

Charge-Transfer Complexes in the Excited State. Laser Photolysis Studies

Michael Ottolenghi

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel

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Intramolecular charge-transfer systems are classified as exciplexes (complexes stable only in the excited state) or electron donor-acceptor (EDA) complexes (also stable in their ground state). EDA complexes¹ are formed in the dark, upon mixing a solution of a molecule having a low ionization potential (electron donor, D) with a solution of a molecule of high electron affinity (electron acceptor, A). The appearance of a new electronic absorption band in the mixed solution, which is not observed in the separated systems, is indicative of complex formation.

The energy of the new band is found to be correlated with the ionization potential of the donor (I_p) and with the electron affinity of the acceptor (E_a), indicating that the transition involves charge transfer from D to A. The energy of the excited (singlet) state, ${}^1(A^-D^+)^*$, is approximated by eq 1, where C

$$E_e = I_p - E_a - C \quad (1)$$

is a Coulomb energy interaction factor.

Intramolecular charge transfer in the excited state was long ago proposed to account for fluorescence quenching phenomena.² It was later unambiguously shown^{3,4} that fluorescence quenching in nonpolar solvents may proceed *via* an excited CT complex ("exciplex" or "hetero excimer"), characterized by a new, red-shifted, emission band. Solvent effects on the complex emission spectrum,⁵ as well as the correlation of both spectrum⁶ and enthalpy of formation⁷ with the oxidation-reduction properties of the fluorescer and quencher, are indicative of the charge-transfer (CT) nature of such exciplexes.

The common quantum mechanical description of EDA complexes and exciplexes is based on the valence-bond (resonance structure) treatment of Mulliken.⁸ The first approximation deals with the interaction between the "no-bond" ground state (AD) and the "dative" charge-transfer structure (A^-D^+), leading to the expressions 2 and 3 for the ground

$$\begin{cases} \psi_g = a_1\psi(AD) + a_2\psi(A^-D^+) \\ \psi_e = a_1'\psi(AD) + a_2'\psi(A^-D^+) \end{cases} \quad \begin{cases} a_1 \approx a_2' \approx 1 \\ a_1' \approx a_2 \approx 0 \end{cases} \quad (2)$$

Michael Ottolenghi was born in Florence, Italy, in 1934, and emigrated to Israel in 1938. Educated at the Hebrew University of Jerusalem, he obtained his Ph.D. in 1962, under the supervision of Professors G. Stein and J. Jortner. After postdoctoral work at Brandeis University with Professor H. Linschitz, and at the University of Chicago, with D. S. McClure, he joined the Department of Physical Chemistry at the Hebrew University, where he is now associate professor and department chairman. His present research interests include primary molecular photoprocesses, with special emphasis on fast excitation techniques, using pulsed lasers.

state (ψ_g) and the first excited singlet state (ψ_e). Actually, additional states such as higher excited CT states^{9a} and locally excited states of the no-bond structure^{9b} should be included, a more general expression being eq 4, where the ij summation is over

$$\psi = a_1\psi(AD) + \sum_{ij} a_{2ij}\psi(D_i^+A_j^-) + \sum_k a_{3k}\psi(D^*A) + \sum_l a_{4l}\psi(DA^*) \quad (4)$$

the possible states of the (D^+A^-) structure. The k and l summations are over the possible excited states of D and A.

In spite of extensive theoretical and experimental data dealing with excited EDA complexes¹ and exciplexes,⁴ little was known of some fundamental aspects of these systems. Experimental difficulties had prevented direct access to problems such as the detection of higher complex excited states, the dynamics of solvation of the fluorescent state, as well as the mechanisms of ionization and intersystem crossing (ISC) which are both important in understanding the photochemistry of CT systems.

However, in the past few years, Q-switched solid-state and pulsed gas lasers became available for excitation in flash photochemical experiments with nanosecond time resolution.¹⁰ Such techniques were extremely useful in providing further insight into the photophysics of CT systems. This Account describes

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(7) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969).

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(9) (a) H. Kuroda, I. Ikemoto, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **39**, 1842 (1965). (b) J. N. Murrell, *Quart. Rev., Chem. Soc.*, **15**, 191 (1961).

progress in this important area of interaction between light and chemical systems. Excluding intermolecular interactions,¹¹ we shall emphasize the contributions of laser excitation techniques to the understanding of both radiation (absorption and emission) and radiationless (ionization and ISC) processes in the excited state of organic CT complexes.

Spectroscopy

Absorption Spectra. A nitrogen-laser photolysis apparatus¹² employed in this laboratory for the detection of fast transient absorbance changes in the nanosecond range¹³⁻¹⁵ consists of a collinear optical arrangement in which both the exciting laser beam and a synchronized analyzing light pulse from a xenon arc are focussed on the solution within an area of $\sim 3 \times 0.8$ mm. The analyzing beam is transmitted to a photomultiplier and its transient intensity variations, due to absorbance changes induced in the solution by the exciting laser pulse, are displayed on an oscilloscope.

As an example of the application of the pulsed laser technique to EDA complexes, we consider those formed between *sym*-tetracyanobenzene (TCNB) and benzene or toluene.¹⁶ In such systems the 337.1-nm N₂ laser line lies within the range of the $\psi_g \rightarrow \psi_e$ charge-transfer band. Exposure to the 10-nsec laser pulse leads to transient absorption spectra around 470 nm whose lifetimes exactly coincide with those of the corresponding 500 nm (~ 100 nsec) CT fluorescence (Figure 1). The laser-induced absorbance is therefore attributed to the fluorescent state of either the TCNB-benzene or the TCNB-toluene complex. As shown in Figure 1, the spectrum of the excited complex is essentially identical with that of the (TCNB)⁻ radical anion prepared by conventional alkali-metal reduction techniques. The same conclusions were also obtained by Masuhara and Mataga by studying the self-reabsorption of the (laser-induced) fluorescence by the emitting state.¹⁷

Such observations constitute direct evidence for the charge-transfer nature of the fluorescent state since, if the latter is essentially composed of the two ions A⁻ and D⁺ (eq 3), it will in first approximation exhibit an absorption spectrum showing the characteristic bands of the separated ions. Such expectation agrees with the above laser-photolysis observations since, in these systems, the contribution of D⁺ to the absorption is negligible. We may therefore postulate that CT fluorescent states of EDA complexes and exciplexes will exhibit two types of transi-

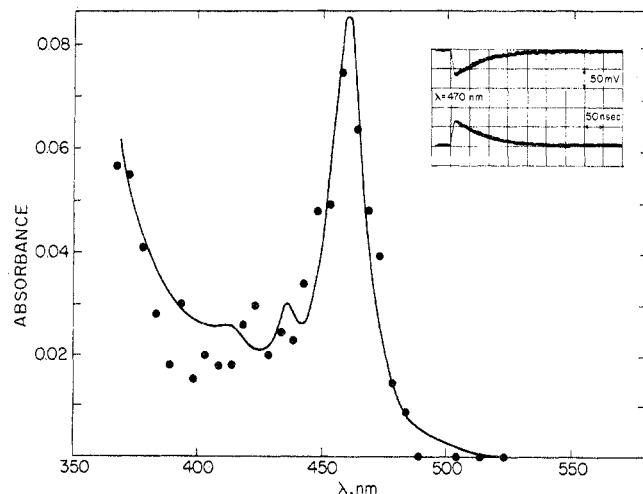
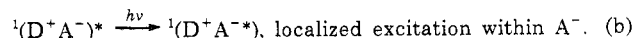
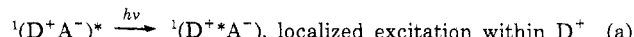


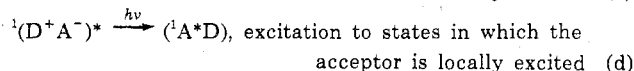
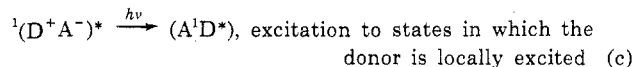
Figure 1. Characteristic oscillograms and transient spectra in the N₂ laser photolysis of the TCNB-toluene complex. The upper trace in the insert was recorded in the absence of the monitoring light. The 10-nsec pulse is fired after one horizontal division, exciting the complex fluorescence which appears as a negative voltage deflection on the oscilloscope screen. The original level of the trace is recovered after the complete decay of the excited state, ~ 200 nsec after excitation. The lower trace was taken in the presence of the monitoring beam and has been corrected for the contribution of the fluorescence scattered light. The light to dark reflection before triggering the laser is 250 mV. This value decreases (the voltage deflection is positive) after firing the laser, due to light absorption by the transient excited complex. Note that the recovery time of the original absorption matches that of the fluorescence. In the spectral curve the points represent the laser-induced absorbance change ~ 20 nsec after triggering. The solid line is the absorption spectrum of the (TCNB)⁻ radical anion produced in an alkali metal-tetrahydrofuran solution (data taken from ref 16).

tions, eq a and b. Obviously, in these transitions, the



CT nature of the complexes is maintained.

When similar laser experiments were extended to exciplexes, excited-state absorption spectra were observed which could not be rationalized by a simple superposition of the A⁻ and D⁺ bands as in the case of the excited EDA complexes reported above.^{18,19} A complete analysis of the numerous bands in the exciplex absorption was carried out by considering "reverse CT transitions" to states in which excitation is localized at the donor or the acceptor¹⁸ (eq c and d).



Apparently the CT state, ${}^1(D^+A^-)^*$, contains enough (A^1D^*) and (${}^1A^*D$) character (and *vice versa*) to make the above transitions allowed. The analysis assumes, however, that the degree of mixing between the corresponding zero-order states (A^-D^+) and,

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(13) C. R. Goldschmidt and M. Ottolenghi, *Chem. Phys. Lett.*, **4**, 570 (1970).

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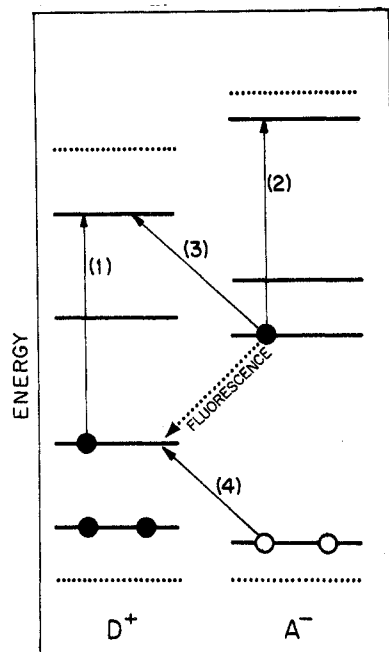


Figure 2. Schematic molecular orbital diagram representing the principal optical transitions in the spectrum of an excited CT complex. The numbers refer to the transitions as described in the text.

e.g., (A^1D^*) is too small to affect significantly their energies. The various transitions are shown in a schematic molecular orbital diagram in Figure 2.

An example clearly demonstrating the above considerations is that of the TMPD-biphenyl exciplex.¹⁹ Transitions of type a are expected to be represented by the characteristic, closely spaced, absorption bands of $TMPD^+$ at 620, 580, and 540 nm. All three bands are present, though slightly shifted, in the exciplex spectrum presented in Figure 3. Localized excitations within A^- are predicted at the characteristic 405-nm and 630-nm bands of the biphenyl negative ion. They are clearly reflected in the exciplex spectrum by the 410-nm peak and by the 650-nm shoulder. Among the transitions to locally excited states only one, involving the $S_3(^1B)$ state of biphenyl, is expected to yield an exciplex band in the 400–900-nm range. Its 0–0 energy lies around 450 nm, fairly coinciding with the 450-nm absorption band of the exciplex.

Thus, absorption spectra of excited CT complexes provide us with a new direct criterion for the charge-transfer nature of the excited state. Hopefully, if put on a more quantitative basis, such absorption measurements may be used to evaluate the degree of charge-transfer contribution to the emitting state of exciplexes and EDA complexes.²⁰ The question arises as to additional information which may be derived from the excited-state absorption spectroscopy of CT systems. It appears that such spectral measurements may provide a new route to the experimental observation of excited singlet molecular states of D or A, which are not detectable in the absorption spectra of the ground state (S_0), or of the lowest excited singlet (S_1) of the corresponding isolated molecules.

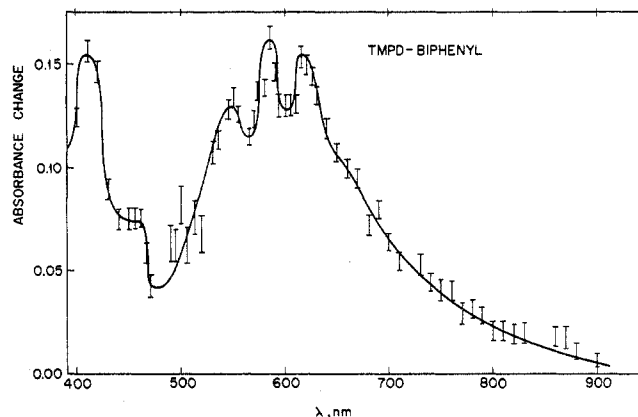


Figure 3. Exciplex absorption spectrum recorded 20 nsec after triggering the nitrogen laser, in a $2 \times 10^{-3} M$ TMPD- $0.1 M$ biphenyl solution in methycyclohexane (data taken from ref 19).

As an example, let us consider the anthracene-*N,N*-diethylaniline (DEA) exciplex whose absorption spectrum is shown in Figure 4. The same figure shows the analysis of the nine bands observed in the available 450–1000-nm spectral range. Two bands (465 and 700 nm) are attributed to transitions of types a and b. Two more are assigned to excitation of the donor (transitions of type c). Out of the five remaining bands, four fairly coincide with transitions to locally excited states of anthracene. Two of such states ($^1B_{3u}^+$ and $^1B_{2u}^+$) are known from the ground-state absorption spectroscopy of the molecule, and two ($^1A_{1g}^-$ and $^1B_{1g}^-$) from excited singlet-singlet laser spectroscopy.^{10e,13} The remaining band at 650 nm is attributed to an anthracene $^1B_{2u}^+$ state, predicted theoretically by Pariser,²¹ which cannot be optically populated from either S_0 or S_1 . Such arguments still await to be generalized in the cases of other exciplex systems.

In the above discussion we have considered the fluorescent CT singlet state. The question arises as to the nature of the corresponding triplet-triplet absorption spectra of the complexes. In view of their relatively long lives, the absorption of triplet states can be recorded by conventional flash-photolysis techniques. Early measurements of this kind led to the detection of triplets which were essentially locally excited states.²² Emission from predominantly charge-transfer triplet states was first reported by Iwata, *et al.*,²³ and by Beens and Weller.²⁴ The CT character of the phosphorescent states was subsequently quantitatively established by esr studies.²⁵

As to the corresponding absorption spectra, an analysis such as presented above for the fluorescent (CT) singlet state should also be applicable to the case of complex triplet states which are predominantly CT in nature. This has been recently confirmed by Matsumoto, *et al.*,²⁶ and by Masuhara, *et*

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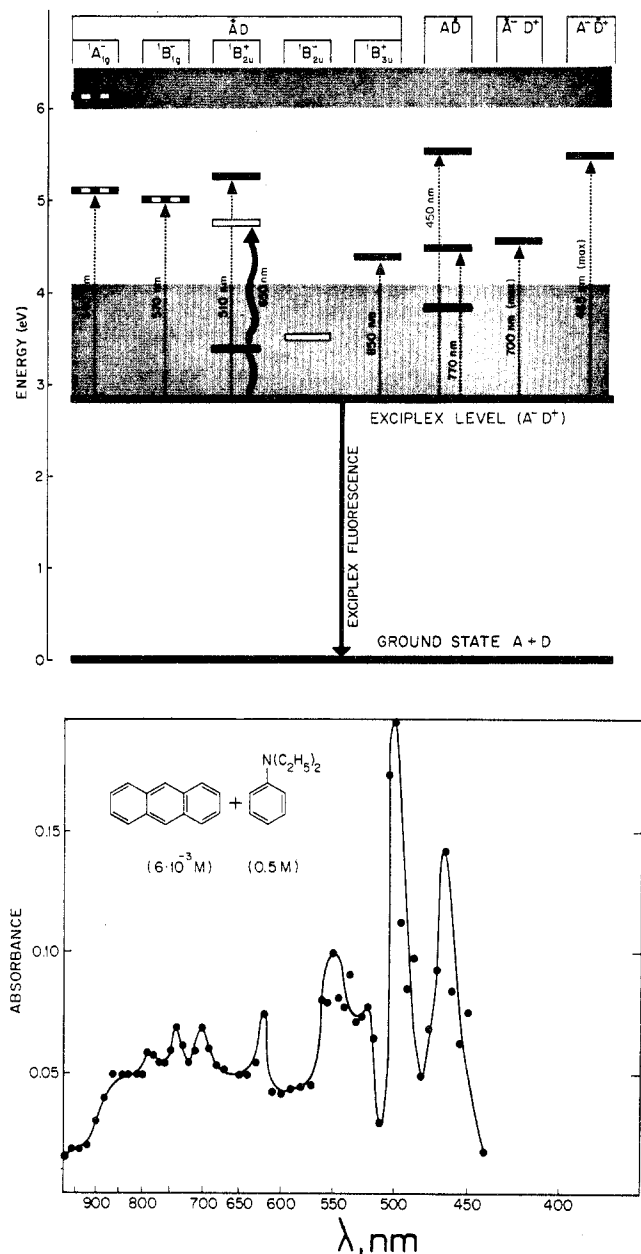


Figure 4. Absorption spectrum of the anthracene-DEA (A-D) exciplex (bottom) and proposed identification of the observed transitions (top). Shaded areas are beyond the experimental observation limits. Closed bars denote anthracene levels observed by ground state (S_0) spectroscopy. Striped bars are levels observed by S_1 absorption spectroscopy (laser photolysis). Open bars are levels unobserved by either one of such techniques. With the exception of the 650-nm band, all marked wavelength values are those predicted for the exciplex (0-0 or peak) transitions. The reader is invited to compare them with the observed spectrum at the bottom (data taken from ref 18).

al.,²⁷ who recorded the absorption spectra of the CT triplets in various TCNB complexes. The presence of the 475-nm band of (TCNB)⁻²⁷ corresponds to the triplet analog of process a: ${}^3(D+A^-)^* \rightarrow {}^3(D+A^*)$. In contrast to observations reported above for the singlet fluorescent state, the triplet spectrum of the TCNB-toluene complex exhibits additional bands above 500 nm. In agreement with the previous analy-

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sis for singlet exciplexes, such bands are assigned²⁶ to the triplet analogs of type d, i.e.: ${}^3(D+A^-)^* \rightarrow (D^3A^*)$.

The failure to observe such reverse CT transitions in the spectrum of the corresponding singlet EDA complexes may be due to relatively poor mixing between the singlet CT and the locally excited configurations. For many EDA complexes, the CT configuration is strongly coupled with the unexcited no-bond configuration (AD), rather than with excited structures, a fact which is responsible for the stabilization of the complex ground state.

Time-Resolved Emission Spectroscopy. The fluorescence spectra of exciplexes and EDA complexes markedly depend on both temperature and solvent polarity. As the static dielectric constant of the solvent increases, the frequency of the fluorescence decreases, a phenomenon which is indicative of the high polarity of the excited state. A quantitative analysis of the effect,²⁸⁻³⁰ based on earlier models,³¹ attributes the fluorescence spectral shifts to the stabilization of the polar excited state by solvation as well as to the fact that during emission the solvent orientation around the complex does not change. A Franck-Condon state is thus reached which lies above the relaxed, nonpolar, ground state.

Such treatments, leading to the evaluation of the exciplex dipole moment, apply when the solvent relaxation time (τ_r) is considerably shorter than the lifetime of the excited state (τ_f), so that emission occurs from a completely solvated complex. At low temperatures and high solvent viscosities the relaxation is slowed down, and when $\tau_r \sim \geq \tau_f$, emission can take place from nonrelaxed solute-solvent configurations.³² This leads to temperature-induced fluorescence shifts such as those observed by Mataga and Murata³³ in the case of the low-temperature TCNB-toluene system. Upon exciting the same complex with a pulsed N_2 laser at 147 K, Egawa, *et al.*,³⁴ observed that as time elapses in the 10^{-9} - 10^{-7} -sec range the emission band undergoes a red shift which directly reflects the solvent reorientation process, from the Franck-Condon to the equilibrium state of the solvated complex. The data were found to be in fair agreement with the theoretical expression of Bakhshiev³⁵ (eq 5), relating the time depen-

$$I(\nu, t) = \text{constant} \times f(\nu, t) \exp(-t/\tau_f) \quad (5)$$

dence of the fluorescence intensity at various wavelengths, $I(\nu, t)$, with the lifetime of the excited com-

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(31) E. Lippert, *Z. Elektrochem.*, **61**, 962 (1967); J. Czekalla and K. O. Meyer, *Z. Phys. Chem. (Frankfurt am Main)*, **27**, 185 (1961); W. Liptay, *Z. Naturforsch. A*, **20**, 1441 (1965).

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plex τ_f . $f(\nu, t)$ is a parameter representing the time-dependent shift of the fluorescence spectrum.

The above considerations strictly apply when the polar fluorescent state of an EDA complex is prepared by the very act of light absorption within the complex CT band. In the case of exciplexes the emitting state is generated *via* a bimolecular, usually diffusion-controlled, quenching reaction. Thus, in order to be detected, the exciplex solvent relaxation process ought to be slower than the quenching reaction which leads from, e.g., $^1A^*$, to $^1(A-D^+)^*$.

Following earlier studies,^{4d,36} Nakashima, *et al.*,³⁷ found suitable experimental conditions for the observation of solvent relaxation around exciplexes. Time resolved spectra for pyrene (acceptor) in highly viscous supercooled tri-*n*-butylamine (donor) at 156 K showed that, within the first 20 nsec, the maximum of the exciplex emission band undergoes a red shift accompanied by a simultaneous increase in intensity (from a nonzero initial value). The first effect is attributed to some specific (AD) pairs having an initial geometrical configuration leading to a very fast formation of the exciplex. A solvent reorientation occurs subsequently, leading to the time-dependent red shift of the fluorescence. The time-dependent increase in intensity is attributed to a rearrangement of solvent-solute configurations which lacked the initial geometry required for the immediate formation of the exciplex. This rearrangement occurs in the same time range as for solvent relaxation around the newly formed dipole.

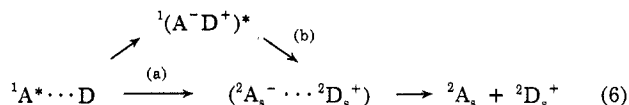
Finally, let us speculate as to the time-resolved absorption (rather than emission) spectra of exciplexes or fluorescent EDA complexes. Our previous analysis predicts that, since the CT nature is maintained, transitions of types a and b will not be significantly affected by solvent reorganization and will not exhibit a time-dependent shift. In fact, a recent observation²⁷ has shown that the 475-nm absorption band of the fluorescent TCNB-toluene complex is present, practically unshifted, also at 77 K, when solvent relaxation does not occur within the fluorescence lifetime. On the other hand, the reverse CT bands c and d, involving a change in complex polarity, should exhibit a time-dependent blue shift, in complete analogy with the time-dependent fluorescence red shift. If verified experimentally, such a prediction may serve as a powerful tool in discriminating between transitions of types a and b and those of types c and d.

Ionization

Exciplexes in Polar Solvents. Upon increasing the solvent polarity, both the exciplex fluorescence intensity and its lifetime decrease.³⁸⁻⁴¹ Ultimately,

in polar solvents such as acetonitrile, the exciplex fluorescence can no longer be detected and, as shown by flash photolysis, the quenching process is associated with the formation of the corresponding radical ions of the donor and the acceptor.⁴²⁻⁴⁴

One desires a detailed model to explain those observations and especially the fact that the fluorescence intensity decreases more rapidly with increasing polarity than does the corresponding fluorescence lifetime. Weller and coworkers⁴² formulated a scheme according to which the yield of formation of the fluorescent exciplex $^1(A-D^+)^*$ (from the initially formed encounter complex, $(^1A^* \cdots D)$, as well as its lifetime, are reduced in polar solvents due correspondingly to processes 6a and 6b. ($^2A_s^- \cdots ^2D_s^+$)



is a solvent-shared ion pair which may subsequently dissociate to the separated ions. An alternative approach attributed the polarity effects to solvent-induced changes in the exciplex radiative as well as nonradiative transition probabilities.³⁹ Although such effects do exist to a certain extent, this interpretation has been criticized on both experimental and theoretical grounds.^{29,45} Experimentally, direct evidence supporting Weller's scheme comes from the recent laser-induced photoconductivity studies of Mataga and coworkers.^{46a,b} Working with pyrene* (or anthracene*) + DMA in pyridine ($\epsilon = 12.3$) they observed that most of the photocurrent is present immediately after the laser pulse, thus confirming process 6a. However, a small fraction grows in slowly at a rate matching the decay of the exciplex fluorescence, in agreement with eq 6b.

Taniguchi, *et al.*,⁴⁶ have also estimated, semiempirically, the free-energy difference between the dissociated ions ($A_s^- + D_s^+$), and the solvated ion pair ($A_s^- \cdots D_s^+$). When $\epsilon \sim 10$ this difference amounts to ~ 0.2 eV, thus being considerably larger than the thermal energy at room temperature. Since ions are still monophotonically generated even in solvents with dielectric constants as low as ~ 6 , this estimate led to the suggestion that the fast dissociation process, circumventing the thermalized exciplex, may take place from nonrelaxed ion-pair^{46a,b} or exciplex⁴⁷ states by-passing also the thermalized ion pair. The question as to whether ionization does quantitatively account for the decrease in the population of the fluorescent state $^1(A-D^+)^*$ at higher polarities is still open. Recent observations of Mataga and coworkers⁴⁷ indicate that the process competing in polar solvents

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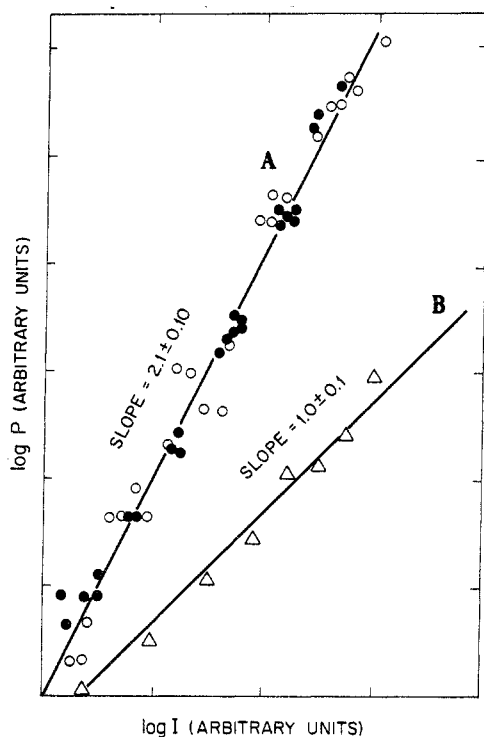


Figure 5. Dependence of peak photocurrents (P) on the laser light intensity (I) in CT quenched systems (data taken from ref 19): (A) $P \sim I^2$ dependence in the case of TMPD quenched by 0.1 M naphthalene (\circ) or biphenyl (\bullet) in isopentane; (B) linear relation between P and I in the case of pyrene quenched by 0.1 M DEA in acetonitrile.

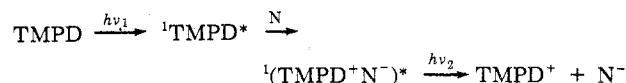
with the formation of ${}^1(A-D^+)^*$ (from nonrelaxed states) may be intersystem crossing (see below) rather than ionization. Evidently, more data are required to obtain a quantitative picture of the primary processes in exciplex systems.

Exciplexes in Nonpolar Solvents. No transient photoconductivity is detectable when the fluorescence of pyrene, excited by the 347.2-nm ruby pulse, is quenched by dimethylaniline in n -hexane ($\epsilon = 1.89$) as solvent.⁴⁶ This fits the semiempirical estimates of Taniguchi, *et al.*, which predict for the free energy of the dissociated ion radical state, ($A_s^- + D_s^+$), a value of 4.93 eV which is not only above the energy of the thermalized exciplex (3.28 eV) but also above the energy of the laser quantum (3.6 eV).

A different situation is, however, encountered in other donor-acceptor systems. Thus, photoconductivity is observed when the fluorescence of TMPD in hydrocarbon solvents, excited by the 337.1-nm N_2 laser line, is quenched by aromatic electron acceptors such as naphthalene (N) and biphenyl (B).¹⁹ Since the energy requirements for photoionization cannot be fulfilled by a single light quantum, this observation can be rationalized only by assuming a two-photon process. This is in fact confirmed by plot A in Figure 5, showing a second-power dependence of the photocurrent (P) on the light intensity (I). Such a nonlinear behavior characterizes biphotonic processes and is in contrast with the linear relationship between P and I observed, for example, in the case of pyrene-DEA in acetonitrile (Figure 5 B and ref 46), where the ionization process (see above) is monophotonic.

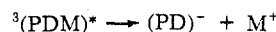
As to the detailed mechanism of the two-quantum

reaction, a detailed analysis¹⁹ suggests that ions are produced *via* light absorption by the thermalized exciplex. Schematically



Such a mechanism implies a substantial extinction coefficient of ${}^1(\text{TMPD}^+\text{N}^-)^*$ at the 337.1-nm laser excitation line. Although due to experimental difficulties direct measurement of such parameters was not possible, the previous analysis of the exciplex absorption spectrum predicts a strong contribution from transitions of types a and b in the cases of both ${}^1(\text{TMPD}^+\text{N}^-)^*$ and ${}^1(\text{TMPD}^+\text{B}^-)^*$.

EDA Complexes. The low fluorescence quantum yields of EDA complexes at room temperature have frequently been attributed to ionic dissociation in the excited state. However, the available evidence concerning the photoionization of EDA complexes is still very limited. We shall refer to a few experiments relevant to this problem. Low-temperature flash excitation of the CT band of the pyromellitic dianhydride (PD)-mesitylene complex leads to the observation of a growing-in of the (PD)⁻ ion at a rate matching the decay of the complex CT phosphorescence.⁴⁸ This is indicative of spontaneous thermal dissociation of the lowest (CT) triplet state.



Ionic dissociation of the CT singlet state has been proposed in the case of some EDA complexes on the basis of laser photoconductivity experiments.⁴⁹ It appears that nonrelaxed Franck-Condon excited states are important in the ionization process.⁴⁷ Both triplet and singlet ionization mechanisms appear to operate in the case of the TCNB- α -methylstyrene complex.⁵⁰ It appears, however, that additional experimental data, such as the effects of light intensity and solvent polarity, studied with fast detection techniques, will be necessary to obtain a comprehensive picture of photoionization mechanisms of EDA complexes.

Intersystem Crossing

"Slow" Intersystem Crossing (ISC) in Nonpolar Solvents. We have previously reported pulsed laser experiments in the TMPD-naphthalene system leading to the observation of a transient absorbance change attributed to the ${}^1(\text{TMPD}^+\text{N}^-)^*$ exciplex. A residual long-lived change in absorbance, after the exciplex decay is completed, can be readily attributed to the triplet state of naphthalene (λ_{max} 415 nm). The result is consistent with previous observations of triplets following CT fluorescence quenching in polar^{3,4b,51,52} and nonpolar⁵³ solvents. As to the

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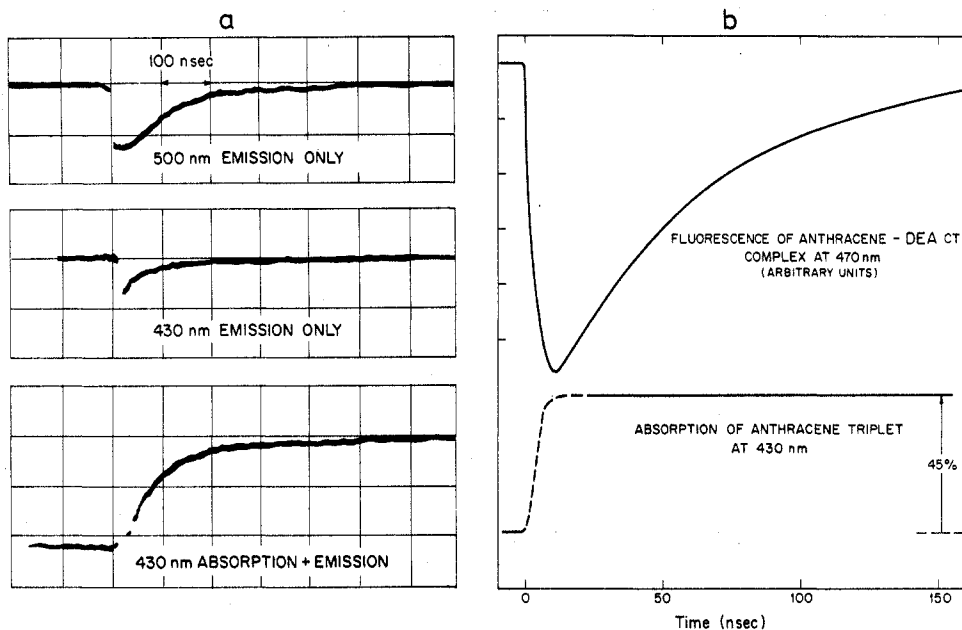
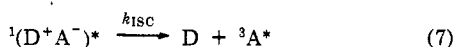


Figure 6. Transient absorbance changes showing the anthracene triplet-state generation at 430 nm in exciplex systems. (a) Slow growing-in process in $3.6 \times 10^{-4} M$ anthracene quenched by $3 \times 10^{-1} M$ DMA in cyclohexane. Note the matching between the absorbance growing-in and the exciplex fluorescence decay (data taken from ref 55, ruby laser photolysis). (b) Fast triplet generation for anthracene ($10^{-2} M$) quenched by DEA ($5 \times 10^{-1} M$) in toluene. Note that the absorbance change at 430 nm is completed prior to any substantial decay of the exciplex (data taken from ref 60, N_2 laser photolysis).

time scale associated with the triplet formation, a distinct growing-in stage of the absorbance at 415 nm indicates that the triplet is generated at the same rate at which the exciplex fluorescence disappears ($\tau_{1/2} \sim 60$ nsec).⁵⁴ This establishes that ISC does occur from the thermalized exciplex in competition with fluorescence.



Similar growing-in processes, matching the exciplex fluorescence decay, have also been observed for the triplet state of biphenyl in the system ${}^1TMPD^* + B$,⁵⁴ for that of anthracene when the latter fluorescence is quenched by dimethylaniline^{54,55} (shown in Figure 6a), and for the naphthalene triplet in the system ${}^1DEA^* + N$.⁵⁴ Independent evidence supporting the mechanism of eq 7 is based on experiments⁵⁴ in which triplet yields (ϕ_{ISC}), recorded in deaerated solutions, are compared with those observed in the same systems in the presence of dissolved oxygen ($\phi_{ISC}(O_2)$). In such systems the exciplex fluorescence is efficiently quenched by O_2 ⁵⁶ so that the observation $\phi_{ISC}(O_2) < \phi_{ISC}$ confirms that ISC and fluorescence emission originate competitively from the thermalized exciplex.

It can therefore be concluded that, as in the case of most aromatic molecules, ISC in the above CT systems occurs in the nanosecond range in competition with fluorescence. It will be referred to as a "slow" ISC path.

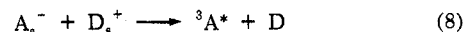
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(56) The same is true for the triplet states. However, the nanosecond time resolution of the laser apparatus allows the measurements of relative triplet yields even when their lifetime is shortened by the reaction with O_2 .

"Slow" ISC in Polar Media. Extensive chemiluminescence studies^{57,58} indicate that the recombination of aromatic radical ions in ethers can lead to the formation of triplet states (eq 8). We saw above that



formation of ions following CT fluorescence quenching is an efficient process at relatively high solvent polarities. Thus, as long as the energy level of the separated ions lies above that of the triplet state, process 8 should be considered as a plausible ISC path for excited EDA complexes or exciplexes.^{51,52} In order to observe process 8 directly in photochemical systems, the rate of bimolecular ion decay (equal to that of the ${}^3A^*$ evolution) should be faster than the decay of ${}^3A^*$, but within the time resolution of the pulsed photolysis apparatus. Such conditions have been achieved using the N_2 laser as the exciting source. Thus, a growing-in of the pyrene triplet, kinetically matching the diffusion-controlled bimolecular decay of the ions, has been observed following the quenching of the pyrene fluorescence by DEA in acetonitrile as well as in several other systems.^{54,59}

"Fast" ISC in Polar and Nonpolar Solvents. A close examination of the laser photolysis data for anthracene* and pyrene* quenched by DEA,⁵³ as well as for pyrene* and 1,2-benzanthracene* quenched by DMA,⁵⁵ indicates that the above "slow" mechanism is not the only ISC path in CT systems.⁵³ Thus, in such cases, the characteristic bands of the corresponding triplets are present immediately after the laser flash, prior to any substantial decay of the exciplex (see Figure 6b). In some cases, e.g., anthracene*

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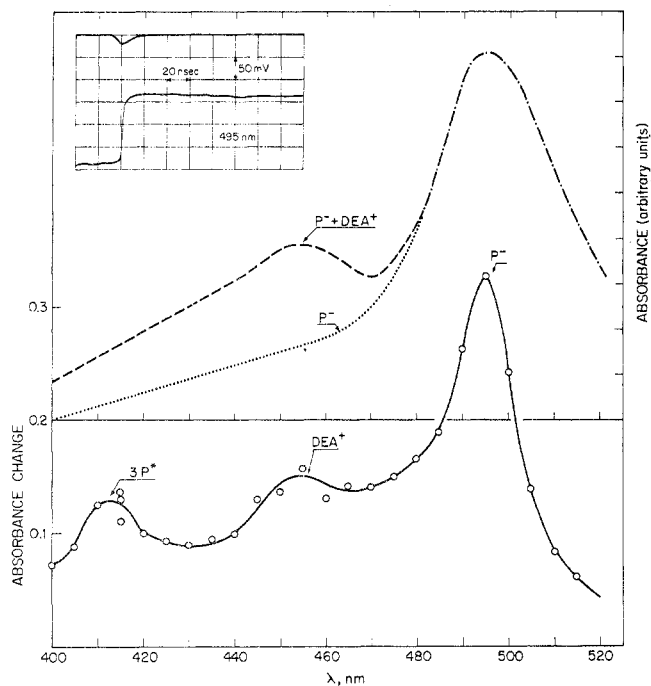


Figure 7. Ions and triplet-state production in the CT quenching of pyrene fluorescence by DEA in a polar solvent. Solid line: transient change in absorbance recorded 25 nsec after firing the nitrogen laser in a methanol solution of 10^{-4} M pyrene quenched by 5×10^{-2} M DEA. Dashed line: superimposed spectra of P^- and DEA^+ reproduced from available data in the literature (details in ref 60). The 415-nm band which is absent in the superimposed spectra of D^- and A^- is due to the triplet state of pyrene. Insert: oscillogram taken at the maximum of the pyrene negative ion absorption band.

+ DMA, the appearance of the triplet growing-in stage, together with a substantial triplet absorption immediately after the pulse, indicate that both "slow" and "fast" mechanisms may operate simultaneously in the same system. Figure 7 shows that a "fast" ISC mechanism is also occurring in a polar solvent such as methanol where no exciplex fluorescence is detectable. The change in absorbance recorded 25 nsec after firing the laser not only exhibits the characteristic bands of pyrene⁻ (at 495 nm) and of DEA^+ (around 460 nm), but also that of the pyrene triplet state at 415 nm. After 25 nsec the bimolecular decay of the ions is still negligible (Figure 7, insert), so that process 8 cannot account for the substantial amount of triplets present at this time.

Independent support for the occurrence of a "fast" ISC mechanism comes from comparison of temperature effects on the triplet yields with those on the yields of exciplex fluorescence (nonpolar solvents) and ion formation (polar solvents).⁶⁰ The data are interpreted by assuming that the initially formed locally excited encounter pair ($^1A^* \cdots D$) (see eq 6) converts first to a nonequilibrium form of the CT state, $^1(A-D)^{\pm}$. In a nonpolar solvent this state can either relax to the fluorescent state, $^1(A-D)^+*$, or undergo ISC. This competition determines the relative yields of the triplet ($^3A^*$) and of the fluorescent state, $^1(A-D)^+*$. In polar systems the process com-

peting with triplet formation is: $^1(A-D)^+ \rightarrow (A_s^- \cdots D_s^+)$, leading finally to the separated ions $A_s^- + D_s^+$. It is argued that $^1(A-D)^{\pm}$ is a Franck-Condon state with excess vibrational energy so that the observed temperature effects on the various yields are due to temperature effects on vibrational relaxation rates.⁶¹

Similar conclusions have recently been extended by Mataga and coworkers to the case of the TCNB-toluene EDA complex²⁷ at 77 K, for which they observed a fast (<20 nsec) generation of the CT triplet, preceding the population of the fluorescent state. At 77 K the fluorescent state is always nonrelaxed with respect to its permanent dipole solvation structure; nevertheless, it does not undergo ISC. This confirms that the excess energy enhancing ISC in the Franck-Condon state is intrinsic within the complex rather than being due to complex-solvent interactions.

Finally, a few words about the high rates involved in the fast ISC path: it was long ago recognized that intermolecular CT interactions can provide a general mechanism for the induction of spin-orbital coupling.⁶² But which coupling scheme is relevant in enhancing spin-orbit coupling in the CT systems previously discussed? Also, why is such coupling very efficiently induced in nonrelaxed levels of the lowest electronically excited singlet state?

Tsubomura and Mulliken in their treatment of fluorescence quenching by molecular oxygen⁶³ have suggested that, due to the $\langle ^1\psi_1 H' ^3\psi_{CT} \rangle$ spin-orbit matrix element, ISC takes place from the localized lowest excited singlet state of the $M \cdot O_2$ CT complex ($^1\psi_1$) to the CT triplet state ($^3\psi_{CT}$). Such a process, followed by the transition to a localized triplet ($^3\psi_1$), has been also assumed by McGlynn, *et al.*, to be responsible for the increased ISC rates in various CT complexes.⁶⁴ However, other coupling schemes due to spin-orbit matrix elements such as $\langle ^1\psi_{CT} H' ^3\psi_{CT} \rangle$, $\langle ^1\psi_{CT} H' ^3\psi_1 \rangle$, and $\langle ^1\psi_{CT} H' ^3\psi_h \rangle$, where $^3(\psi_1)$ and $^3(\psi_h)$ are correspondingly the lowest and a higher localized triplet state, should also be taken in consideration.⁶²

Discrimination between the various alternatives is at present impossible. Moreover, it is difficult to speculate as to the dramatic effect of nonrelaxed states in enhancing the process. One possibility is that excess vibrational energy is needed to reach an intersection point of the two potential energy curves involved [*e.g.*, those of $^1\psi_{CT}$ and $^3(\psi_1)$]. Another possibility is that the excess energy in $^1\psi_{CT}$ allows the transition to a higher triplet state [$^1(\psi_{CT})$ or $^1(\psi_h)$] which is closer to it in energy than $^3\psi_1$. Obviously, much more experimental and theoretical work will be required for quantitative description of the prethermalized ISC path.

Most of the experimental data from this laboratory reported in this Account are from research sponsored by the U. S. National Bureau of Standards.

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