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Electronic Structures of Exciplexes and Excited Charge-Transfer Complexes

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Abstract: For the exciplexes and excited charge-transfer (CT) complexes formed between 9,10-dicyanoanthracene and 2,6,9,10-tetracyanoanthracene as electron acceptors and alkylbenzenes as donors, the radiative rate constants (k_f) increase with increasing emission energy. The increase in k_f is attributed to a corresponding decrease in the charge-transfer character of the emitting species. This is explained in terms of the relative contributions of pure ion-pair and locally excited states to the emitting state. With decreasing solvent polarity and with increasing redox energy of the acceptor/donor pair ($E^{ox}{}_D - E^{red}{}_A$), the energy of the pure ion-pair state is raised and mixing with the locally excited states increases. The dependence of k_f on emission energy is analyzed quantitatively using a three-state model in which mixing among the first locally excited singlet state of the cyanoanthracenes, the pure ion-pair state, and the neutral state is taken into account. Simplified methods for data analysis are also discussed. From the analyses, the relationship between the electronic structures of the exciplex/excited CT complexes and the emission frequency is obtained. For these acceptor/donor systems, the emitting species can be considered to be essentially pure contact radical-ion pairs (>90% CT character) when their emission maxima are lower in energy than the 0,0 transition of the acceptor excited singlet states by ca. 5000 cm^{-1}. Values of ca. 1300–1350 cm^{-1} are obtained for the electronic matrix elements coupling the locally excited and ion-pair states. The corresponding matrix elements for coupling the ion-pair and the neutral states are ca. 750–900 cm^{-1}, which are similar to those estimated previously from studies of the rates of nonradiative electron transfer in closely related species.

I. Introduction

An important issue related to exciplex and excited charge-transfer (CT) complex photophysics is the extent to which charge is transferred from the donor (D) to the acceptor (A). The mechanisms and rates of the radiative and nonradiative deactivation processes of these species, and also of any chemical reactions, should depend upon the extent of charge transfer. For example, nonradiative deactivation represents an energy-wasting step for excited CT species, and consequently, methods for predicting absolute rate constants for this process are of great importance. This issue has recently been addressed in a study of excited CT complexes in which the rates of nonradiative decay were successfully predicted, with no adjustable parameters, from data obtained from measurements of the corresponding CT emission.[1] It was assumed that the nonradiative decay processes were return electron transfer reactions, i.e. that the excited CT complexes were fully ionic. Before this approach could be applied to any particular excited CT species, however, it would have to be first established that charge separation is, in fact, complete. Estimates of fractional charge transfer have, in fact, been made previously for several exciplex and excited CT complexes, using a variety of techniques.[2] Nevertheless, no generally applicable simple method has been described, and as a result, this important property has been quantified for very few systems.

The electronic states of both exciplexes and excited CT complexes are usually described as linear combinations of neutral, ion-pair, and locally excited states of the acceptor and donor, e.g. $\Psi_0[AD]$, $\Psi_1[A^{\bullet-}D^{\bullet+}]$, and $\Psi_2[A^*D]$ (eq 1).[3] The representation

$$\Psi_{Ex} = c_0\Psi_0[AD] + c_1\Psi_1[A^{\bullet-}D^{\bullet+}] + c_2\Psi_2[A^*D] \quad (1)$$

in eq 1 is appropriate for the case of a good electron acceptor and a good electron donor, where the energy of the lowest singlet excited state of A is considerably lower than that of D. In eq 1, Ex represents either an exciplex or an excited CT complex. The extent of charge transfer in the Ex is determined by the values of the expansion coefficients c_1 and c_2; the coefficient c_0 is usually small. The fractional charge transfer in the Ex, f_{CT}, can be defined as $c_1{}^2$.[4,5] In the limiting case when c_1 (and therefore f_{CT}) approaches unity, the Ex is essentially a contact radical-ion pair (CRIP, $A^{\bullet-}D^{\bullet+}$).[3b,4] The extent of mixing among the various basis states of eq 1 will depend upon the magnitudes of the appropriate electronic coupling matrix elements, which can be rather large for Ex species.[1] The Ex of eq 1 can, of course, be taken to represent the CT excited state of any AD system. For example, the extent of charge transfer is also an important issue in linked donor/acceptor systems.[6] As a result of the large through-bond electronic couplings which are sometimes found in

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[5] This is correct if Ψ_0, Ψ_1, and Ψ_2 are orthogonal. For the more general case, see ref 4.

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such systems, it is important to be able to assess the possibility of mixing among locally excited and pure ion-pair states in these cases too.

In the electron-transfer literature, there has been considerable discussion of the relationship between the electron-transfer matrix elements and the strengths of the corresponding CT radiative transitions. Such relationships for CT absorptions are well-known.[4,7] Of particular relevance to the present study, there has been recent interest in the determination of electron-transfer matrix elements from CT radiative rate studies.[1,8] In the accompanying paper, we described a detailed study of the radiative rates for the Ex formed between cyanoanthracene acceptors and alkyl-substituted benzene donors in various solvents.[9] The radiative rate constants exhibit a smooth dependence on the Ex emission frequency, which is readily explained in terms of variations in the extent of mixing of locally excited and ion-pair states. With increasing solvent polarity and/or with increasing donor and acceptor abilities, the energy of the ion-pair state decreases relative to that of the locally excited state. As a result, the emission energy decreases, the extent of charge transfer in the Ex increases, and the radiative process changes from intramolecular to intermolecular in nature, leading to a decrease in the radiative rate constant.[10]

In this paper, we describe a quantitative analysis of the cyanoanthracene/alkylbenzene Ex radiative rate data which then allows the f_{CT} of these systems to be evaluated. The data are analyzed in terms of the three-basis-state model indicated in eq 1, and the matrix elements which couple Ψ_1 to Ψ_0 and to Ψ_2, respectively H_{01} and H_{12}, are determined. Mixing of neutral, ion-pair, and locally excited states has been considered previously in various CT absorption and emission studies.[3,10,11] In some cases, the coupling matrix elements have been estimated from molecular orbital calculations,[3b,11b,d] and in others, estimates of H_{12} have been made from analyses of experimental data.[3c,11e] In this work, we describe methods for analysis of CT radiative rates in terms of the three-basis-state model, which allows the determination of *both* of the matrix elements H_{01} and H_{12}. Some of the results described here, and a simplified form of the data analysis, have been published previously in a communication.[12] In the present work, we discuss a more comprehensive set of radiative rate data and describe a detailed model for analysis of the radiative rate data in addition to the simplified form discussed previously. Independently, and as this work was in progress, Bixon, Jortner, and Verhoeven described another simple method for analysis of CT radiative rate data.[13] This data analysis method is also discussed here.

From the data analyses, values for the electronic coupling matrix elements and hence the f_{CT} for the cyanoanthracene/alkylbenzene systems are determined. As indicated above, in other recent work on excited CT states, the relationship between the radiative and nonradiative electron-transfer reactions in excited CT states and the applicability of current electron-transfer theories have been explored.[1,8,14] The values for the matrix elements obtained in the present work are found to be consistent with those estimated from the measured rates of nonradiative electron transfer within related CRIP species.[14]

Table 1. Average Emission Frequencies, Measured and Calculated Radiative Rate Constants, and Percentages of Charge Transfer of 2,6,9,10-Tetracyanoanthracene (TCA)/Alkylbenzene Excited CT Complexes in Different Solvents

D[a]	solvent[b]	$\tilde{\nu}_{av}$[c] (10^3 cm^{-1})	$(k'_f)_{measd}$[d] (10^6 s^{-1})	$(k'_f)_{calcd}$[e] (10^6 s^{-1})	$\%_{CT}$[f]
p-Xy	CHX	19.69	6.96	6.47	67
TMB	CHX	18.89	3.67	3.65	80
Dur	CHX	17.82	1.89	1.99	89
PMB	CHX	17.41	1.70	1.65	91
HMB	CHX	16.56	1.22	1.18	93
p-Xy	CTC	18.98	4.72	3.87	79
TMB	CTC	18.09	2.61	2.29	87
Dur	CTC	16.89	1.59	1.33	92
PMB	CTC	16.45	1.26	1.13	93
HMB	CTC	15.63	0.98	0.88	95
p-Xy	TCE	18.41	2.77	2.72	85
TMB	TCE	17.53	1.85	1.74	90
Dur	TCE	16.27	1.13	1.07	94
HMB	TCE	14.75	0.75	0.70	96
Dur	Diox	14.91	0.76	0.73	96
HMB	Diox	13.74	0.54	0.57	97
PMB	Tol	14.98	0.78	0.74	96
HMB	Tol	14.15	0.69	0.62	97
p-Xy	FB	17.20	1.38	1.51	91
TMB	FB	16.21	1.00	1.05	94
Dur	FB	14.91	0.79	0.73	96
PMB	FB	14.45	0.64	0.66	96
HMB	FB	13.52	0.60	0.55	97
p-Xy	DCM	16.68	1.10	1.23	93
Dur	DCM	14.45	0.68	0.66	96
PMB	DCM	13.93	0.59	0.59	97
HMB	DCM	13.11	0.44	0.51	97

[a] The alkylbenzene donors are *p*-xylene (*p*-Xy), 1,2,4-trimethylbenzene (TMB), durene (Dur), pentamethylbenzene (PMB), and hexamethylbenzene (HMB). [b] The solvents and their refractive indices are cyclohexane (CHX, 1.426), carbon tetrachloride (CTC, 1.4595), trichloroethylene (TCE, 1.4755), *p*-dioxane (Diox, 1.422), toluene (Tol, 1.496), fluorobenzene (FB, 1.465), and dichloromethane (DCM, 1.424). [c] The average emission frequency of the excited CT complex as determined from eq 19. [d] Measured Ex radiative rate constant, corrected for the solvent refractive index (eq 3b,c). [e] Calculated Ex radiative rate constant based on the parameters given in Table 5 and calculated as described in section III.A. [f] Percentage of charge transfer of the Ex, defined as 100 × c_1^2 (eq 1) and calculated as described in section IV.

II. Radiative Rate Data

The electron acceptors discussed here are 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA), and the donors are the methyl-substituted benzenes *p*-xylene (*p*-Xy), 1,2,4-trimethylbenzene (TMB), durene (Dur), pentamethylbenzene (PMB), and hexamethylbenzene (HMB).[15] As discussed in detail in the accompanying paper, excitation of these acceptors in the presence of the donors in argon-purged solution in solvents with varying polarity gives typical Ex emission spectra.[9] The Ex emissions occur at longer wavelength and have smaller radiative rate constants with increasing solvent polarity. The Ex emissions also occur at longer wavelengths and with smaller radiative rate constants with decreasing E_{redox} (eq 2), where $E^{ox}{}_D$ and $E^{red}{}_A$ are the donor oxidation potential and the acceptor reduction potential, measured in a polar solvent against the same reference electrode. (The redox parameters for the present donors and acceptors are given in ref 9.)

$$E_{redox} = E^{ox}{}_{D} - E^{red}{}_{A} \qquad (2)$$

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Table 2. Average Emission Frequencies, Measured and Calculated Radiative Rate Constants, and Percentages of Charge Transfer of 9,10-Dicyanoanthracene (DCA)/Alkylbenzene Exciplexes in Different Solvents

D[a]	solvent[b]	$\tilde{\nu}_{av}$[c] (10^3 cm^{-1})	$(k'_f)_{measd}$[d] (10^6 s^{-1})	$(k'_f)_{calcd}$[e] (10^6 s^{-1})	$\%_{CT}$[f]
Dur	CHX	20.33	8.69	9.94	57
PMB	CHX	19.80	6.27	6.49	71
HMB	CHX	18.97	3.64	3.71	83
Dur	TCE	19.42	6.15	4.94	77
PMB	TCE	18.82	3.99	3.40	84
HMB	TCE	18.02	2.22	2.27	89
PMB	Diox	18.25	2.69	2.52	88
HMB	Diox	17.35	1.73	1.73	92
PMB	*p*-Xy	18.67	3.48	3.13	85
HMB	*p*-Xy	17.89	2.04	2.14	90
Dur	FB	18.71	3.65	3.20	85
PMB	FB	18.04	2.42	2.32	89
HMB	FB	17.08	1.62	1.57	93
PMB	DCM	17.32	1.90	1.71	92
HMB	DCM	16.35	1.29	1.26	94
PMB	*o*-DCB	17.82	2.01	2.08	90
HMB	*o*-DCB	16.90	1.41	1.48	93
Dur	BN	16.76	1.58	1.42	94
PMB	BN	16.20	1.29	1.21	95
HMB	BN	15.40	0.88	1.00	96
Dur	AN	16.12	1.30	1.18	95
PMB	AN	15.52	1.07	1.02	96

[a] The alkylbenzene donors are durene (Dur), pentamethylbenzene (PMB), and hexamethylbenzene (HMB). [b] The solvents and their refractive indices are cyclohexane (CHX, 1.426), trichloroethylene (TCE, 1.4755), *p*-dioxane (Diox, 1.422), *p*-xylene (*p*-Xy, 1.495), fluorobenzene (FB, 1.465), dichloromethane (DCM, 1.424), *o*-dichlorobenzene (*o*-DCB, 1.551), butyronitrile (BN, 1.384), and acetonitrile (AN 1.344). [c] The average emission frequency of the Ex as determined from eq 19. [d] Measured Ex radiative rate, corrected for the solvent refractive index (eq 3b,c). [e] Calculated Ex radiative rate based on the parameters given in Table 5 and calculated as described in section III.A. [f] Percentage of charge transfer of the Ex, defined as 100 × c_1^2 (eq 1) and calculated as described in section IV.

Table 3. Average Emission Frequencies, Measured and Calculated Radiative Rate Constants, and Percentages of Charge Transfer for the Excited Cyanoanthracene Acceptors[a] in Aromatic Solvents

A[a]	solvent[b]	$\tilde{\nu}_{av}$[c] (10^3 cm^{-1})	$(k'_f)_{measd}$[d] (10^7 s^{-1})	$(k'_f)_{calcd}$[e] (10^7 s^{-1})	$\%_{CT}$[f]
DCA	FB	21.57	2.56	2.56	(4)
DCA	Tol	21.44	2.19	2.40	(8)
DCA	*o*-DCB	21.37	2.13	2.30	(11)
DCA	*p*-Xy	21.23	1.97	2.10	18
DCA	TMB	20.76 ± 0.06[g]	1.32	1.36 ± 0.6	41 ± 2
TCA	FB	21.16	1.93	2.00	(10)
TCA	*o*-DCB	20.93	1.69	1.70	21

[a] DCA is 9,10-dicyanoanthracene, and TCA is 2,6,9,10-tetracyanoanthracene. [b] The solvents and their refractive indices are fluorobenzene (FB, 1.465), toluene (Tol, 1.496), *o*-dichlorobenzene (*o*-DCB, 1.551), *p*-xylene (*p*-Xy, 1.495), and 1,2,4-trimethylbenzene (TMB, 1.504). [c] The average emission frequency calculated according to eq 18. [d] Measured Ex radiative rate, corrected for the solvent refractive index (eq 3b,c). [e] Calculated Ex radiative rate constant based on the parameters given in Table 5 and calculated as described in section III.A. [f] Percentages of charge transfer of the Ex, defined as 100 × c_1^2 (eq 1) and calculated as described in section IV. The low values of $\%_{CT}$ (given in parentheses) are susceptible to a large error, as they are very sensitive to the value chosen for $\bar{\nu}_{A^*}$. [g] The percentage of CT of excited DCA in TMB is nearly halfway between those of the A* and the ion-pair state. The difference, however, between ν_{av} calculated according to either eq 18 or eq 19 is small (20.71 × 10^3 and 20.82 × 10^3 cm^{-1}, respectively). The ranges given for $(k'_f)_{calcd}$ and for $\%_{CT}$ are the result of using these two values of $\bar{\nu}_{av}$.

Table 4. Average Emission Frequencies and Radiative Rate Constants for the Excited Cyanoanthracenes[a] in Nondonating Solvents

	DCA		TCA	
solvent[b]	$\tilde{\nu}_{av}$[c] (10^3 cm^{-1})	k'_f[d] (10^7 s^{-1})	$\tilde{\nu}_{av}$[c] (10^3 cm^{-1})	k'_f[d] (10^7 s^{-1})
CTC	21.88	2.82	21.73	2.54
DCM	21.56	2.71	21.51	2.39
AN	21.56	2.73	21.46	2.48

[a] DCA is 9,10-dicyanoanthracene, and TCA is 2,6,9,10-tetracyanoanthracene. [b] The solvents and their refractive indices are carbon tetrachloride (CTC, 1.4595), dichloromethane (DCM, 1.424), and acetonitrile (AN, 1.344). [c] Average emission frequency calculated according to eq 18. [d] Radiative rate constant corrected for the solvent refractive index according to eq 3b,c.

The radiative rate constants and the average emission frequencies (defined below) for the Ex are summarized in Tables 1 and 2. The equivalent data for the acceptors in various solvents, but in the absence of an added alkylbenzene donor, are given in Tables 3 and 4. The data for these A*/solvent systems also indicate varying degrees of CT character in the emitting species, although to a smaller extent than in the conventional Ex.[9] The radiative rate constants, k_f, of the Ex and the A*/solvent systems exhibit a smooth dependence upon emission frequency.[9] The data represent a comprehensive data set for quantitatively studying the consequences of varying degrees of ion-pair and locally excited character in the Ex states. In order to analyze the variations in k_f for the various emitting species, the factors which control this quantity must be considered.

III. Theoretical Analysis of the Radiative Rate Data

It is well-known that k_f is given by an expression of the form shown in eq 3a, in which $f(n)$ is a function of the solvent refractive index and **M** is the electronic transition moment for the emission process.[16] The average emission frequency for the present systems, ν_{av}, is defined below. The refractive-index factor $f(n)$ (eq 3b) is used rather than the more familiar n^3 because it has a somewhat firmer theoretical basis[17] (see Appendix A). For the solvents used here, the dependencies of $f(n)$ and n^3 on the refractive index are virtually identical, except that $f(n)$ is 11% smaller. To compare data from measurements in different solvents, it is convenient to use the radiative rate constants corrected for the refractive index, k'_f (eq 3c).

$$k_f = \frac{64\pi^4}{3hc^3} f(n) \nu_{av}^{\ 3} M^2 \tag{3a}$$

$$f(n) = n\left(\frac{n^2+2}{3}\right)^2 \tag{3b}$$

$$k'_f = \frac{k_f}{f(n)} \tag{3c}$$

M depends upon the electronic nature of the initial and final states involved in the emission process, as shown in eq 4, in which

$$\mathbf{M} = \langle \Psi_{Ex} | \hat{\mu} | \Psi_G \rangle \tag{4}$$

$\hat{\mu}$ is the dipole moment vector operator and Ψ_G is the ground state formed upon emission. For the limiting case when the contribution of the locally excited state to the Ex is minimal (i.e., $c_2 \sim 0$ in eq 1), f_{CT} is essentially unity and the Ex is essentially a pure ion pair. The transition moment under these circumstances, $\mathbf{M}_{A^-D^+}$, arises from mixing of a small amount of ion-pair character into the ground state and should depend upon the emission frequency approximately as indicated in eq 5.[18] In eq 5, $\Delta\mu$ is the difference

$$\mathbf{M}_{A^-D^+} = -\frac{H_{01}\,\Delta\mu}{h\nu_{av}} \tag{5}$$

between the static dipole moments of the pure ion-pair state $\Psi_1[A^{\bullet-}D^{\bullet+}]$ and the neutral state $\Psi_0[AD]$, here assumed to be

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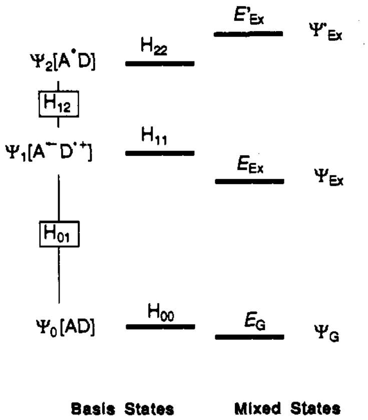

Figure 1. States involved in the formation of exciplexes/excited charge-transfer complexes (Ex). The basis states (neutral (Ψ_0[AD]), ion-pair ($\Psi_1[A^{\bullet-}D^{\bullet+}]$), and locally excited ($\Psi_2[A^*D]$) states) are mixed to form the ground (Ψ_G) and the Ex (Ψ_{Ex}) states with energies E_G and E_{Ex}. The energies associated with Ψ_0, Ψ_1, and Ψ_2 *at the geometry of the Ex state are* H_{00}, H_{11}, and H_{22}, respectively. The electronic matrix element coupling Ψ_0 and Ψ_1 is H_{01} and that coupling Ψ_1 and Ψ_2 is H_{12}.

orthogonal, and H_{01} is the electronic matrix element coupling these states.[19] Thus, $M_{A^-D^+}$ should decrease as ν_{av} increases, and k'_f should be directly proportional to ν_{av}, for a constant H_{01}.[20] As discussed in the accompanying paper, however, k'_f increases much more rapidly than ν_{av} for the Ex with higher emission frequencies, due to a corresponding increase in M as a result of an increasing admixture of the locally excited to the pure ion-pair state.[9] When an Ex is essentially a pure radical-ion pair, the radiative transition to the essentially nonionic ground state is an intermolecular electron-transfer process and is thus expected to have a relatively small value of **M**. In contrast, for the other limiting case of a pure locally excited state, the transition moment, $\mathbf{M}_{A^*}$, corresponds to an allowed intramolecular process and is therefore relatively large compared to $\mathbf{M}_{A^-D^+}$. As the energy of $\Psi_1[A^{\bullet-}D^{\bullet+}]$ increases, the energy of the Ex emission should increase, the contribution to the Ex of the locally excited state $\Psi_2[A^*D]$ should also increase, and so, therefore, should the magnitude of **M**. Evidently, a description of k'_f is required, in which contributions from all three of the states indicated in eq 1 are taken into account.

A. Three-State Mixing Model. The mixing of pure ion-pair and locally excited states has been treated previously several times.[3,10,11] The present model is somewhat different in the manner in which the electronic polarization of the solvent is treated, as detailed in Appendix A. Other explicit and implicit assumptions in the treatment are also discussed in Appendix A. As indicated in eq 1, the emitting Ex is assumed to be described by a three-state electronic basis (cf. Figure 1). The ground state is given analogously by eq 6. The expansion coefficients c_i (eq 1)

$$\Psi_G = d_0\Psi_0[AD] + d_1\Psi_1[A^{\bullet-}D^{\bullet+}] + d_2\Psi_2[A^*D] \quad (6)$$

and d_j (eq 6) and the energies of the two states E_{Ex} and E_G are solutions of the matrix eigenvalue eqs 7 and 8, where **H** is the

$$\mathbf{Hc} = E_{Ex}\mathbf{c} \quad (7)$$

$$\mathbf{Hd} = E_G\mathbf{d} \quad (8)$$

Hamiltonian matrix and **c** and **d** are the column eigenvectors containing the c_i and d_j. In the present case we are interested in geometries characteristic of the Ex species. Thus, E_{Ex} and E_G are the electronic energies of the Ex and the ground state *at the nuclear geometry of the Ex* (cf. Figure 2).

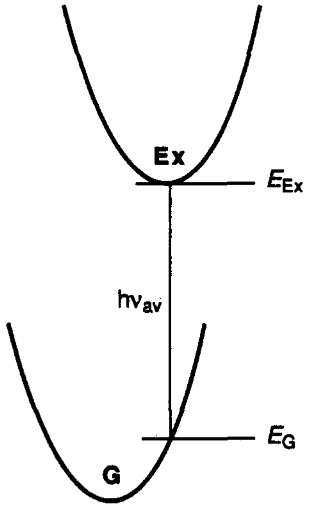

Figure 2. Schematic energy diagram of the ground (G) and the Ex states. E_G is the electronic energy of the ground state *at the Ex equilibrium configuration.* The average emission energy ($h\nu_{av}$) corresponds to the energy difference $E_{Ex} - E_G$.

The basis functions Ψ_0, Ψ_1, and Ψ_2 are assumed to be orthonormal and real-valued, so that $H_{ij} = H_{ji}$ for all i and j.[21] Any influence of the donor on the intramolecular properties of the acceptor is ignored. Thus, the (electronic) excitation energy ($H_{22} - H_{00}$) of the locally excited species A*D is assumed to be the same as that of the acceptor A* in the absence of any donor. In order to relate all energies to that of Ψ_0[AD], we set H_{00} = 0. Then the energy of the pure A*D state, H_{22}, is given by eq 9 with $h\nu_{A^*}$ as an average value of the energy of the fluorescence of A* in nondonating solvents (defined below), neglecting the modest dependence of this energy on the solvent. The matrix elements coupling Ψ_0[AD] and $\Psi_2[A^*D]$ are assumed to be negligibly small (eq 10). The remaining unknown quantities are

$$H_{22} = h\nu_{A^*} \quad (9)$$

$$H_{02} = H_{20} = 0 \quad (10)$$

the energy of the pure ion-pair state, H_{11}, and the matrix elements coupling $\Psi_1[A^{\bullet-}D^{\bullet+}]$ to Ψ_0[AD] and to $\Psi_2[A^*D]$, H_{01} and H_{12}. By suitable choices of phase for the Ψ_i, it may be arranged that H_{01} and H_{12} are both nonnegative. It is assumed that H_{01} and H_{12} are the same for all donor/solvent combinations and that differences in ν_{av} and k'_f are due to variations in H_{11}, the energy of the pure ion-pair state.

The transition moment **M** is given by eq 4 with Ψ_{Ex} and Ψ_G given by eqs 1 and 6. The Ψ_0[AD] and $\Psi_2[A^*D]$ states are assumed to have the same static dipole moment (eq 11), which is small in any case, and any "direct" neutral-to-ionic or ionic-to-locally-excited contribution to the transition moment is neglected (eq 12).

$$\mathbf{M}_{00} = \mathbf{M}_{22} \quad (11)$$

$$\mathbf{M}_{10} = \mathbf{M}_{12} = 0 \quad (12)$$

$$\text{where} \quad \mathbf{M}_{ij} = \langle\Psi_i|\hat{\mu}|\Psi_j\rangle = \mathbf{M}_{ji} \quad (13)$$

As an intramolecular property of the acceptor, the "local excitation" transition moment, $\mathbf{M}_{20}$, is assumed to be the same as that of A* in the absence of donors (eq 14), as discussed above. The remaining contribution to **M** is the difference in the static

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[19] H_{01} is usually denoted V in the electron-transfer literature.

[20] As discussed later, the electronic transition moment of the Ex varies with nuclear coordinates. For the case where $f_{CT} \approx 1$, it can be shown[1b] that k'_f is nevertheless directly proportional to ν_{av}, with ν_{av} defined as in eq 19 (Section III.B).

[21] To say that a many-electron wave function is real-valued means that the spatial function multiplying each many-electron spin function is real-valued. If the Hamiltonian contains only kinetic energy and Coulombic terms, its eigenfunctions may be taken to be real-valued. We assume the same for the approximate eigenfunctions Ψ_i.

dipole moment between the pure ion-pair and pure neutral states (eq 15). Expansion of eq 4 in terms of the $\mathbf{M}_{ij}$ results in eq 16.

$$\mathbf{M}_{20} = \mathbf{M}_{\mathrm{A}^*} \tag{14}$$

$$\mathbf{M}_{11} - \mathbf{M}_{00} = \Delta\mu \tag{15}$$

$$\mathbf{M} = c_1 d_1 \Delta\mu + (c_2 d_0 + c_0 d_2)\mathbf{M}_{\mathrm{A}^*} \tag{16}$$

For the present Ex, $d_0 \sim 1$, $|c_1|$ and/or $|c_2|$ is ca. 1, and c_0, d_1, and d_2 are small. The contribution to $\mathbf{M}$ from the $\mathbf{M}_{\mathrm{A}^*}$ term is large when c_2 is large, i.e., when the Ex has extensive locally excited character. (The product of small terms ($c_0 d_2$) is generally negligible compared to $c_2 d_0$.) The contribution to $\mathbf{M}$ from the $\Delta\mu$ term is large when the Ex has extensive ion-pair character. Because $\Delta\mu$ is much larger than $\mathbf{M}_{\mathrm{A}^*}$ (see below), its contribution to the total transition moment can become dominant when f_{CT} and c_1 are large, even though d_1 is always fairly small. A perturbation theory based on the fact that H_{01} and H_{02} are small relative to the excitation energy ($E_{\mathrm{Ex}} - E_{\mathrm{G}}$) (Appendix B) shows that c_1, c_2, E_{Ex}, and E_{G} are approximately independent of H_{01}, while d_1 is approximately equal to $(-H_{01}/(E_{\mathrm{Ex}} - E_{\mathrm{G}}))$. Hence, to a good approximation, $\mathbf{M}$ actually depends only on the product $(H_{01}\Delta\mu)$ and not on H_{01} or $\Delta\mu$ alone (cf. eq 5). The significance of this observation will become clear later.

The preceding describes the electronic part of the problem. However, E_{Ex}, E_{G}, and $\mathbf{M}$ depend upon nuclear coordinates, including high-frequency vibrational and low-frequency librational and solvent coordinates. To treat the fluorescence spectrum and k'_{f} properly would require an elaborate vibronic and statistical-mechanical analysis. For simplicity, we consider instead a nuclear configuration representative of the Ex at equilibrium, with E_{G} and E_{Ex} as the energies at *this* geometry. (E_{G} is not the energy of the ground state at *its* equilibrium geometry.) The "vertical" (fixed geometry) energy difference is identified with $h\nu_{\mathrm{av}}$ (eq 17, see Figure 2). The evaluation of $h\nu_{\mathrm{av}}$ as a suitable average over the fluorescence spectrum is discussed in the next section.

$$E_{\mathrm{Ex}} - E_{\mathrm{G}} = h\nu_{\mathrm{av}} \tag{17}$$

For the closely related systems discussed here, it is assumed that the only quantity that varies is H_{11}, the energy of the purely ionic state $\mathrm{A}^{\bullet -}\mathrm{D}^{\bullet +}$. The correlation between k'_{f} and $h\nu_{\mathrm{av}}$ then arises from the dependence of each of these quantities on H_{11}. Given a set of values for H_{01}, H_{12}, and H_{22}, one can plot k'_{f} as a function of ν_{av} by evaluating each as a function of H_{11}. In practice, however, in order to actually fit the data, we determined k'_{f} as a function of ν_{av} as follows. We regarded eqs 7 and 8 as defining $(E_{\mathrm{Ex}} - E_{\mathrm{G}})$ as a function of H_{11}, and we solved numerically for the value of H_{11} that gave $(E_{\mathrm{Ex}} - E_{\mathrm{G}}) = h\nu_{\mathrm{av}}$. With that value, eqs 7 and 8 gave the c_i and d_j, eq 16 then gave $\mathbf{M}$, and eq 3 gave k'_{f}. The fractional charge-transfer character of the Ex was then simply obtained as c_1^2.

B. Evaluation of Average Emission Energies. If $\mathbf{M}$ were independent of nuclear coordinates, as is usually assumed for intramolecular excited states, eq 3 would give $\mathbf{M}$ correctly when ν_{av} is evaluated using the Strickler–Berg formula (eq 18).[22] In eq

$$\nu_{\mathrm{av}}(\mathrm{A}^*) = \left(\frac{\int I_{\mathrm{f}}\,\mathrm{d}\nu}{\int \nu^{-3} I_{\mathrm{f}}\,\mathrm{d}\nu}\right)^{1/3} \tag{18a}$$

$$\nu_{\mathrm{av}}(\mathrm{A}^*) = \left(\frac{\int \nu^{-2} I_{\lambda}\,\mathrm{d}\nu}{\int \nu^{-5} I_{\lambda}\,\mathrm{d}\nu}\right)^{1/3} \tag{18b}$$

18, I_{f} or I_{λ} is the emission intensity expressed in photons per unit time per unit spectral energy or wavelength, respectively. For an Ex state, on the other hand, the energy of the ion-pair state relative to the neutral and locally excited states varies with some solvent, intermolecular, and intramolecular coordinates. As a result, H_{11} varies with nuclear coordinates and so, therefore, do E_{Ex} and $\mathbf{M}$. As discussed above, however, when f_{CT} is essentially unity, $\mathbf{M}$ is equivalent to $\mathbf{M}_{\mathrm{A^-D^+}}$ (eq 5). In this case, eqs 3 and 5 give accurate values for $(H_{01}\Delta\mu)$ when ν_{av} is evaluated using eq 19.[1]

$$\nu_{\mathrm{av}}(\mathrm{A}^{\bullet -}\mathrm{D}^{\bullet +}) = \frac{\int I_{\mathrm{f}}\,\mathrm{d}\nu}{\int \nu^{-1} I_{\mathrm{f}}\,\mathrm{d}\nu} \tag{19a}$$

$$\nu_{\mathrm{av}}(\mathrm{A}^{\bullet -}\mathrm{D}^{\bullet +}) = \frac{\int \nu^{-2} I_{\lambda}\,\mathrm{d}\nu}{\int \nu^{-3} I_{\lambda}\,\mathrm{d}\nu} \tag{19b}$$

Many of the Ex and A*/solvent systems studied here actually fit neither limiting case, and in the quantitative analysis of the radiative rate data, we have somewhat arbitrarily used $\nu_{\mathrm{av}}(\mathrm{A}^{\bullet -}\mathrm{D}^{\bullet +})$ from eq 19 for the systems with higher CT character, i.e. the conventional acceptor/donor Ex systems (Tables 1 and 2), and $\nu_{\mathrm{av}}(\mathrm{A}^*)$ for those with mostly locally excited character, i.e. the A*/solvent systems (Table 3).

C. Evaluation of the Fixed Parameters. The theory described above gives k'_{f} as a function of ν_{av} with the parameters $\Delta\mu$, $\mathbf{M}_{\mathrm{A}^*}$, H_{01}, H_{12}, and H_{22}. Because $\Delta\mu$ and $\mathbf{M}_{\mathrm{A}^*}$ are vector quantities, the angle between them, θ, must be determined. It is reasonable to assume that $\mathbf{M}_{\mathrm{A}^*}$ is directed along the 9,10 axis of the cyanoanthracene acceptors, as in anthracene itself.[23] The $\Delta\mu$ is presumably directed along a line joining the centers of the acceptor and the donor, and therefore, $\theta = 90°$, as long as the center of the donor lies over the acceptor's long axis. It seems unlikely that θ should be significantly different from 90°, and indeed, it is found that values near 90° are required to fit the data. Hence we have chosen to fix θ at 90° in order to decrease the number of variable parameters (however, see below for further discussion).

Values for H_{22} (identified with ν_{A^*}) and $\mathbf{M}_{\mathrm{A}^*}$ can be obtained from the fluorescence properties of A* in solvents where CT interactions are likely to be negligible. Three solvents of low, medium, and high polarity that meet this requirement are carbon tetrachloride, dichloromethane, and acetonitrile. Both $(k'_{\mathrm{f}})_{\mathrm{A}^*}$ (the radiative rate constant of A*, corrected for the solvent refractive index) and ν_{A^*} for DCA are slightly higher than those for TCA in each of these solvents (Table 4), which indicates that the parameters H_{22} and $\mathbf{M}_{\mathrm{A}^*}$ are somewhat different for the two acceptors. Therefore, the data for the DCA and TCA Ex were treated separately. In these least interacting solvents, the average values of $\tilde{\nu}_{\mathrm{A}^*}$ and $(k'_{\mathrm{f}})_{\mathrm{A}^*}$ for TCA are 21.6×10^3 cm^{-1} and 2.47×10^7 s^{-1}, respectively. The corresponding parameters for DCA are 21.8×10^3 cm^{-1} and 2.75×10^7 s^{-1}.[24] These values yield transition moments ($\mathbf{M}_{\mathrm{A}^*}$) for TCA and DCA of 2.80 and 2.91 D, respectively (Table 5).

As discussed above, k'_{f} actually depends only on the product $(H_{01}\Delta\mu)$ and not on H_{01} or $\Delta\mu$ alone. Therefore, a value must be known for $\Delta\mu$ in order to determine the value of H_{01}. If the distance between the centers of the acceptor and the donor (r) is 3.3 Å, an *a priori* estimate of $\Delta\mu$ is $|e|r = 16$ D. This may be an overestimate, however, as it neglects the dipole moment induced in $\mathrm{A}^{\bullet -}$ by the charge distribution of $\mathrm{D}^{\bullet +}$ and vice versa. The most common experimental method for evaluating $\Delta\mu$ is a solvato-

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[22] Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

[23] (a) Craig, D. P.; Hobbins, P. C. *J. Chem. Soc.* **1955**, 539. (b) Craig, D. P. *J. Chem. Soc.* **1955**, 2302. (c) Craig, D. P.; Hobbins, P. C. *J. Chem. Soc.* **1955**, 2309.

[24] The value obtained for the $\tilde{\nu}_{\mathrm{A}^*}$ of DCA is 21.7×10^3 cm^{-1} when the data in Table 4 are used. However, a much better fit to the Ex data is obtained when using the slightly higher value of 21.8×10^3 cm^{-1} for this parameter.

Table 5. Average Emission Frequencies, Radiative Rate Constants, and Transition Moments for the Excited Cyanoanthracenes[a] and the Electronic Coupling Matrix Elements[b,c] for Their Exciplexes and Excited CT Complexes with Alkyl-Substituted Benzene Donors

A[a]	$\tilde{\nu}_A$* or $\tilde{H}_{22}$ (10^3 cm^{-1})	$(k'_f)_A$* (10^7 s^{-1})	M_A* (D)	$\tilde{H}_{01}$[b] (cm^{-1})	$\tilde{H}_{12}$[b] (cm^{-1})
TCA	21.6	2.47	2.80	750	1350
DCA	21.8	2.75	2.91	900	1300

[a] DCA is 9,10-dicyanoanthracene, and TCA is 2,6,9,10-tetracyanoanthracene. [b] Determined as described in section III.D. using 13 D for $\Delta\mu$ and 90° for θ.

chromic study of Ex emissions.[25] In order for the standard analysis to apply, the extent of charge transfer in the Ex under consideration should be essentially independent of the solvent polarity. This can be the case if the Ex is equivalent to a pure radical-ion pair, i.e. significant mixing with the A* state does not occur in the range of solvents used. As discussed in more detail below, the excited CT complex formed between TCA and HMB is of high CT character in all of the solvents used in this study, and a plot (not shown) of its emission maximum versus the standard solvent polarity function[25] is linear with a slope of ca. -7×10^3 cm^{-1}. Similar results were obtained for other acceptor/donor pairs, such as TCA/PMB, TCA/Dur, and DCA/HMB, in solvents where the extent of CT was also high (see below). The average value obtained for the slopes is $(-7 \pm 0.6) \times 10^3$ cm^{-1}. The slopes are related to $(\Delta\mu^2/\rho^3)$, in which ρ is the radius of the solvent cavity surrounding the Ex.[25] Estimates based upon the volume of the acceptor and donor molecules give a value for ρ of ca. 5 ± 0.5 Å. The range in $\Delta\mu$ which corresponds to this value of ρ is ca. 13 ± 2 D. Because the model for the solvatochromic measurements is based on a point dipole in a spherical cavity, with a strong dependence on the radius of the cavity, this value for $\Delta\mu$ is taken with some reservation. In support of this value for $\Delta\mu$, however, is a value of 9.8 D obtained by electrooptical methods for the exciplex formed between DCA and hexamethylbenzene in hexane.[26] As discussed below, charge transfer in this particular exciplex is not complete and, in fact, is estimated to be ca. 83%.[27] Linear extrapolation of this dipole moment to 100% charge transfer indicates a value for $\Delta\mu$ of ca. 12 D, which is similar to the estimate of 13 D from the solvent dependence of the emission maxima. Thus, in the following analysis, we assume $\Delta\mu$ to be 13 D.

D. Fitting Procedure and Determination of the Matrix Elements. The remaining parameters are the matrix elements H_{01} and H_{12}. As discussed above in connection with eq 16, k'_f actually depends only on the product $(H_{01}\Delta\mu)$ and not on H_{01} or $\Delta\mu$ alone. In fitting the data using the exact expression for **M** (eq 16), it was indeed found that varying $\Delta\mu$ was entirely equivalent to varying H_{01}. Hence, the two adjustable parameters really are $(H_{01}\Delta\mu)$ and H_{12}. With only two adjustable parameters, their values could be determined with reasonable reliability by a nonlinear least squares procedure that minimizes the rms deviation between experimental and theoretical values of k'_f as a function of ν_{av}.

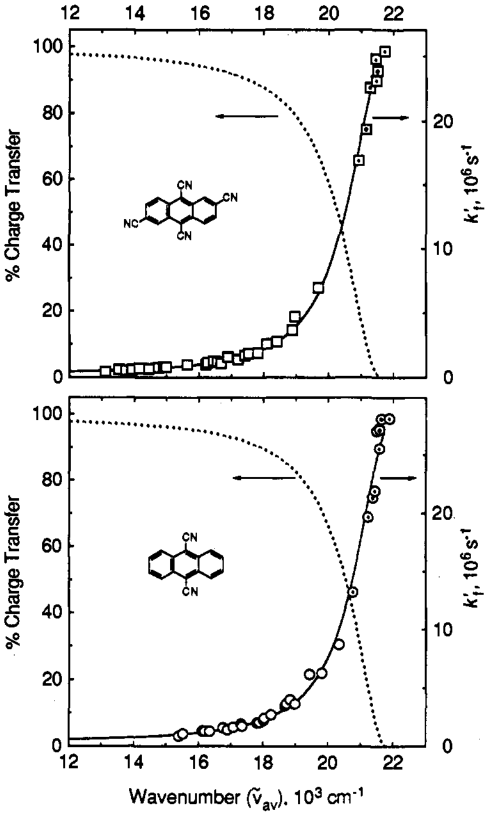

Figure 3. Plots of (symbols, right axis) radiative rate constants corrected for the solvent refractive index, k'_f, and (dotted curve, left axis) percentages of charge transfer, $\%_{CT}$ (defined in text), as a function of average emission wavenumber, $\tilde{\nu}_{av}$ (defined in the text), for the exciplexes and excited CT complexes of (top) 2,6,9,10-tetracyanoanthracene and (bottom) 9,10-dicyanoanthracene as acceptors, with methyl-substituted benzenes as donors, in various solvents at room temperature (Tables 1 and 2). The dotted circles and squares are the corresponding data for the same acceptors in various solvents in the absence of added donors (see the accompanying paper, ref 9). The solid curves through the data points represent fits to the three-state theory described in the text using the parameters given in Table 5. The dotted curves showing the dependence of $\%_{CT}$ on $\tilde{\nu}_{av}$ are calculated using the same values of the fitting parameters.

Shown in Figure 3 are the radiative rate constants corrected for the solvent refractive index (k'_f) plotted versus the average emission wavenumbers ($\tilde{\nu}_{av}$) for the Ex of TCA and DCA (open circles and squares, Tables 1 and 2) and the A*/solvent only systems (dotted circles and squares, Tables 3 and 4), determined as described above. Preliminary fitting indicated that it was important to accurately define the region of lower ν_{av}, i.e. the parts of the plots where the dependence of k'_f on ν_{av} is weaker. Because there are more data points in this region for TCA as the acceptor, this data set should be more reliable. The best fit to the TCA data, shown as the curve through the data points, was obtained using 1350 cm^{-1} for H_{12} and 9.8×10^3 cm^{-1} D for $(H_{01}\Delta\mu)$, with uncertainties of ca. 5% for both parameters. For DCA, values of 1300 cm^{-1} for H_{12} and of 11.7×10^3 cm^{-1} D for $(H_{01}\Delta\mu)$ gave the best fit (Figure 3), although the uncertainty is somewhat higher in this case, ca. 10%. Thus, upon the basis of a $\Delta\mu$ of 13 D, as discussed above, the matrix element H_{01} can be estimated to be ca. 750 cm^{-1} and ca. 900 cm^{-1} for the TCA and for the DCA Ex systems, respectively (Table 5). The values of H_{01} and H_{12} are positive by convention. The radiative rate constants calculated for the TCA and DCA Ex using these values of the parameters, together with the f_{CT}, are summarized in Tables 1 and 2.

The H_{01} and H_{12} might be expected to vary from donor to donor if the HOMO of the donor cation were different for the different donors. The degeneracy of the HOMO in benzene is lifted for most of the present donors, and in fact, there is evidence that there are two types of HOMO for the donor radical cations, depending upon the methyl-group substitution pattern.[15] If the HOMO in the Ex is the same as in the isolated radical cations, then the data might be expected to fall into two groups of H_{01}

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[25] (a) Mataga, N.; Okada, T.; Yamamoto, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2562. (b) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183. The Ex emission maxima ($\bar{\nu}_{max}$) are plotted versus the solvent parameter shown in the following equation, where $\bar{\nu}_{max}(0)$ is the Ex emission frequency in the vacuum, ρ is the radius of the Ex solvent cavity, ϵ is the solvent dielectric constant, and n is the refractive index. The dipole moment of the ground state of the Ex is assumed to be zero.

$$\bar{\nu}_{max} = \bar{\nu}_{max}(0) - \frac{(\Delta\mu)^2}{hc\rho^3}\left\{2\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \left(\frac{n^2 - 1}{2n^2 + 1}\right)\right\}$$

[26] Groenen, E. J. J.; van Velzen, P. N. T. *Mol. Phys.* **1978**, *35*, 19.

[27] We assume that the DCA/hexamethylbenzene/cyclohexane Ex studied here is similar to the DCA/hexamethylbenzene/hexane Ex studied in ref 26.

and H_{12}. The fact that no such pattern can be discerned in the k'_f versus ν_{av} data (Figure 3) suggests that the HOMO in the Ex is essentially the same for the different donors. This might be explained if the important interaction in resolving the degeneracy in the Ex is the interaction with the $A^{\bullet-}$ rather than the effect of methyl substitution.

We have assumed that for each acceptor the various parameters ($H_{01}, H_{12}, \Delta\mu, \theta$) are constant for all of the donor/solvent systems. The good fits shown in Figure 3 and in Tables 1 and 2 are certainly consistent with this assumption. It is possible *a priori*, however, that the parameters vary systematically to some extent with, for example, donor ionization potential and that this contributes to the observed dependence of k'_f on ν_{av}. The fact that k'_f exhibits the same dependence on ν_{av}, whether the variation in ν_{av} is brought about by changing the donor or the solvent, argues against significant variation of the parameters from donor to donor. A variation of the parameters with the energy of the Ex alone cannot be ruled out, however. For example, the geometry of the Ex might vary with f_{CT} and thus ν_{av}.

In order to fit the data, it is obvious that both H_{01} and H_{12} are sizeable, and hence, in the equilibrium geometry of the Ex, the Ψ_0, Ψ_1, and Ψ_2 all have the same symmetry. DCA itself has a vertical mirror plane containing the long axis, and its molecular ground and first excited states have different symmetries with respect to this plane.[28] The donor cannot be placed so that the Ex has the same mirror plane, or else Ψ_0 and Ψ_2 would likewise have different symmetries and either H_{01} or H_{12} would vanish. Therefore, either the donor is not, in fact, centered above the long axis of the DCA or it is centered above that axis and oriented asymmetrically. In the former, more likely case, θ cannot be exactly 90°. Although TCA lacks the mirror plane in question, the fact that both acceptors have similar values for the Ex parameters suggests that both form Ex with similar geometries.

From a consideration of simple molecular models, it is evident that θ can not be very different from 90°. In the simplest picture of the Ex, the cyanoanthracene and the alkylbenzene can be assumed to have a face-to-face geometry with a separation of 3.5 Å. In any relative position of the two species such that at least one-half of the benzene ring lies over one of the rings of the anthracene, θ cannot differ from 90° by more than 15°. Good fits to the data can, in fact, be obtained with values for θ ranging from 75° to 105°. The changes in the values of H_{01} and H_{12} required to give the best fits for this range of θ are less than 15%.

As indicated above, in certain geometries of the DCA Ex, either H_{01} or H_{12} should vanish by symmetry. Molecular orbital calculations indicate that the vanishing element would be H_{01} (see for example ref 26). The fact that H_{01} is considerably smaller than H_{12} may be a consequence of a geometry that is nearly symmetric, or it may be coincidental. Presumably the same situation applies for the Ex of TCA.

E. Simplified Treatment of the Data. In this section, we compare the exact treatment described above with simplified versions. The latter can provide preliminary estimates of the fitting parameters H_{01} and H_{12} for further refinement by the exact treatment. Alternatively, within the approximations described here, the simplified model provides a more direct method for determining the values of H_{01} and H_{12}. In the following, we express all matrix elements and average frequencies in wavenumber form (10^3 cm^{-1}) with the notations $\tilde{H}$ and $\tilde{\nu}$. The dipole and transition moments ($\Delta\mu$ and **M**) are in debye. Thus eq 3 becomes eq 20.

For the current systems, $\tilde{H}_{01}$ is much smaller than the energy difference between the AD and $A^{\bullet-}D^{\bullet+}$ states ($\tilde{H}_{11}$) and we have assumed that there is no direct coupling between Ψ_0[AD] and Ψ_2[A*D]. As a result, c_0, d_1, and d_2 are small. The following perturbation scheme (developed further in Appendix B) is appropriate. At zeroth order, we neglect the coupling between Ψ_0[AD] and $\Psi_1[A^{\bullet-}D^{\bullet+}]$. Then the ground state is approximated by Ψ_0[AD] and E_G by 0. The Ex state is approximated by $c_1\Psi_1[A^{\bullet-}D^{\bullet+}] + c_2\Psi_2[A^*D]$; the E_{Ex}, c_1, and c_2 are solutions of a two-state problem analogous to eq 7, and $h\nu_{av} = E_{Ex}$. The coupling between Ψ_0[AD] and $\Psi_1[A^{\bullet-}D^{\bullet+}]$ is treated as a perturbation. With some further simplifications (see Appendix B), **M** can be given by eq 21, i.e. in terms of the two limiting transition moments discussed above, $\mathbf{M}_{A\text{-}D^+}$ (eq 22) and $\mathbf{M}_{A^*}$ (eq 23), and the fractional CT character (f_{CT}) in the Ex. As discussed in Appendix B, eq 24 provides a very good approximation to f_{CT} in terms of the matrix element $\tilde{H}_{12}$ and the difference between the average emission wavenumber of A* ($\tilde{\nu}_{A^*}$) and that of Ex ($\tilde{\nu}_{av}$).[3b]

$$k'_f = 313.7\tilde{\nu}_{av}{}^3M^2 \tag{20}$$

$$\mathbf{M} = (f_{CT})^{1/2}\mathbf{M}_{A\text{-}D^+} - (1 - f_{CT})^{1/2}\mathbf{M}_{A^*} \tag{21}$$

$$\mathbf{M}_{A\text{-}D^+} = -\frac{\tilde{H}_{01}\Delta\mu}{\tilde{\nu}_{av}} \tag{22}$$

$$(M_{A^*})^2 = (0.003\ 19)\frac{(k'_f)_{A^*}}{\tilde{\nu}_{A^*}{}^3} \tag{23}$$

$$f_{CT} = \left[1 + \left(\frac{\tilde{H}_{12}}{\tilde{\nu}_{A^*} - \tilde{\nu}_{av}}\right)^2\right]^{-1} \tag{24}$$

Thus, from eqs 20–24, the dependence of k'_f on $\tilde{\nu}_{av}$ is given directly in terms of measurable quantities, with only ($\tilde{H}_{01}\Delta\mu$) and $\tilde{H}_{12}$ (and θ) as variable parameters. Calculations of k'_f versus $\tilde{\nu}_{av}$ using eqs 20–24 and those using the exact theory described above give nearly identical results (with $\theta = 90°$ in both), indicating that the simplified treatment is quite accurate for data analysis. As a further test of this simplified treatment, we calculated the f_{CT} values for the DCA and TCA Ex using eqs 20–24. When these were compared with the values determined using the exact theory, it was found that the two sets of calculated numbers were the same within ca. 0.5%, thus further supporting the validity of the simplified treatment.

For the case of $\theta = 90°$, eq 21 reduces to the particularly simple form of eq 25. A simple method for data analysis results

$$(\text{for } \theta = 90°) \quad M^2 = f_{CT}(M_{A\text{-}D^+})^2 + (1 - f_{CT})(M_{A^*})^2 \tag{25}$$

from rearranging eqs 20–25 to give a linear function (eq 26), which we described briefly in a recent communication.[12] According to eq 26, a plot of the quantity W_{Ex} vs $k'_f/\tilde{\nu}_{av}$ should be

$$W_{Ex} \equiv \left(1 - \frac{\tilde{\nu}_{A^*}{}^3}{(k'_f)_{A^*}}\frac{k'_f}{\tilde{\nu}_{av}{}^3}\right)\left(\frac{\tilde{\nu}_{A^*}}{\tilde{\nu}_{av}} - 1\right)^{-2} = a + b\left(\frac{k'_f}{\tilde{\nu}_{av}}\right) \tag{26a}$$

$$\text{where} \quad a = -\left(\frac{\tilde{H}_{01}\Delta\mu}{\tilde{H}_{12}M_{A^*}}\right)^2 \qquad b = \frac{\tilde{\nu}_{A^*}{}^3}{(k'_f)_{A^*}}\frac{1}{\tilde{H}_{12}{}^2} \tag{26b}$$

linear, with $\tilde{H}_{12}$ and ($\Delta\mu\tilde{H}_{01}$) determined simply from the slope and intercept (eq 26b). Plots according to eq 26 for the TCA and DCA Ex radiative rate data are shown in Figure 4. With increasing $k'_f/\tilde{\nu}_{av}$, i.e. as the CT character of Ex decreases and the difference between $\tilde{\nu}_{A^*}$ and the $\tilde{\nu}_{av}$ of the Ex decreases, the error associated with the calculation of the function W_{Ex} increases sharply. The sensitivity to slight variations in the radiative rates and the average emission frequencies of the Ex and of the reference (A*) state is particularly large when $k'_f/\tilde{\nu}_{av}$ exceeds ca. 200 cm s^{-1}. The few points for each data set for which $k'_f/\tilde{\nu}_{av}$ is larger than this value were excluded, therefore, from the analysis. The slope and intercept of Figure 4a gave values for $\tilde{H}_{01}$ and $\tilde{H}_{12}$ of 750 and 1360 cm^{-1}, respectively, which are nearly identical to those obtained from the analysis of the TCA data using the exact treatment described above (750 and 1350 cm^{-1}). Even the

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[28] Birks, J. B. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 1.

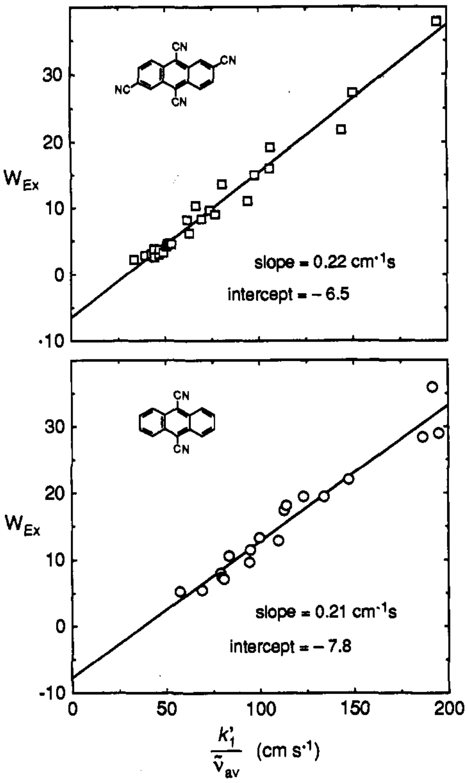

Figure 4. Plot of the quantity W_{Ex} (eq 26) vs $k'_f/\tilde{\nu}_{av}$ for the cyanoanthracene Ex systems with (top) 2,6,9,10-tetracyanoanthracene as the acceptor and (bottom) 9,10-dicyanoanthracene as the acceptor.

corresponding data for DCA (Figure 4b), which are more limited especially in the sensitive range of low $k'_f/\tilde{\nu}_{av}$, gave values for $\tilde{H}_{01}$ and $\tilde{H}_{12}$ of 850 and 1360 cm^{-1}, respectively, in very good agreement with those obtained from the exact treatment (900 and 1300 cm^{-1}).

Recently, Bixon, Jortner, and Verhoeven[13] independently derived another simple expression for the dependence of k_f on emission frequency, which is most applicable for data with high ionic character. With our choice of refractive-index correction and "representative frequency", their result is equivalent to the expression given by eq 27 for the transition moment. For $\theta = 90°$, eqs 3 and 27 give eq 28,[13] with the dipole moments expressed

$$\mathbf{M} = \mathbf{M}_{A\text{-}D+} - \left(\frac{\tilde{H}_{12}}{\tilde{\nu}_{A^*} - \tilde{\nu}_{av}}\right)\mathbf{M}_{A^*} \qquad (27)$$

$$\frac{k'_f}{\tilde{\nu}_{av}} = 313.7\left[(\tilde{H}_{01}\Delta\mu)^2 + (\tilde{H}_{12}M_{A^*})^2\left(\frac{\tilde{\nu}_{av}}{\tilde{\nu}_{A^*} - \tilde{\nu}_{av}}\right)^2\right] \qquad (28)$$

in debye and the wavenumbers in 10^3 cm^{-1}. Thus a plot of $k'_f/\tilde{\nu}_{av}$ vs $[\tilde{\nu}_{av}/(\tilde{\nu}_{A^*} - \tilde{\nu}_{av})]^2$ should be a straight line with an intercept proportional to $(\tilde{H}_{01}\Delta\mu)^2$ and a slope proportional to $(\tilde{H}_{12}M_{A^*})^2$. Plots for the TCA and DCA Ex data according to eq 28 are shown in Figure 5. Because eqs 27 and 28 are valid for highly ionic states,[13] the few data points for which $(\tilde{\nu}_{A^*} - \tilde{\nu}_{av})$ is less than 3×10^3 cm^{-1} (corresponding to CT character less than 85%) are not included in the analysis. In addition, the uncertainty in $(\tilde{\nu}_{A^*} - \tilde{\nu}_{av})^{-2}$ becomes large for these data points because of imprecision in the proper determination of $\tilde{\nu}_{av}$ (see also above). The slope and intercept of Figure 5 (top) (TCA data) give values for $\tilde{H}_{01}$ and $\tilde{H}_{12}$ of 780 and 1240 cm^{-1}, respectively, which are close to those obtained from the analysis using the exact treatment discussed above (750 and 1350 cm^{-1}). The corresponding data for the DCA Ex (Figure 5 (bottom)) give values for $\tilde{H}_{01}$ and $\tilde{H}_{12}$ of 890 and 1220 cm^{-1}, respectively. Again, these results are similar to those obtained from nonlinear fitting of the k'_f data using the exact treatment (900 and 1300 cm^{-1}).

Equation 27 is equivalent to eq 21 with the approximation that $\mathbf{M}$ is replaced by $(f_{CT})^{1/2}\mathbf{M}$. Equations 20–25 can thus be combined to give eq 29. Equation 29 is equivalent to eq 28 when

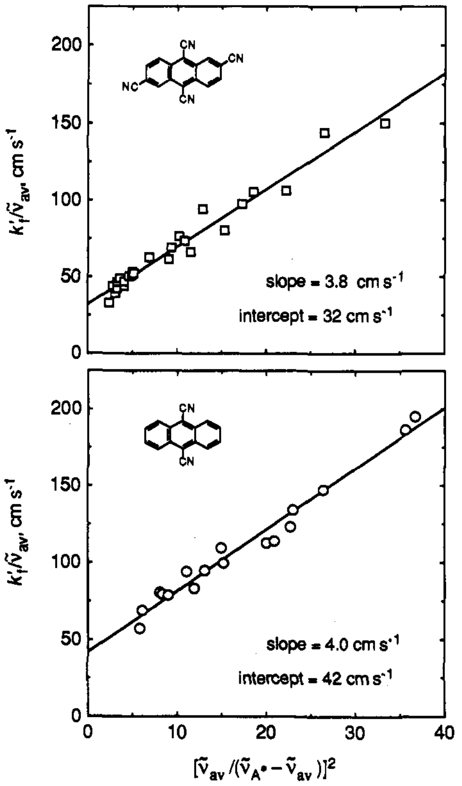

Figure 5. Plots of the radiative rate constant (corrected for the solvent refractive index) divided by the average emission wavenumber ($k'_f/\tilde{\nu}_{av}$) vs the wavenumber function $[\tilde{\nu}_{av}/(\tilde{\nu}_{A^*} - \tilde{\nu}_{av})]^2$ (eq 28) for the exciplexes and excited CT complexes of (top) 2,6,9,10-tetracyanoanthracene and (bottom) 9,10-dicyanoanthracene as acceptors, with methyl-substituted benzenes as donors, in various solvents at room temperature (Tables 1 and 2).

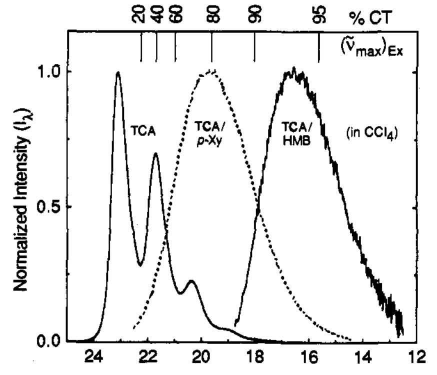

Figure 6. Emission spectra of 2,6,9,10-tetracyanoanthracene (TCA) and the excited CT complexes (Ex) of TCA with *p*-xylene (p-Xy) and with hexamethylbenzene (HMB) in carbon tetrachloride at room temperature. Also indicated on the top scale are the approximate percentages of charge transfer character (%$_{CT}$) in the Ex for different Ex emission maxima.

$$\frac{k'_f}{\tilde{\nu}_{av}}\left[1 + \left(\frac{\tilde{H}_{12}}{\tilde{\nu}_{A^*} - \tilde{\nu}_{av}}\right)^2\right] = 313.7\left[(\tilde{H}_{01}\Delta\mu)^2 + (\tilde{H}_{12}M_{A^*})^2\left(\frac{\tilde{\nu}_{av}}{\tilde{\nu}_{A^*} - \tilde{\nu}_{av}}\right)^2\right] \qquad (29)$$

the quantity in brackets on the left side (which is equal to $(f_{CT})^{-1}$, eq 24) is approximated to unity. In fact, the parameters obtained above can be refined by replotting the entire left side of eq 29 vs $[\tilde{\nu}_{av}/(\tilde{\nu}_{A^*} - \tilde{\nu}_{av})]^2$; for the $\tilde{H}_{12}$ on the left side, we use the initial estimate from eq 28. After very few iterations, convergence was achieved for the current data sets, i.e. values for $\tilde{H}_{12}$, derived

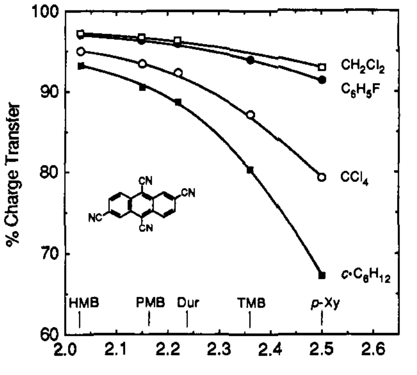

Figure 7. Plot of the percentage of charge transfer in excited complexes of 2,6,9,10-tetracyanoanthracene/alkylbenzenes in cyclohexane, carbon tetrachloride, fluorobenzene, and dichloromethane (Table 1) vs the redox energy of the A/D pair (eq 2).

from the slope of the plot according to eq 29, were equal to those used to calculate the function on the left-hand side. The values of $\tilde{H}_{01}$ and $\tilde{H}_{12}$ (750 and 1360 cm^{-1}, respectively), obtained from the slope and intercept of such a plot (Figure not shown), for the Ex of TCA are essentially identical to those obtained from the nonlinear fitting according to the exact model (Table 5). The corresponding values for the DCA data (830 and 1380 cm^{-1}, respectively) are also in good agreement with those from the exact treatment discussed above (Table 5).

IV. Electronic Properties of the Ex

Once H_{12} has been evaluated by one of the methods described above, the electronic structures of the Ex can be determined in terms of a percentage of charge transfer ($\%_{CT}$), evaluated as 100 $\times f_{CT}$. In Figure 3, plots of $\%_{CT}$ (dotted curves, left axes) are superimposed on plots of k'_f (data and solid curves, right axes) for both sets of Ex. When $h\nu_{av}$ is equal to the emission energy of the pure locally excited state, $H_{11} = \infty$ and $\%_{CT} = 0$, by definition. As the emission frequency decreases, H_{11} decreases, and the $\%_{CT}$ increases.

The approximate vertical mirror-image relationship (evident in Figure 3) between $\%_{CT}$ and k'_f is readily understood in terms of eq 30, which provides a rough estimate of $\%_{CT}$ directly from the experimental data (i.e., without any fitting), when the $\%_{CT}$ is less than ca. 90%. Equation 30 is obtained from eq 25 by neglecting the CT contribution involving $\mathbf{M}_{A\text{-}D^+}$ and substituting for M^2 and $(M_{A^*})^2$ using eq 3 or eqs 20 and 23.

$$\%_{CT} \approx 100\left[1 - \frac{k'_f}{(k'_f)_{A^*}}\left(\frac{\tilde{\nu}_{A^*}}{\tilde{\nu}_{av}}\right)^3\right] \tag{30}$$

The $\%_{CT}$ reaches a value of ca. 90 at an average emission energy of ca. 17 $\times$ 10^3 cm^{-1} for both the DCA and TCA systems, i.e. ca. 5 $\times$ 10^3 cm^{-1} lower than the average emission energy of the A* alone. The Ex species which emit at frequencies lower than this can be considered for most purposes to be essentially pure radical-ion pairs ($\geq$90% CT). The energies of the 0,0 transitions of the A* are higher than the average emission energies by ca. 1350 cm^{-1}. The emission maxima of the Ex ($\tilde{\nu}_{max}$) are higher than the corresponding emission averages ($\tilde{\nu}_{av}$) by a similar value (ca. 800–1100 cm^{-1}). *Thus, the CT character of these Ex species is $\geq$90%, i.e. these Ex are essentially pure contact radical-ion pairs, when their emission maxima are lower than that of the 0,0 transition of the A* by $\geq$5 $\times$ 10^3 cm^{-1}* (see Figure 6).

It is interesting to consider which of the acceptor/donor/solvent systems studied here are in fact nearly pure CRIP. The variations in the $\%_{CT}$ with E_{redox} and solvent polarity for the present Ex are summarized in Tables 1 and 2 and illustrated in Figure 7. For the better acceptor TCA with the best donor hexamethylbenzene, even in the nonpolar solvent carbon tetrachloride, the $\tilde{\nu}_{av}$ for the excited CT complex is 15.6 $\times$ 10^3 cm^{-1}, which corresponds to 95% CT character. For the same acceptor in the same solvent with the poorer donor *p*-xylene, the emission occurs at considerably higher energy ($\tilde{\nu}_{av} \approx$ 19 $\times$ 10^3 cm^{-1}) and the $\%_{CT}$ is only ca. 79 (Table 1). The TCA/*p*-xylene pair attains greater than 90% CT character only in solvents as polar as fluorobenzene.

The highest energy Ex included in the present work is that of DCA/durene in cyclohexane. Weaker donors do not form exciplexes with DCA in this solvent at conventional concentrations ($\leq$0.2 M). From the radiative rate data, this Ex has a 57% CT character (Table 2). In acetonitrile, however, the $\%_{CT}$ of the same pair increases to ca. 92%. Since this A/D pair has the highest E_{redox} (2.69 eV) of those included in the present work,[15] all of the other acceptor/donor systems will have even higher CT character in such polar solvents. That is, the Ex's of DCA and TCA with alkylbenzenes as donors which have E_{redox} values lower than $\sim$2.7 eV are all essentially pure radical-ion pairs in acetonitrile.

The extent of charge transfer in exciplexes and excited CT complexes is clearly one of the more important properties of such species and, as discussed above, should play a major role in determining the rates of their various deactivation processes. The importance of the extent of charge transfer might be different for the different deactivation processes, however. Radiative decay, the subject of this investigation, is an extreme case. For an Ex with partial A*D character, k'_f is larger than that for a hypothetical Ex with 100% ionic character and with the same average emission frequency by a factor F (eq 31). For 90% or 95% charge transfer, this factor F is 4.2 or 2.1, respectively.[29] Thus, for some Ex that would be considered as essentially pure radical-ion pairs by most criteria, a substantial proportion of the radiative rate comes from residual mixing with the A*D state.

$$F = f_{CT} + \frac{(1 - f_{CT})(M_{A^*})^2}{(M_{A\text{-}D^+})^2} \tag{31}$$

At present it is not possible to similarly evaluate the influence of the extent of charge transfer on the rates of the other deactivation processes, although several qualitative observations can be made. When the extent of charge transfer in the Ex is high, the chemical reactivity of the Ex should resemble that of a radical-ion pair. When the extent of charge transfer decreases, the radical-ion-like reactivity should decrease. In fact, such behavior has been observed for some exciplexes of DCA.[30] When naphthalenes are used as the donors, addition of a second naphthalene to the Ex to form an ADD triple exciplex can occur, which can be taken as a simple example of a chemical reaction of the Ex species. The formation of such triple complexes is related to the readiness of substituted naphthalenes to form dimer radical cations. In fact, the rate constant for interception of the DCA/naphthalene Ex by a second naphthalene to form a triple complex increases substantially with increasing solvent polarity.[30] This is almost certainly due in large part to the fact that, in the less polar solvents, extensive mixing of the pure ion-pair and A* states occurs, thus decreasing the radical-cation character of the donor in the Ex. The extent of mixing decreases with increasing solvent polarity, the radical-cation character of the donor increases, and the efficiency of interception by a second naphthalene increases.

Intersystem crossing in the DCA and TCA Ex's studied here yields the lowest energy triplet states, which are the locally excited triplet states of the acceptors, ^{3}DCA* and ^{3}TCA*.[31] When the extent of charge transfer is high, the process Ex $\rightarrow$ ^{3}A* represents an electron-transfer reaction. As the extent of mixing increases, however, the resemblance to electron-transfer reactions will decrease. In fact, studies of the rates of intersystem crossing in

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[29] The parameters used to fit the TCA data shown in Figure 3 were used in these calculations.

[30] Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4814.

[31] Boiani, J.; Goodman, J. L.; Gould, I. R.; Farid, S. Manuscript in preparation.

the Ex of DCA and TCA are entirely consistent with these processes being electron-transfer reactions when $\%_{CT}$ is high, and significant deviations from the behavior expected for electron-transfer reactions are observed when the $\%_{CT}$ decreases.[31]

The matrix elements obtained from the analysis of the radiative rate data are relevant to the quantitative evaluation of the rates of electron transfer in the radical-ion pairs. When the emitting species are essentially pure radical-ion pairs, then both the radiative and nonradiative deactivations are return electron transfer processes.[32] We have previously studied these processes for the radical-ion pairs of DCA and TCA in considerable detail.[14,15] Of particular relevance are measurements of the rates of return electron transfer in the excited CT complexes of TCA with the alkylbenzene donors in acetonitrile.[14] It was previously assumed that these species were CRIP, which is confirmed in the present study. From a quantitative analysis of the rates of these electron-transfer reactions, an estimate for H_{01} of 750–1200 cm^{-1} was obtained.[14] The lower value is the same, within error bounds, as that obtained in the current study. Thus, essentially the same value for H_{01} is obtained from measurements of the rates of nonradiative return electron transfer in the CRIP and from the analyses of radiative electron transfer (emission) in closely related systems described here. This important result further confirms the close relationship between radiative and nonradiative electron-transfer processes.[1,8,14,33]

The cyanoanthracene/alkylbenzene systems appear to be particularly amenable to the study of locally excited/ion-pair mixing because the energies of the these states are so close in these cases. In related studies of the tetracyanobenzene/alkylbenzene acceptor/donor pairs, no systematic dependence of k_f on ν_{av} could be detected.[1b] The energy of the lowest excited singlet state of tetracyanobenzene is higher than those of the cyanoanthracenes by ca. 8×10^3 cm^{-1}. As a consequence, mixing of the locally excited and ion-pair states appears to be considerably smaller for tetracyanobenzene than for the cyanoanthracene acceptors (with these donors) so that it is undetectable in radiative rate measurements.

V. Conclusions

From a quantitative analysis of the radiative rate data of a family of exciplexes and excited CT complexes, estimates of their electronic structures are obtained and the conditions for essentially complete charge transfer (i.e., the conditions under which these species are essentially contact radical-ion pairs) are established. In contact radical-ion pairs, the close quantitative relationship between nonradiative and radiative electron transfer is confirmed by the good agreement in the electronic coupling matrix elements obtained from studies of the two processes.

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Appendix

A. Further Comments on the Theoretical Treatment. 1. Electronic States and Matrix Elements. The present work is based on a new formulation of the electronic states of the joint system, solute (acceptor/donor pair) plus solvent.[34] Each basis function, $\Psi_0[AD]$, $\Psi_1[A^{\bullet-}D^{\bullet+}]$, or $\Psi_2[A^*D]$, is the product of a factor representing the state of the solute, $\psi_0[AD]$, $\psi_1[A^{\bullet-}D^{\bullet+}]$, or $\psi_2[A^*D]$, and a factor representing the state of the solvent (S), as adjusted for the electrostatic influence of the solute in its respective state, $\phi_0[S|AD]$, $\phi_1[S|A^{\bullet-}D^{\bullet+}]$, or $\phi_2[S|A^*D]$. Equation 1, for instance, has the form of eq A1. Thus, the electronic state

$$\Psi_{Ex} = \sum_{i=0}^{2} c_i\psi_i[AD]\phi_i[S|AD] \qquad (A1)$$

of the solvent "follows" (is correlated with) that of the solute. In using a product form, we have neglected the antisymmetry requirement and electron exchange. The ψ_i are assumed to be orthonormal; the ϕ_i are normalized but not orthogonal. Although the difference between the various solvent states ϕ_i is physically important, it is typically small in the sense that $\langle\phi_i|\phi_j\rangle \sim 1$. Earlier treatments of Ex problems were based on a contrary assumption that (in essence) the solvent adjusts electronically to the *overall* state of the solute (self-consistent field approximation), i.e. the same ϕ was associated (tacitly) with each ψ_i.[3b,c] This assumption is no longer accepted except as a limiting case.[34,35] A fringe benefit of the present formalism is that it does not involve a nonlinear Schrödinger equation or reaction-field estimates of solvent shifts, and various eigenstates of the complete system are orthogonal. The reaction field effects are built into the H_{ij}.

In the formalism of ref 34, the matrix elements are affected by the polarization (electronic and orientational) of the solvent. Presumably the quantity most strongly affected is H_{11}, the energy of the pure ionic state. This has no consequence, however, since we make no assumptions about how H_{11} varies from case to case. We neglect the solvent dependence of the other diagonal energy term, $H_{22} - H_{00}$. (In the text, we take H_{00} as the zero of energy for each Ex. In this Appendix, for clarity, we do not.) It should not be too strongly affected by polarization of the solvent, since the states involved are neutral and have no net dipole moment. To the degree that $H_{22} - H_{00}$ is affected by solvent polarization, one is tempted to equate it in each solvent with the energy of the fluorescence of the unquenched acceptor, $h\nu_{A^*}$, in the same solvent. Such a procedure would be incorrect, however, for two reasons. First, unlike the uncomplexed acceptor, the acceptor molecule in the Ex is not completely solvated on the side facing the donor. Second, the orientational polarization of the solvent will generally be greater for the Ex than for the unquenched acceptor. We also neglect any effect of the solvent on the off-diagonal matrix elements, H_{01} and H_{12} (see ref 34).

It seems to be generally accepted that neutral–ionic mixing, as represented by the contribution of Ψ_1 to our Ψ_G, is too small to explain the stability of the "charge-transfer" complexes that form in some acceptor/donor systems. The TCA/alkylbenzene complexes,[9] have equilibrium constants (K_{CT}) of ca. ≤ 10 M^{-1}, implying stabilization free energies on the order ≤ 500 cm^{-1}. A simple estimate of the CT contribution to this stabilization, $H_{01}{}^2/h\nu_{av}$, is a mere 60 cm^{-1}. The additional effects that stabilize the ground state may also affect the locally excited state and may, therefore, affect $H_{22} - H_{00}$ in a manner that cannot be predicted *a priori*. Such effects should not exceed a few hundreds of cm^{-1}, however. As the ionic character of the Ex varies, the equilibrium bond lengths and bond angles in the acceptor and the donor must change and, again, $H_{22} - H_{00}$ presumably changes somewhat. We neglect these changes too.

We have arbitrarily assumed that the no-bond, ion-pair, and locally excited states are orthogonal. If not, one might orthogonalize them and take Ψ_0, Ψ_1, and Ψ_2 to be the result. These states, however, could no longer be interpreted as purely neutral or ionic, and the definition of f_{CT} would become somewhat problematic.

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(32) (a) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078. (b) Gould, I. R.; Farid, S.; Young, R. H. *J. Photochem. Photobiol. A: Chem.* **1992**, *65*, 133.

(33) See, for example: (a) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (b) Barqawi, K. R.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 47. (c) Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712. (d) Barbara, P. F.; Walker, G. C.; Smith, T. P. *Science* **1992**, *256*, 975. (e) Zeng, Y.; Zimmt, M. B. *J. Phys. Chem.* **1992**, *96*, 8395.

(34) Young, R. H. *J. Chem. Phys.* **1992**, *97*, 8261.

(35) (a) Gehlen, J. N.; Chandler, D.; Kim, H. J.; Hynes, J. T. *J. Phys. Chem.* **1992**, *96*, 1748. (b) Kim, H. J.; Hynes, J. T. *J. Chem. Phys.* **1992**, *96*, 5088. (c) Marcus, R. A. *J. Phys. Chem.* **1992**, *96*, 1753.

2. The Transition Moment. As illustrated by eq A1, the initial and final states of an optical transition involve the electronic structure of the solvent as well as the AD pair in an inseparable manner. The appropriate formulation of transition probabilities has not been worked out. Hence we lack a proper formula for the radiative rate constant or the absorption oscillator strength. In this work we have assumed *ad hoc* the standard formulas, eqs 3 and 4, with $\hat{\mu}$ representing the dipole moment of the AD pair and not the solvent. (In the first instance, $\hat{\mu}$ should include just the electronic contribution to this moment, but we may add the nuclear contribution, since it is constant and therefore does not affect the value of the transition moment between orthogonal states. Only then do $\mathbf{M}_{00}$, $\mathbf{M}_{11}$, and $\mathbf{M}_{22}$ represent the static dipole moments of the Ex in the three "pure" states.) Strictly speaking, $\mathbf{M}_{A^*}$ now includes an "electronic Franck–Condon factor" for the solvent, e.g. (A2), but that factor, $\langle\phi_2|\phi_0\rangle$, should be very nearly unity, since the AD pair in a pure no-bond or a pure locally excited state should perturb the solvent in small and nearly identical ways.

$$\mathbf{M}_{A^*} = \langle\psi_2|\hat{\mu}|\psi_0\rangle\ \langle\phi_2|\phi_0\rangle \qquad \text{(A2)}$$

Although reasonable and probably close to correct, the above assumptions lack a firm theoretical basis. It is tempting to assume, instead, that eqs 3 and 4 hold, but $\hat{\mu}$ includes the dipole moment of the solvent as well as the AD pair. (Again, in the first instance, $\hat{\mu}$ should include only electronic contributions, but the transition matrix element is unchanged if nuclear contributions are added.) One problem with that assumption is that it introduces one aspect of the influence of the solvent, entanglement of the states of the solute and solvent (see eq A1), without addressing another, the local-field effects that give rise to the enhancement factor $f(n)$. A second problem, and an indication that a thorough analysis will be required, is encountered when one tries to use eq 16. The $\Delta\mu$ includes the change in dipole moment of the solvent; the contribution of molecules far from the AD pair is divergent or conditionally convergent. (It is approximately equal to an integral of $\mathbf{P}_d \propto (n^2 - 1)\mathbf{E}_d$, where $\mathbf{E}_d$ is the electric field of a suitable "effective dipole moment" representing the long-range influence of the AD pair in its $A^{\bullet-}D^{\bullet+}$ state and $\mathbf{P}_d$ is the corresponding bulk electronic polarization. $\mathbf{E}_d$ decreases as r^{-3}, where r is the distance from the AD pair.) Evidently, the local-field problem will not be solved simply by partitioning the solvent into a "near region" that contributes to the overall transition moment (as part of a supermolecule including the AD pair) and a "far region" that gives rise to the local fields. To sidestep these difficulties, we neglect the possible contribution of solvent electrons to the transition moment.

We return to the conventional formulation of the transition moment, which does not consider solute–solvent correlations. It is usually assumed, either tacitly or on the basis of very rough arguments, that "direct" transition matrix elements such as $\mathbf{M}_{01}$ and $\mathbf{M}_{12}$ are small.[3a,36] The assumption about $\mathbf{M}_{12}$ is safe because the corresponding coefficient $(c_1d_2 + c_2d_1)$ is small anyway. The assumption about $\mathbf{M}_{01}$ is harder to justify. Hence we consider, briefly, an alternative model in which H_{01} vanishes but, of course, H_{12} does not. Consider the case of DCA and suppose, for the sake of argument, that the reason that $H_{01} = 0$ is that the Ex retains one of the vertical mirror planes of the DCA and Ψ_0 and Ψ_1 have different symmetries under the mirror operation. (It seems unlikely that the Ex would adopt a geometry retaining the C_2 axis of DCA but neither vertical mirror symmetry.) For H_{12} not to vanish, Ψ_2 must have the same symmetry as Ψ_1, which differs from that of Ψ_0. The vertical mirror plane with this effect runs through the DCA long axis, with Ψ_0 symmetric and Ψ_1 and Ψ_2 antisymmetric. With these symmetries, however, $\mathbf{M}_{01}$ would necessarily be parallel to the DCA short axis and therefore to $\mathbf{M}_{A^*}$. We have been unable to fit k'_f data with parallel transition moments, so this model fails. Although TCA lacks these mirror planes, it is reasonable to expect approximately the same polarization properties as for DCA.

All things considered, it seems unlikely that $H_{01} = 0$. It is possible that neither H_{01} nor $\mathbf{M}_{01}$ vanishes. If so, the present estimate of H_{01} would have to be adjusted either upward or downward, depending on the direction of $\mathbf{M}_{01}$. However, the good fits obtained with $\mathbf{M}_{01} = 0$ imply that additional parameters describing $\mathbf{M}_{01}$ cannot be extracted from the data. The conventional neglect of "direct" transition moments like $\mathbf{M}_{01}$ could profitably be reinvestigated with high-quality molecular-orbital calculations on smaller, model systems.

3. Refractive Index Correction. The refractive index factor $f(n)$ is used in eq 3 for the following reasons. The more familiar factor n^3 was derived by Strickler and Berg[22] from the density of photon (polariton) states in a medium of refractive index n. The possibility of a further refractive index effect was overlooked in the course of assuming that the Einstein absorption coefficients $(B_{1a\to ub})$ are proportional to the vibronic transition moments via a lumped proportionality constant K. The $B_{1a\to ub}$ were used to evaluate k_f via an Einstein detailed-balance argument. Adapting an argument by Chako,[17a] one finds that K depends on n so that the factor n^3 is replaced by $f(n)$, (eq 3b), assuming that the AD pair occupies a spherical cavity in the solvent.[17b,36] (Precisely the same factor has been found recently in a detailed quantum-electrodynamic treatment of the radiative decay rate of an impurity atom in a simple-cubic host crystal.[17c]) For an ellipsoidal cavity, the corresponding factor depends on the aspect ratio of the cavity and the orientation of the transition moment.[37] The experimental evidence for DCA and other anthracene derivatives favors a factor of n^2.[17b,38,39] The proper factor undoubtedly depends on the orientation of the transition moment relative to the axes of the cavity (or of the Ex) and, therefore, on the degree of mixing between pure ionic and locally excited states. Although a factor of n^2 is preferable for a pure locally excited state, it may not be so for mixed states. Hence we have stayed with the factor $f(n)$. The refractive index factor might affect our results in two ways. First, if it varies with the degree of charge transfer, f_{CT}, it may alter the dependence of k_f on f_{CT} or $h\nu_{av}$. Second, for highly ionic Ex, it affects the magnitude of the transition moment, and therefore of $H_{01}\Delta\mu$, required to account for the value of k_f. It is hard to assess either of these effects, in part because the direction of $\Delta\mu$ is incompletely determined by experiment (only the angle between $\Delta\mu$ and $\mathbf{M}_{A^*}$ is needed for the interpretation) and in part because existing theoretical models employ highly idealized geometries (spherical or ellipsoidal cavities;[17b,37] simple cubic lattices[17c,40]).[41]

4. Mixing with Other States. In addition to a large number of higher energy states, in the present systems, there are two nearby states that might mix significantly into the Ψ_{Ex}. (a) The absorption spectra of the acceptors (e.g., Figure 2 of ref 9) show a structure that is not mirrored in the emission spectra. The additional structure in the absorption spectra is presumably due to a second electronic state that has some intensity and is nearly degenerate with the A* state considered here. It is almost certainly derived from the ^1L_b state of anthracene.[42] In principle, the corresponding locally excited state could contribute to Ψ_{Ex}. Further

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(36) (a) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005. (b) Also see ref 4, Chapter 3, with our added assumption that Ψ_0 and Ψ_1 are orthogonal.

(37) (a) Shibuya, T. *Chem. Phys. Lett.* **1983**, *103*, 46. (b) Shibuya, T. *J. Chem. Phys.* **1983**, *78*, 5175.

(38) Hirayama, S.; Iuchi, Y.; Tanaka, F.; Shobatake, K. *Chem. Phys.* **1990**, *144*, 401.

(39) Lampert, R. A.; Meech, S. R.; Metcalfe, J.; Phillips, D.; Schaap, A. P. *Chem. Phys. Lett.* **1983**, *94*, 137.

(40) Fulton, R. L. *J. Chem. Phys.* **1974**, *61*, 4141.

(41) (a) For a discussion of solvent effects on molecular clusters, see: Shalev, E.; Ben-Horin, N.; Jortner, J. *J. Chem. Phys.* **1991**, *94*, 7757. (b) Since the effect of solvent on k_f is closely related to the effect on absorption, the literature of the latter is germane. See, for instance: Iweibo, I.; Obi-Egbedi, N. O.; Chongwain, P. T.; Lesi, A. F.; Abe, T. *J. Chem. Phys.* **1990**, *93*, 2238 and references therein.

(42) Friedrich, D. M.; Mathies, R.; Albrecht, A. C. *J. Mol. Spectrosc.* **1974**, *51*, 166.

analysis indicates that mixing with this second locally excited state should have little effect on k'_f for highly ionic Ex. These were the Ex used to evaluate $\tilde{H}_{01}$ and $\tilde{H}_{02}$ using eqs 26 and 29. Hence, little effect on these parameters is expected. The theoretical predictions in the region of high energies and small f_{CT} may be affected, however. (b) Each donor possesses two high-energy filled orbitals. These are in fact degenerate and isolated in benzene and HMB, although this degeneracy is presumably lifted in the presence of the $A^{\bullet-}$. However, a second ion-pair state could arise as a result of electron transfer from the second highest energy occupied orbital of the donor. If the energy difference between the two ion-pair states is small (ca. a few hundred cm^{-1}) and both states are strongly coupled to the locally excited state, the relative contributions of the two ion-pair states to Ψ_{Ex} could vary systematically with the average energies of the ion-pair states and the meaning of the fitting parameters $\tilde{H}_{01}$ and $\tilde{H}_{02}$ would be not clear. However, one might also expect the energy differences and relative contributions of the ion-pair states to vary from donor to donor, resulting in distinctly different plots of k'_f versus $\tilde{\nu}_{av}$ for different donors. No such variation is detected. In any case, because good fits are obtained without considering contributions from these (or other) states, it would be impossible to extract coupling parameters involving such additional states and, in fact, the good fits suggest that additional states may not be important.

5. Vibronic Coupling. Our treatment of partially ionic states as a purely electronic problem amounts to a simple Born–Oppenheimer approach. It neglects the possibility that different vibronic sublevels will mix to different degrees, as incorporated in the recent treatment by Bixon, Jortner, and Verhoeven.[13] This neglect is most problematic when the difference in energy between the ion-pair and locally excited states is small, say on the order of a vibrational quantum for a typical intramolecular skeletal mode (ca. 1400 cm^{-1}), and a detailed consideration of near-degenerate vibronic coupling is required. Because H_{12} is of approximately the same size, these cases correspond to $f_{CT} \approx 0.5$. Fortuitously, such cases are few: most of the Ex correspond to considerably larger f_{CT}, and all but one of the examples of A^* in a donor solvent correspond to considerably smaller f_{CT}. Thus, the energy of the ion-pair state is usually well below, or well above, that of the locally excited state.

B. Simplified Mixing Model. Because H_{01} is always much smaller than H_{11}, the ground state and its energy are approximately $\Psi_0[AD]$ and H_{00}, i.e. $d_0 \approx 1$, $d_1 \approx 0$, $d_2 \approx 0$, and $E_G \approx 0$. For the same reason, the Ex state has little $\Psi_0[AD]$ character, i.e. $c_0 \approx 0$, while $|c_1|$ and/or $|c_2|$ are comparable to 1. The energy and the large coefficients of the Ex state can be approximated by solving eq B1, the two-dimensional analog of eq 7. Moreover, since $E_G \approx 0$, eq 17 reduces to eq B2.

$$\begin{pmatrix} H_{11}-E_{Ex} & H_{12} \\ H_{12} & H_{22}-E_{Ex} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad (B1)$$

$$E_{Ex} = h\nu_{av} \qquad (B2)$$

The approximations in eqs B1 and B2 would be exact if H_{01} were zero, i.e. if the Hamiltonian matrix were replaced by the zeroth-order approximation (eq B3). We use the rest of the Hamiltonian matrix as a perturbation (eq B4) in first-order perturbation theory to estimate d_1 (eq B5), where E'_{Ex} is the second eigenvalue of $\mathbf{H}^{(0)}$. Trace conservation gives eq B6.

$$\mathbf{H}^{(0)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & H_{11} & H_{12} \\ 0 & H_{12} & H_{22} \end{pmatrix} \qquad (B3)$$

$$\mathbf{H}^{(1)} = \begin{pmatrix} 0 & H_{01} & 0 \\ H_{01} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (B4)$$

$$d_1 \approx -\left(\frac{c_1^{\,2}}{E_{Ex}} + \frac{c_2^{\,2}}{E'_{Ex}}\right)H_{01} \qquad (B5)$$

$$E'_{Ex} = H_{22} + (H_{11} - E_{Ex}) \qquad (B6)$$

Starting with eq 16, we can replace d_0 by 1 and $c_0\,d_2$ by 0 and use eq B5 for d_1 to obtain eq B7. At this level of approximation,

$$\mathbf{M} = -c_1\left(\frac{c_1^{\,2}}{E_{Ex}} + \frac{c_2^{\,2}}{E'_{Ex}}\right)H_{01}\Delta\mu + c_2\mathbf{M}_{A^*} \qquad (B7)$$

c_1, c_2, E_{Ex}, and E'_{Ex} are independent of H_{01} and the only important role of H_{01} is to govern the contribution of $\Delta\mu$ to the total transition moment. In that role, it is only the product $H_{01}\Delta\mu$ that matters and not H_{01} or $\Delta\mu$ individually. The simplified expression that was used in section III.A. to make the same point is obtained from eqs B5 and B9, below, with E_{Ex} replaced by $E_{Ex} - E_G$.

We now write $c_1^2 = 1 - c_2^2$ to obtain eq B8. The factor multiplying c_2^2 on the right is smaller in magnitude than $1/E_{Ex}$.

$$\left(\frac{c_1^{\,2}}{E_{Ex}} + \frac{c_2^{\,2}}{E'_{Ex}}\right) = \frac{1}{E_{Ex}} + c_2^{\,2}\left(\frac{1}{E'_{Ex}} - \frac{1}{E_{Ex}}\right) \qquad (B8)$$

Moreover, c_2^2 is small unless the Ex has considerable locally excited character and the CT contribution to $\mathbf{M}$, involving d_1, is relatively minor anyway. Hence, it is a good approximation to neglect the term involving c_2^2 on the right of eq B8, and eq B9 follows. Inserting eq B9 in eq B7 gives eqs B10 and B11. The fractional CT character

$$\left(\frac{c_1^{\,2}}{E_{Ex}} + \frac{c_2^{\,2}}{E'_{Ex}}\right) \approx \frac{1}{E_{Ex}} \qquad (B9)$$

$$\mathbf{M} = c_1\mathbf{M}_{A^-D^+} + c_2\mathbf{M}_{A^*} \qquad (B10)$$

$$\text{where } \mathbf{M}_{A^-D^+} = -\frac{H_{01}\Delta\mu}{E_{Ex}} \qquad (B11)$$

is $f_{CT} = c_1^2$. Without loss of generality, we may take c_1 to be nonnegative, so $c_1 = (f_{CT})^{1/2}$. Within the present approximations, $c_2^2 = 1 - f_{CT}$. The sign of c_2 is fixed by eq B12, which is part of the two-dimensional eigenvalue equation (eq B1). Since H_{12}

$$H_{12}c_1 + (H_{22} - E_{Ex})c_2 = 0 \qquad (B12)$$

is nonnegative by convention and $E_{Ex} < H_{22}$, eq B12 implies that $c_2 \leq 0$; hence $c_2 = -(1 - f_{CT})^{1/2}$. In addition, using eq B12 with $c_2^2 = 1 - c_1^2$, we obtain eq B13.[3b] Eq 24 follows upon replacing H_{22} by $h\nu_{A^*}$ and E_{Ex} by $h\nu_{av}$.

$$f_{CT} = c_1^{\,2} = \left[1 + \left(\frac{H_{12}}{H_{22} - E_{Ex}}\right)^2\right]^{-1} \qquad (B13)$$