecules where the rotating group is bulky [e.g arylamino group in (*p*-toluidino)naphthalenesulfonate (TNS)] an increase in viscosity is found to retard the TICT process, even at low viscosity.[308]

With rise in polarity the quantum yield and lifetime of the "nonpolar" emission decreases monotonically with slight red-shift of emission maxima. For the TICT emission, however, with an increase in polarity, the quantum yield initially increases and after reaching a maximum decreases with a further rise in polarity while the emission maxima monotonically shifts to the red.[204,205,213] This observation is quite general and is observed in both hydrogen bonded[204,205] and in non-hydrogen-bonded solvents.[213] Before explaining this result, we will discuss the solvent effect on the rate of TICT and the nonradiative decay from the TICT state.

The formation time for the TICT state (τ_M) can be determined experimentally either from the rate of decay of the "nonpolar" emission or from the rate of formation (growth) of the TICT emission.[192-194] The solvent dipoles relax around the newly created solvent dipoles at a rate corresponding to "longitudinal" relaxation time (τ_L).[231,245,247] Depending on the relative fastness of the molecular relaxation rate (τ_M^{-1}) and the solvent relaxation rate (τ_L^{-1}), two distinct cases may arise. When solvation (τ_L^{-1}) is slower than the molecular relaxation rate (τ_M^{-1}), the overall rate is governed by solvation. This is called the dynamic polarity effect. In this case creation of the TICT state can be considered instantaneous and after formation the TICT state gradually loses energy due to solvation. As a consequence the TICT emission exhibits a time dependent or dynamic Stokes shift.[231,232,250] A dynamic Stokes shift is conclusive evidence for dynamic polarity effect. The other extreme is a static polarity effect, where molecular rate (τ_M^{-1}) is slower than solvation and hence is rate determining. For DMABN, Hicks et al. observed that the TICT rate is slower than the solvent relaxation time and there is no dynamic Stokes shift.[192-194] Hence, the TICT process of DMABN is a case of static polarity effect. To dissect the effect of polarity and viscosity on the TICT process of DMABN, a series of careful experiments has been done by Eisenthal et al.[192-194] To isolate the effect of polarity, the TICT rate (τ_M) is determined for a number of nitriles at different temperatures while the viscosity is kept the same. Under such isoviscous conditions, it was found that the TICT rate increases with increase in polarity. Different polarity parameters, e.g. dielectric constant (ϵ), Lippert function

$$\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

and Dimroth's $E_T(30)$ value, have been tried. It has been observed that when the logarithm of the TICT rate ($k_T = \tau_M^{-1}$) is plotted against these parameters the best straight line is obtained for $E_T(30)$. This indicates that $E_T(30)$ reports the microscopic polarity experienced by the DMABN molecule more truthfully than the bulk parameters (e.g. ϵ, n). The relatively lower efficacy of the bulk parameters may be due to clustering of the polar solvent molecules around the polar solute, causing "dielectric enrichment".[297] Since $E_T(30)$ is the absorption energy of a charge transfer dye, it itself is a microscopic polarity parameter related to solvation energy. This is why the observed rate correlates so well with $E_T(30)$. To explain the polarity dependence in a Arrhenius picture, it has been proposed[192-194] that the activation energy for the TICT process is polarity dependent. With a rise in polarity the polar TICT state is stabilized more than the "nonpolar" or LE state, and hence the crossing of the two potential energy (PE) curves occur at a lower energy at higher polarity (Figure 9). Since the activation barrier is the energy difference between the lowest point of the PE curve of the "nonpolar" state and the crossing point, the barrier decreases with rise in polarity. To explain the experimental results quantitatively, Eisenthal et al.[192-194] proposed the empirical relation according to which the barrier (E_B) decreases linearly with increase in $E_T(30)$ as

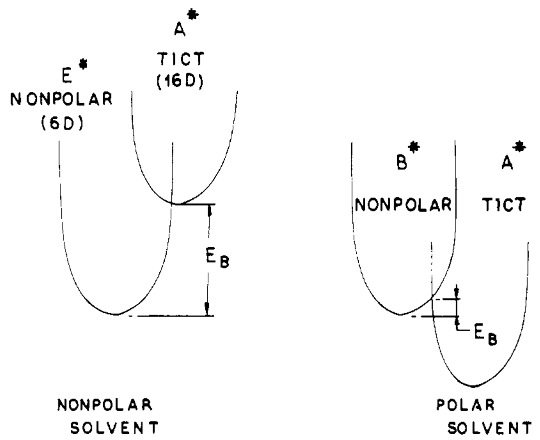

Figure 9. Relative energies (schematic) of "nonpolar" and TICT excited states in nonpolar and polar solvents.

$$E_B = E_B^\circ - A[E_T(30) - 30] \qquad (8)$$

where E_B° is the barrier in a hydrocarbon having a $E_T(30)$ value 30 kcal/mol. The overall rate k_T is thus, given by

$$k_T = k_T^\circ \exp(-E_B^\circ/RT) \exp[A\{E_T(30) - 30\}/RT] \qquad (9)$$

This explains the linear relation between ln k_T vs $E_T(30)$. The polarity-corrected rate ($k_T \exp[-A\{E_T(30) - 30\}/RT]$) is found to be independent of viscosity at low viscosity. This indicates that the TICT process for DMABN is polarity controlled and viscosity has little or no effect. The concept of a polarity-dependent barrier has subsequently been extended to other molecules such as sulfones,[199] aniline aryl sulfonates,[218,219] and rhodamine laser dye.[219,220]

In cases where the TICT state is nonfluorescent,[199,218,219] the TICT rate can be obtained from the decay of the "nonpolar" (LE) emission as follows. In this case the reciprocal of the fluorescence lifetime of the "nonpolar" emission (τ_{NP}) is the sum of the radiative (k_r) and nonradiative (k_{nr}) rates. k_{nr} includes the TICT rate (k_T) and other nonradiative rates (k_{nr}^x). Thus

$$\tau_{NP}^{-1} = k_r + k_{nr} = k_r + k_T + k_{nr}^x \qquad (10)$$

The radiative rate (k_r) is obtained from fluorescence quantum yield of "nonpolar" emission (ϕ_{NP}^f) as

$$k_r = \frac{\phi_{NP}^f}{\tau_{NP}} \qquad (11)$$

From eqs 10 and 11 is easily calculated k_{nr}. Using the polarity-dependent barrier (eq 8) one can write

$$k_{nr} = k_{nr}^x + k_T^\circ \exp(-E_B^\circ/RT) \exp[A\{E_T(30) - 30\}/RT] \qquad (12)$$

At high polarity, when the TICT rate (k_T) is much greater than other nonradiative rates (k_{nr}^x)

$$k_{nr} \cong k_T^\circ \exp(-E_B^\circ/RT) \exp(A[E_T(30) - 30]/RT) \qquad (13)$$

In this case ln k_{nr} vs $E_T(30)$ should be a straight line.

The polarity range where such relation holds depends on the molecule concerned.[218]

2. TICT versus ISC

While an increase in polarity accelerates formation of the TICT state, it also affects the nonradiative decay rate (ISC) from TICT singlets to low-lying triplets. The dipole moment of DMABN in the TICT singlet state is more than that in the triplet state.[267] Thus with a rise in polarity the preferential solvation of the TICT state decreases the energy gap between the TICT state and the triplet. According to energy gap law of nonradiative transitions,[26,346] the rate of ISC from the TICT singlet state increases as the singlet–triplet energy gap decreases. Due to the enhanced ISC rate from TICT singlet, triplet yields of DMABN and related molecules increase as polarity increases.[212] Evidently, polarity affects the yield of TICT emission (ϕ^f_{TICT}) in two opposing ways. While acceleration of the TICT process tends to increase ϕ^f_{TICT}, the increase of nonradiative (ISC) rates from the TICT state tends to decrease ϕ^f_{TICT}. Due to these two opposite effects, ϕ^f_{TICT} exhibits a rise and fall behavior with a rise in polarity.[204,205,213]

The external heavy atom effect on "nonpolar" and the TICT state has been the subject of several studies.[215–218] For the "nonpolar" (LE) excited state ISC competes with the TICT process. Under conditions where the TICT rate is very slow (e.g. cryogenic inert gas matrices[215] or in fluid solutions at low polarity[218]), the main nonradiative pathway is ISC. In this case, an appreciable heavy atom effect is observed. In cryogenic matrices relative to smaller argon in the heavy xenon matrix a dramatic increase in the phosphorescence yield and concommitant decrease in fluorescence yield and lifetime is observed.[215] However, at high polarity in fluid solution where the TICT process is much faster than the ISC process, ISC and the external heavy atom effect becomes relatively unimportant.[215,217] To summarize, the ISC rate and heavy atom effect depend on the S–T interval and the TICT rate, both of which depend strongly on the polarity of medium.

3. Superhigh Viscosity: Polymer Solutions and High Pressure

In solutions of polymers it is observed that as the polymer concentration increases the relative intensities of LE, and the TICT emission of *p*-(dimethylamino)benzoic acid ester (DMABE) remains unchanged up to a polymer concentration of 70% by weight.[214] Above this concentration, marked suppression of TICT emission is observed. To explain this it is proposed that, above 70%, the mesh size in the polymer network decreases so much that there is very little free volume for the twisting to occur. The microviscosity of such a polymer environment is very high and is comparable to glassy medium.[329] The free volume needed for rotation of the twisting group is estimated to be 5.4 mL/mol.[329] In the highly viscous polymer media, the interconversion of different ground-state rotamers of DMABE is very slow and hence they coexist as distinct species. Excitation of different rotamers leads to different ratios of intensities of the "nonpolar" and TICT emissions. This is known as the red edge emission (REE) effect. REE is observed for a number of polymer environments.[329,334–336] It is also observed that the solutions of DMABE bonded to polymers exhibited marked blue-shift compared to free DMABE in the same solvent. This is attributed to reduced solvation of the polymer-bound DMABE molecules as the polymer backbone prevents solvent molecules from approaching the DMABE molecule. The sensitivity of the TICT emission to polymer environment is utilized to probe mobilities of polymer segments[331–333] and to monitor the kinetics of polymerization.[333] It should be noted that though the free-volume effect[328,329] plays a major role in the TICT processes in polymer environment, polarity effects are still very important. Thus while TICT is readily observed in polar polymers, no TICT emission is observed in nonpolar polystyrene polymer.[335] The importance of specific interactions like hydrogen-bonding effects on TICT is also the subject of considerable debate.[193,204,278,334]

Recently the effect of very high pressure on DMABE[229] and bianthryl (BA)[230] have been studied. For DMABE the ratio of intensities of TICT and nonpolar emission was found to decrease with increase in pressure in solution and to a much greater extent when DMABE is bonded to polymers.[229] This is ascribed to a decrease of free volume with an increase in pressure. For BA in picosecond transient absorption, an anthracene-like state (LE) and a polar TICT state are detected.[230] At high pressure, due to pressure-induced changes in polarity and viscosity, the electron-transfer rate changes considerably and the decay of the TICT state becomes highly nonlinear. An appreciable portion of the TICT emission is independent of viscosity, has a rise time shorter than the excitation pulse, and is assigned to some BA molecules which are already twisted in the ground state. This has implications in photosynthetic bacterial reaction center.[230]

C. Theoretical Approaches to Solvent Effects on TICT

The dramatic dependence of the TICT process on solvents has inspired a large number of theoretical studies on the solvent effects on TICT. These studies can be broadly classified into two types. In the first type, or stochastic models,[184,185,198,231–260] the overall rate is obtained from statistical mechanical models (e.g. Langevin equations) incorporating the solvent effect as a friction term. The potential energy (PE) surface on which the molecule moves during the course of TICT is not calculated a priori in this model. On the other hand, in the second approach the PE surface is first constructed using quantum chemical methods[260–267] for isolated molecules and then solvation energy is calculated and added to get the PE surface in the presence of solvents. Afterward a dynamical theory is used to calculate the rate.

1. Stochastic Models

The main task of this model is to take into account the effect of solvent suitably in the Langevin equation. The solvent hinders the twisting motion through friction and by continuously buffeting the solute molecule, thereby resulting in a fluctuating force. The randomness of the buffeting (i.e. collisions) necessitates statistical models. The other important effect is the reorganization of the solvent dipoles around the instantaneously created polar TICT state. For solvation of electrons it is proposed that the *solvent relaxation time* (τ_L) is[247]

$$\tau_L = \frac{\epsilon_0}{\epsilon_\infty}\tau_D \tag{14}$$

where τ_D is Debye relaxation time, and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively. The subsequent modifications and extension of this model to ultrafast solvation of molecules have been discussed by a number of authors.[198,231-233,238,244,250,253] In case of molecules the solvation time is determined from dynamic Stokes shift. Thus, if the TICT process of a particular molecule exhibits the *dynamic polarity effect*, the overall rate should be compared with the solvent relaxation time given in eq 14 or the more recent expressions. Experimentally one measures the emission energies at times zero ($\nu(0)$), t ($\nu(t)$), and infinity ($\nu(\infty)$). The dynamic solvent shift is described by[231-232,249,259]

$$c(t) = \frac{\nu(t) - \nu(0)}{\nu(\infty) - \nu(0)} \tag{15}$$

In general, it is observed that in many cases the decay of $c(t)$ is highly nonexponential. Thus it is not possible to correlate the rate of decay of $c(t)$ directly to the longitudinal relaxation time, τ_L. However, in some cases the average solvation time (τ_s), defined as

$$\tau_s = \int_0^\infty c(t)\,dt \tag{16}$$

agrees well with τ_L. It is also observed that the differences in solvation time for some solute probes in the same solvent is smaller than the differences for the same solute in different solvents. This emphasizes that for this set of molecules solvation plays an important role.

In the above models solvent is taken as a continuous medium. More recently there has been some attempts to take into account the structure of solvents.[240-242] In the so-called dynamic mean sphere approximation (MSA) model the solvents are treated as dipolar spheres whose structure is calculated by MSA. The major limitation of this model is that the results are in a very complicated form and the predicted rate is much slower than actual experimental results. The success and limitations of the various stochastic models have been summarized in several recent reviews.[231,232,244,259]

2. Quantum Chemical Calculation

In the stochastic models the structure of the solute is completely neglected. This leads to serious error for the static polarity effect, where the molecular rate processes of the solute are the rate-determining step, as discussed in section IV.B.1. In this case the experimental rate deviates markedly from stochastic models. In many cases[192-194,199,218,219] the TICT dynamics are found to exhibit a static polarity effect. In such cases the success of the stochastic models ignoring the structure of the probe solute is doubtful. An alternative approach is to construct the PE surface of the solute using quantum chemical methods taking into account solvation effects and then to use a dynamic model. Semiempirical and ab initio quantum chemical calculations have been performed for DMABN and related molecules.[260-267] Unfortunately some of these calculations did not take into account solvation at all[263,264] and hence do not provide much insight into the TICT problem, as it is crucially dependent on solvent. In an early calculation Lipinsky et al.[261] used the INDO/CI method to calculate the energies and dipole moments of the planar and the perpendicular excited states of DMABN taking into account the solvation using Onsagar's theory. Though this calculation is consistent with some general experimental trends, it does not explain the complete course of the TICT process as the calculations were done only at two points. Further, the ground-state geometry is not optimized in this calculation and hence it cannot explain whether the abnormal red-shift of the TICT emission is due to the difference in the energies of the excited state conformers or to the energy differences in the ground states. In two recent calculations the ground-state geometrical parameters of DMABN were optimized.[265,267] Majumdar et al.[267] used the standard MNDO method for complete optimization of the geometrical parameters of DMABN in the ground state for each value of the dihedral angle θ (ring – NMe_2). For each ground-state conformation total energy and dipole moment are calculated. Then for each conformation a CNDO-S/CI calculation is performed to get the transition energy. The excited state PE surface is generated by adding the transition energy to the energy of the corresponding ground state conformation. The solvation energy for a state of dipole moment μ is, according to Onsagar's theory,[347] $-\vec{\mu}\cdot\vec{R}$. The reaction field $\vec{R}$ is given by, $\vec{R} = (2/a^3)f\vec{\mu}'$, $\vec{\mu}'$ being the solute dipole causing polarization in the cavity of radius a. The form of $f(\mu')$ depends on the time scale concerned. When solvent is fully equilibrated around the dipole μ (e.g. for ground state or long-lived excited states), f is given by $f = (\epsilon - 1)/(2\epsilon + 1)$ and $\vec{\mu} = \vec{\mu}'$. In this case the solvation energy is

$$\Delta E_s(\theta) = \frac{2\mu(\theta)^2}{a^3}\left[\frac{\epsilon - 1}{2\epsilon + 1}\right] \tag{17}$$

When the solvation energy is given by eq 17 the state may be considered fully solvated. During the TICT process the molecule passes from the "nonpolar" state to a highly polar state so quickly that the solvent dipoles cannot reorient, but electrons belonging to the solvent molecules are instantly polarized. Thus if μ and μ' denote dipole moments of the "nonpolar" and the TICT state, the solvation energy for the TICT state (dipole moment μ') immediately after creation from the "nonpolar" state (dipole moment μ) is given by

$$\Delta E_s(\theta) = \frac{2\vec{\mu}(\theta)\cdot\vec{\mu}'(\theta)}{a^3}\left[\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] - \frac{2\mu'(\theta)^2}{a^3}\left[\frac{n^2 - 1}{2n^2 + 1}\right] \tag{18}$$

When the solvation energy is given by eq 18 the state may be considered partially solvated. To summarize, at the time of creation of the TICT state the solvation energy for the TICT state is given by eq 18. Subsequently the solvent dipoles reorient according to the new dipole μ' and solvation energy increases. The final solvation energy when the solvent reorientation is complete is given by eq 17. It should be noted that the dipole moment of DMABN are found to vary with the dihedral angle (θ) describing the twisting motion,[267] and thus it is incorrect to assume a single dipole moment

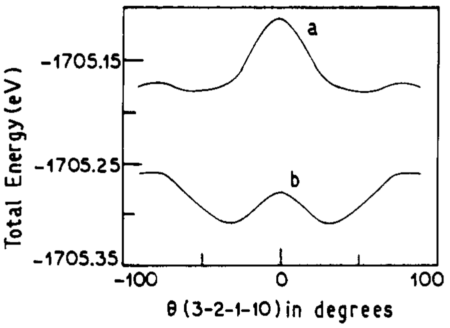

Figure 10. Ground-state energy of DMABN as a function of twisting, τ, as obtained by MDNO methods, (a) in isolated molecules and (b) in water (from ref 267; copyright 1991 American Chemical Society).

throughout the entire TICT process. Majumdar et al.[267] calculated the dipole moments for each torsion θ and then used the torsion-dependent dipole moment in eqs 17 and 18 to calculate solvation energy.

Figure 10 gives the ground state energy surface[267] of isolated DMABN and in water ($\epsilon = 78$). In isolated DMABN, there is a shallow minimum around a dihedral angle 50° and there is a maximum at 0° (planar geometry), the barrier being 0.08 eV. In polar solvent the barrier for twisting decreases to 0.03 eV, the minimum shifts to about 30°, and the energy difference between the 90° geometry and minimum is 0.04 eV. Since these energy differences are not much greater than thermal energy (kT) rotation about the bond joining the ring and the NMe_2 is nearly free in the ground state. Thus the large red-shift of the TICT emission relative to the "nonpolar" emission is not due to the energy difference between ground-state rotamers and is due exclusively to the differences in the excited-state energies.[267] Figure 11 describes energies of the four excited states (S_{1-3} and S_5) of DMABN under isolated conditions (Figure 11a) and fully solvated (Figure 11b) in a solution of 0.8 M butyronitrile in *n*-octane. The calculated dipole moment, geometry (90°), and position of emission energies in a number of solvents for the state S_5 agrees extremely well with the experimental data on the TICT state and thus the state S_5 is assigned to be responsible for the TICT emission. Similarly the "nonpolar" emission is attributed to either or both of S_{1-2}. Figure 11c describes the crossing of PE surfaces of the fully solvated curves for the "nonpolar" state (S_{1-2}) and the partially solvated surface for the TICT state. It is observed that the energy of the TICT state is greater than the energy of the "nonpolar" state for $\epsilon < 2.2$. Thus the minimum or threshold value of ϵ needed for observation of the TICT process is 2.2. The activation barrier for the TICT process is obtained from the crossing of the PE curves in Figure 11c, and the calculated values agree with those obtained experimentally by Eisenthal et al.[192-194] The decrease of the energy gap between the TICT singlet and low-lying triplets with a rise in solvent is as discussed in the earlier section is also accounted for by this calculation.[267]

Kato and Amatatsu[265] used the ab initio SCF-MO method to analyze the TICT process of DMABN. In this case the ground-state geometry was optimized using the analytic energy gradient method of the STO-3G basis. A diabatic representation for the excited states were constructed. The electrostatic solvation energy was incorporated as a multipole expansion using the

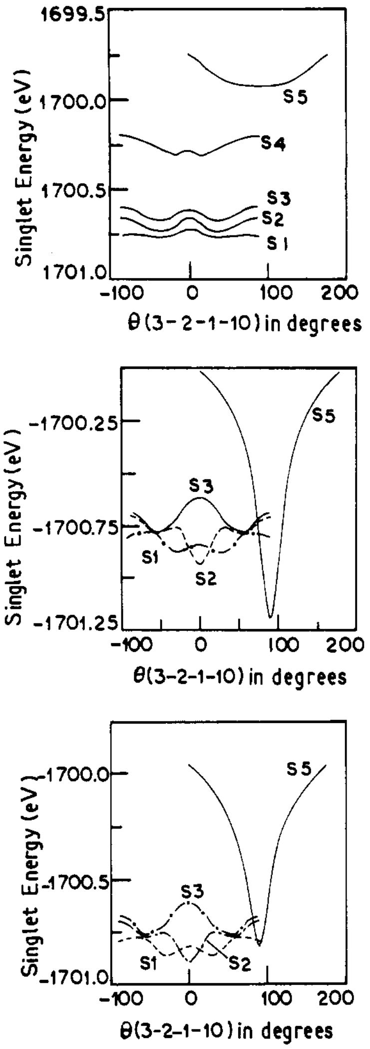

Figure 11. Excited state energies of DMABN, (a) in isolated molecules and (b) in those fully solvated in 0.8 M butyronitrile (BuN) in n-octane and (c) crossing of fully solvated S_{1-3} states and the partially solvated S_5 states in 0.4 M BuN (from ref 267; copyright 1991 American Chemical Society).

calculated electron densities. No attempt was made, however, to distinguish between the short-time and long-time solvation energies as described in eqs 17 and 18. The calculated geometry, dipole moments, and ground-state barrier agree with experimental results. However, activation energy for the TICT process or singlet–triplet gaps are not calculated by Kato and Amatatsu. They also used Monte Carlo simulation to calculate the structure of the DMABN–H_2O complex. Other simulation methods for DMABN–water clusters are used by Cazeau-Dubroca et al.[250] and Bernstein et al.[279,280] These calculations will be discussed in a later section in connection with the spectroscopy of such clusters in supersonic jet.

Though the quantum chemically calculated PE surface using torsion-dependent dipole moment and solvation may be a better description of the PE surface, a simple transition-state description may not be adequate to describe the details of the dynamics.[231-233] The stochastic models using a reasonably good PE surface constructed by quantum chemical methods is certainly a more attractive alternative particularly in the case of the static polarity effect. Recent molecular dynamic simulations also hold much promise.[232,233-237,244,245]

D. TICT Process in Isolated Molecules and Clusters: Supersonic Jets and Supercritical Fluids

In order to get precise knowledge about the geometry and PE surface of DMABN and related molecules in the ground state as well as in the excited states, a number studies have been made in supersonic jet.[279-294] In supersonic jet DMABN and its analogues with near-planar ground-state geometry do not exhibit the TICT emission even when excited at wavelengths much shorter than the 0-0 transition. The lack of TICT emission in an isolated jet-cooled molecule may be attributed to the extreme nonpolar environment and the consequent large barrier for TICT. In such a nonpolar environment the TICT state remains at a higher energy. On excitation above the barrier quick vibrational relaxation brings the molecule to the minimum of the lower energy potential well corresponding to the "nonpolar" state.[284] The excitation spectra of DMABN is similar to that of N,N-dimethylaniline (DMA) and is dominated by a low-frequency vibration at 61 cm^{-1} which is attributed to the torsion about the bond joining the ring and the NMe_2 group.[279-282,284-292] Microwave studies in free jet[290] indicate that in the ground-state DMABN deviates slightly from planarity, the dihedral angle being 15°. This is in agreement with recent quantum chemical calculations.[265,267] The laser-induced fluorescence and time-of-flight mass spectra (TOFMS) of DMABN and related molecules have been analyzed in considerable detail in terms of the torsional vibration involving the NMe_2 group.[279-281,290] Such analysis indicates that the minimum in the first excited state S_1 of DMABN shifts by about 30°, which is also consistent with the recent calculations.[265,267]

To understand the role of solvents in the TICT process, a number of solvent clusters of DMABN and related molecules involving a wide range of solvents, e.g. argon, water, methanol, and acetonitrile, have been studied. Like bare molecule, solvated DMABN also does not exhibit the TICT emission. However, DMABN derivatives which are partially twisted in the ground state exhibit TICT emission on complexation with methanol and acetonitrile.[285] For planar DMABN analogues, solvation does not alter the general features of the excitation spectra. This indicates that the NMe_2 is not affected by solvation and hence in these clusters the solvent molecules presumably do not stay near the NMe_2 group. The structure of the DMABN clusters has been the subject of several theoretical studies.[204,265,279,280,290] In DMABN-Ar cluster a sharp Q branch is observed which suggests that the Ar atom is situated just above the ring.[290] Lennerd-Jones cluster calculations performed by Bernstein et al.[279-280] indicate three cluster configurations for DMABN-H_2O. More than one kind of DMABN-H_2O is also indicated by the Monte Carlo simulations done by Kato and Amatatsu.[265] The experimental proof in favor of more than one kind of complex is provided by TOFMS.[280] Since fluorescence excitation (LIF) spectra indicate only one kind of complex, it is proposed that there are two kinds of complexes, one fluorescent and the other nonfluorescent, both of which appear in TOFMS, while in the LIF spectra only the fluorescent complex is detected.[279,280]

Though no solvent cluster of DMABN exhibits TICT emission 9,9′-bianthryl (BA) readily undergoes TICT on solvation by the polar solvent acetone.[283,289] No TICT emission is observed for bare BA or BA solvated by a nonpolar solvent such as cyclohexane.

More recently the effect of solvent clustering about the TICT probe molecule was also investigated in supercritical fluids.[294-296] Supercritical fluids refer to fluids just above their critical temperature. By slight change in pressure under supercritical conditions, one can go from near vacuum to an almost liquidlike condition. The solvent shift data on TICT emission in superfluids shows large positive deviation from the Lippert plot.[294] Such deviation indicates solvent clustering around the probe solute undergoing TICT. Kajimoto et al.[294] determined that in such aggregates there are three CF_3H molecule per DMABN molecule. It is also observed that relative intensity of the TICT emission increases as density of the supercritical phase increases. Sun et al.[296] studied DMABN and DMABE in a number of supercritical fluids and identified three phases.

E. TICT in Organized Assemblies

In recent times there has been a very vigorous interest in the spectroscopy organized assemblies because of their obvious biological implications.[299] The interior of any organized assembly is markedly different from bulk solutions. For organized assemblies in aqueous solutions (e.g. micelles, cyclodextrins, and proteins), the interior is quite nonpolar while the bulk aqueous phase is highly polar. The situation is just the opposite in the case of reversed micelles, where there is a polar water pool inside and the bulk solution outside is nonpolar. The local viscosity of organized assemblies is also appreciably different from bulk values. The substantially altered local polarity and viscosity of the organized environment and the restrictions imposed on the molecular motions inside the finite-sized assemblies influence the TICT process in a highly interesting way. The extraordinary sensitivity of the quantum yield, lifetime, and position of the TICT emission is utilized to probe the microscopic polarities of a number of organized assemblies.

In polar aqueous phase quantum yield and lifetime of both "nonpolar" and TICT emission are extremely small because of very high TICT rates and rapid ISC from the TICT singlet to the triplets. When the probes are transferred from the polar aqueous phase to relatively less polar organized environments, the reduction in polarity leads to a marked blue-shift of the TICT emission and a dramatic increase in the emission yields from both "nonpolar" and TICT emission. The emission quantum yields, maxima, and lifetime serve as excellent indicators of the microscopic polarity of the organized assemblies. We will now elaborate these ideas with specific examples.

1. Cyclodextrins

Cyclodextrins (CDx) are cyclic polymers of α-amylose. In aqueous solutions they form a very well-defined hydrophobic cavity and encapsulate molecules of suitable size and the resulting supramolecules often exhibit properties drastically different from those of the free guest molecules in aqueous solutions.[298] The α-, β-,

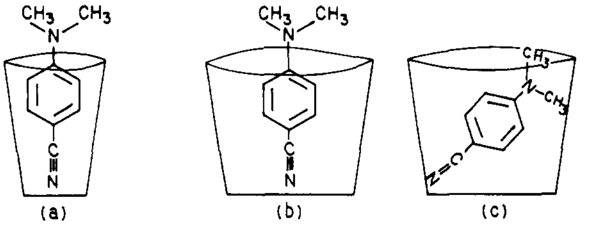

Figure 12. Proposed structures of DMABN–cyclodextrin complexes, (a) with α-CDx and (b and c) with β-CDx.

and γ-cyclodextrins (CDx) contain six, seven, and eight amylose units, respectively. For each of them the height of the cavity is 8 Å while the diameter of the inner rim of the cavities are approximately 4.5, 6.5, and 8 Å, respectively. In aqueous CDx solutions one encounters three regions of distinctly different polarity, namely, the interior of the cavity, the rim of the cavity, and bulk aqueous solution. The interior of the CDx cavity resembles cyclic ethers (e.g. dioxane) and is relatively nonpolar while the rims are moderately polar due to the hydroxyl groups and nearby water molecules. The main aim of studying the TICT process in CDx solutions is to find out how the cavity affects the dynamics of the charge transfer and the twisting and whether it is due to the reduced polarity of the cavity or to the restrictions imposed on the twisting motion. It is also interesting to ascertain whether the dynamics in the interior of the cavity are different from those at the rims.

Cramer et al.[305] observed dramatic fluorescence enhancement of p-toluidinonaphthalenesulfonate (TNS) in a CDx environment long before the introduction of the TICT concept. In the light of the discussions in section IV.B.1, it is now evident that suppression of the nonradiative TICT process in the relatively nonpolar CDx environment leads to enhancement of the emission yield from the "nonpolar" state.[306,307,345] Turro et al. observed a large enhancement of the TICT emission of DMABN and DEABN in α- and β-CDx.[300] However, as they studied only the TICT emission and did not study the effect of CDx on the "nonpolar" emission at all, they could not distinguish between the DMABN molecules at the interior of the cavity from those at the rim. A more detailed study of the phenomena has been done by Nag et al.[301] On addition of α-CDx to an aqueous solution of DMABN, the "nonpolar" emission remains more or less unaffected while there is a very dramatic increase in the yield, energy, and lifetime of the TICT emission.[301] In the case of β- and γ-CDx, both the "nonpolar" and TICT emissions exhibit an increase of yield and lifetime. At the highest concentration of β- or γ-CDx, the excitation spectra and lifetime of the TICT emission are found to be different from those of the "nonpolar" emission. This indicates that the enhanced "nonpolar" and the enhanced TICT emission are due to different sets of molecules. An increase in the yield and lifetime of the emission from the "nonpolar" state is obviously due to suppression of the main nonradiative pathway (TICT) in the "nonpolar" excited state of DMABN. Thus, the enhanced "nonpolar" emission in case of β- and γ-CDx can be attributed to those DMABN molecules which are confined entirely inside the nonpolar cavity (Figure 12c). The enhanced TICT emission obviously originates from those molecules which are in a more polar environment i.e. at the rims (Figure 12b). In this case, the enhancement of the TICT emission occurs because of the lower polarity of the rim of the CDx cavities compared to bulk water and the consequent decrease in the nonradiative (ISC) rates in the TICT state. The increase in the lifetime of the TICT emission on complexation with CDx substantiates this contention.

It is worthwhile to discuss the restriction or hindrance imposed on the twisting motion by the CDx cavity. The observation of TICT in the case of the smallest α-CDx indicates that the twisting motion of the NMe_2 group is not restricted, even on complexation with α-CDx. One might argue that the twisting motion is not restricted when the molecules are partially enclosed (e.g. in α-CDx; Figure 12a) because the part of the molecule projected out of the cavity is free to rotate. By extending this argument, one expects TICT would be inhibited when the guest molecules are totally inside the cavity. If this were the case, the hindrance should have been more for molecules inside β-CDx than for those in γ-CDx and in the latter case the TICT process should not have been suppressed. The enhanced "nonpolar" emission in the spacious γ-CDx suggests that the TICT emission is suppressed in γ-CDx also.[301] This conclusively proves that the TICT process for DMABN where the small rotating group is inhibited inside the CDx cavity due to reduced polarity and not due to the restrictions imposed on the molecular motion inside the cavity.

The emission properties of TICT molecules have been used to estimate the polarity of the interior and the rims of the CDx cavities.[300,301,345] On the basis of the emission maximum of the TICT emission of DMABN at the highest CDx concentration, Turro et al.[300] estimated the $E_T(30)$ for β-CDx to be around 57, which is greater than that of ethylene glycol (56.3) and slightly less than that of water. If β-CDx were so polar the yield of "nonpolar" emission of DMABN in β-CDx would have been extremely low. But subsequent measurements by Nag et al.[301] indicate that the yield of the "nonpolar" emission in β-CDx is about 30 times that in water. It may be mentioned that the yields of "nonpolar" emission of DMABN in dioxane and in acetonitrile are respectively 75 and 5 times that in water.[205] Thus this measurements suggest that the polarity of the interior of β-CDx is intermediate between that of dioxane ($E_T(30) = 36$) and acetonitrile ($E_T(30) = 46$). The apparent discrepancy between the measurements of Turro et al. and Nag et al. can easily be reconciled if one recognizes that the enhanced "nonpolar" emission is due to the molecules at the interior of the cavity CDx and the enhanced TICT emission due to those at the rims (Figure 12). To summarize, the $E_T(30)$ at the rim is 57 while that at the interior of the cavity is between 36 and 46. More recently Sarkar et al.[345] compared emission parameters of TNS in CDx to those in a dioxane–water mixture and concluded that the polarity at the rims of α- and β-CDx are 55 and 54, respectively. The suppression of the TICT process and consequent enhancement of "nonpolar" emissions and lasting action inside the CDx cavities have recently been observed for rhodamine, fluorescin, and 7-(diethylamino)coumarin laser dyes.[302-304]

2. Micelles, Reversed Micelles, and Vesicles

In recent years TICT probes have been utilized to follow micellization and to determine critical micellar concentration (CMC). It is well-known that in aqueous solutions below CMC the surfactant molecules are randomly arranged. Above CMC micellar aggregates of surfactant molecules are formed. The interior of any micelle is quite nonpolar and resembles hydrocarbons while the micellar surface is quite polar due to presence of polar head groups. As soon as micellar aggregates are formed the fluorescent TICT probes migrates into the nonpolar region inside the micelles. In the micellar aggregate the TICT process is largely inhibited due to reduction in polarity, and hence the yield and lifetime of the "nonpolar" emission increase markedly above the CMC. The change of slope of the yield of the "nonpolar" emission has been shown to be a sensitive indicator to determine the CMC and relative polarity of different micellar environments.[308-310]

Similar studies have been extended to estimate the polarity of reversed micelles.[311-315] Reversed micelles are aggregates of certain surfactant molecules in hydrocarbon solvent where the surface of the aggregates are nonpolar with polar water molecules trapped inside. The water pool inside the reversed micelles mimics a biomembrane and hence there has been a lot of interest in the study of the local polarity of the water pool in reversed micelles. To estimate the local polarity of reversed micelles anilino sulfonates[311-312] and (dimethylamino)phenyl-3*H*-indole[313] have been used as probes. From fluorescence lifetime measurements it was concluded that as the water-to-oil ratio (*W*) increases from 0 to 12, the dielectric constant of aerosol-OT (AOT) reversed micelles increases from 2.3 to 9.0. Similar studies were also extended to vesicles.[314]

3. Proteins

It has been known for a long time[316] that the emission intensity and lifetime of certain fluorophores (e.g. anilinoaryl sulfonates) increase dramatically on binding to proteins. Several mechanisms have been proposed to explain the remarkable sensitivity of these fluorescent probes.[268,318,326] Recently it has been established that this sensitivity is due to the polarity-dependent TICT process.[218,219,324] The polarity of the biological pockets can be estimated from the yield, lifetime, and λ_{max} of the TICT or the "nonpolar" emission. On binding to proteins the TICT process is seriously inhibited because of reduction in the polarity and this causes a marked increase of the yield and lifetime of fluorescence from the "nonpolar" state. The recognition of the importance of the polarity-dependent TICT process in the fluorescence sensitivity of biological probes has significantly enlarged the list of such probe molecules. As an example it has been demonstrated that the common 7-(diethylamino)coumarin laser dyes are much more sensitive than conventional biological probes.[324] Further, the relative magnitudes of the fluorescence enhancement of 4-methyl- and 4-(trifluoromethyl)-7-(diethylamino)-coumarin dyes indicate that the microscopic polarity rather than the microscopic viscosity of the biomolecules are chiefly responsible for the inhibition of the TICT process for these molecules on binding to proteins.[324]

4. Effect of Urea

The TICT processes have also been utilized to study the interaction of urea with fluorophores bound to micelles, cyclodextrins, and proteins.[344,345] Urea is known to inhibit formation of micelles and to cause denaturation of proteins. Two mechanisms have been proposed to explain the action of urea.[343] According to the first one, urea "breaks" the hydrogen-bonding structure of water. The second mechanism envisages replacement of a few water molecules around a hydrophobic group by the urea molecule, causing a change in solvation of the latter. Though the first mechanism has been quite popular a number of recent experiments seem to contradict this.[338] Further, computer-simulation studies[339] indicate urea hardly affects water structure, which goes against the first mechanism. The simulations also indicate that urea replaces a few water molecules around a hydrophobic group, which is consistent with the second mechanism. To test this mechanisms fluorescence of *p*-toluidinonaphthalenesulfonate (TNS) has been studied in aqueous surfactant solutions in the presence of urea. It is observed that the CMC increases on addition of urea.[344] It is also observed that above the CMC the yield of "nonpolar" emission is considerably decreased on addition of urea. At first sight it might appear that the decrease in the emission yield is due to quenching of TNS molecules bound to micelles by urea. But in that case the lifetime of the "nonpolar" emission of TNS should have been decreased on addition of urea. However, it is observed that above the CMC the lifetime of TNS is found to be more or less unaffected by addition of urea. Thus, the decrease of "nonpolar" emission yield cannot be due to urea-induced quenching. It has been observed[337] that urea increases viscosity of the micellar surface. This also fails to explain the decrease of "nonpolar" emission as an increase of viscosity is known to increase the "nonpolar" emission of TNS.[308] To explain this it is proposed that addition of urea causes removal of TNS molecules along with some water molecules from the micellar surface. Since TNS is almost nonfluorescent in water, removal of TNS molecules from the micellar surface causes reduction of the overall emission yield. The lifetime remains unaffected because only the fraction of TNS molecules bound to micelle surfaces contributes effectively to the total emission. The relative magnitude of urea-induced changes for a neutral surfactant (Triton-X 100) and an anionic one (SDS) supports this. Similar studies are extended to the CDx cavities having a more well-defined and stable structure.[345] In case of CDx the binding constant of TNS with CDx with and without urea is determined from emission measurements.[345] For α-CDx the results indicate that the number of TNS molecules bound to CDx decreases in the presence of urea. For β-CDx two-kinds of β-CDx–TNS complexes, 1:1 and 2:1, are detected. It is observed that for the 1:1 complex addition of urea causes a decrease in the number of TNS molecules bound to β-CDx. The 2:1 complex however remains more or less unaffected, presumably because of the fact that the two CDx molecules attached to the TNS molecule protects it on both side from the influence of urea. The change of emission yield on addition of urea is quantitatively explained in terms of the number of bound TNS molecules and their emission quantum yields.[345] Similar results are also observed for TNS molecules bound to a protein, bovine serum albumin.[345]

V. Concluding Remarks: Future Prospects

The age-old subject of solvent effects in chemistry is still extremely invigorating and seems to be ever-expanding. In the coming years the fascinating effects of environment on the photoinduced CT phenomena is likely to proliferate in a number of new directions. It appears that the microscopic details of the solvent–solute interaction as unraveled by the clean experiments on clusters in supersonic jet and the increasingly detailed theoretical models will continue to supplement the picosecond and subpicosecond studies in homogeneous liquid solutions. The resulting knowledge is expected to enhance our understanding of the more complex and certainly more interesting case of CT phenomena in organized assemblies and biological systems. While the studies in many of the organized environments have already begun, the very interesting case of CT phenomena in two dimensions, e.g. at solid[299g] or liquid surfaces and in Langmuir–Blodgett films,[299l] remain quite unexplored. Such studies will provide greater insight in the electron transfer processes across biomembranes.

Unlike solvent effects, the subtle effects of magnetic field have only been felt over the last 2 decades, and the subject of spin chemistry has graduated from sporadic, ill-defined reports to a mature, well-structured subject. Charge-transfer luminescence, as described in this review, is only one of the methods of monitoring MFE in electron-spin-forbidden chemical reactions. It has certain advantages over resonance techniques. For instance, it can directly follow the dynamics with high time resolution and is applicable to low and high fields, whereas CIDNP and CIDEP techniques are difficult to apply at low fields and further, it is applicable under conditions where resonance techniques are difficult to apply, namely in viscous or heterogeneous solution or even in the rigid state. However, the exciplex luminescence techniques, unless combined with microwave techniques, cannot provide sublevel-dependent kinetic data. In recent times there has been considerable progress in time-resolved FT-ESR, CIDEP, CIDNP, and RYDMR techniques. These techniques hold considerable promise in unraveling sublevel-dependent kinetics.[44u,v] Moreover, MFE is more pronounced in triplet-born radical pairs which do not fluoresce and can only be studied by transient absorption, transient photocurrent, and other techniques.[44g,t,p] It is therefore necessary to combine the exciplex luminescence data with the results obtained from other techniques. Analysis of exciplex luminescence yield data also suffers from our lack of knowledge of initial distance and state at which radical pairs are generated, and of the precise shape of the PE curve at close intermolecular separations. These complications in MFE arise due to coupling of the spin motion with the spatial motion and can be largely avoided by choosing D–A pairs at fixed distances such as in rigid molecules, matrices, or crystals. Fluorescence studies on such systems should be able to throw light on the spin Hamiltonian, particularly on anisotropicities of Zeeman, dipolar, and hyperfine interactions. More time-resolved studies on isotropic systems are also necessary for obtaining reliable optimized kinetic parameters.

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