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Electronic Coupling Matrix Elements in Acceptor–Donor Excited States and the Effect of Charge-Transfer Character on Their Radiative Rate Constants

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It is well known that charge-transfer (CT) oscillator strengths and radiative rate constants, k_f, are functions of the appropriate electronic coupling matrix elements.[1] For CT excited states, an important issue is the extent to which mixing of locally excited states is important. Exciplexes,[2a] excited states of acceptor (A)/donor (D) CT complexes,[1b] and those of rigidly linked A/D systems,[2b] designated here collectively as Ex, are usually described within a minimal basis set consisting of the neutral (AD), the ion pair ($A^{\bullet-}D^{\bullet+}$), and the locally excited states (A^*D), as indicated in eq 1 for the case where the energy of D^* is much higher than that of A^*.[3] Mixing among the basis states, which we assume

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

to be orthonormal, depends upon the electronic matrix elements that couple the AD and $A^{\bullet-}D^{\bullet+}$ states (H_{01}) and the $A^{\bullet-}D^{\bullet+}$ and A^*D states (H_{12}). If H_{12} and H_{01} are known, the fractional charge-transfer character of the Ex, f_{CT}, defined as $|c_1|^2$, can be determined. If $f_{CT} < 1$ due to significant admixture of the A^*D state, then k_f, for example, is expected to be larger than for an essentially pure $A^{\bullet-}D^{\bullet+}$ state ($f_{CT} \approx 1$).[3] Here we describe a simple method for analyzing the k_f for a series of exciplexes and excited CT complexes, which allows H_{12} and H_{01} to be determined, and thus f_{CT}. The experimental data represent a comprehensive data set covering $f_{CT} \approx 0$ to $f_{CT} \approx 1$. In the nonadiabatic limit and when the Ex is essentially a pure ion pair, H_{01} controls the rate constant for the nonradiative return-electron-transfer process Ex → AD.[4] Recently, H_{01} for some Ex has been estimated from k_f by assuming that the Ex are, in fact, pure ion pair states.[5] The method described here can be used to test this assumption.

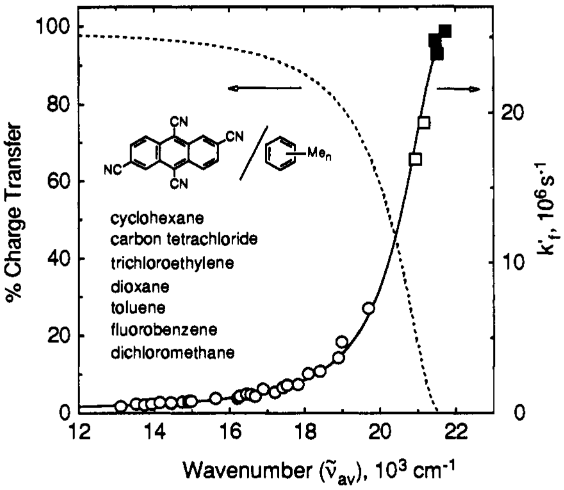

Figure 1. Right axis: plot of radiative rate constants corrected for solvent refractive index (k'_f) vs average emission wavenumber ($\bar{\nu}_{av}$), for TCA/alkylbenzene exciplexes and excited CT complexes (○), for TCA* in nondonating solvents[11] (■), and for TCA* in weakly donating aromatic solvents (□). The solid curve through the points represents a fit to the data as described in the text. Left axis: plot of percentage charge transfer vs $\bar{\nu}_{av}$ (dashed curve).

Radiative rate constants[6] for CT emission were measured for a series of exciplexes and excited CT complexes with 2,6,9,10-tetracyanoanthracene (TCA) as the acceptor and the methyl-substituted benzenes *p*-xylene, 1,2,4-trimethylbenzene, durene, pentamethylbenzene, and hexamethylbenzene as the donors. Solvents of varying polarity (cyclohexane to dichloromethane) were used. The k_f values plotted versus an average emission frequency, ν_{av},[7] are shown as the circles in Figure 1. Also included in Figure 1 are k_f data for TCA* without an alkylbenzene donor in carbon tetrachloride, dichloromethane, and acetonitrile (filled squares), and in fluorobenzene and *o*-dichlorobenzene (open squares). The former solvents, though of varying polarity, are relatively nondonating. The latter two solvents exhibit partial donor character as evidenced by the smaller ν_{av} and k_f. The k_f values clearly depend strongly on the emission frequency. The emission properties of the TCA*/solvent only systems are clearly related to those of the Ex.

The dependence of k_f on emission frequency is usually expressed as shown in eq 2, in which $f(n)$ is a function of the solvent refractive index[8] and M is the electronic transition moment.

$$k'_f = \frac{k_f}{f(n)} = \frac{64\pi^4}{3hc^3}\nu_{av}{}^3M^2 \qquad (2)$$

To compare measurements in different solvents, the observed radiative rate constants are corrected for refractive index, giving the solvent-independent k'_f. For an Ex, M is expected to decrease with increasing f_{CT}.[3] At the limit where $f_{CT} = 0$, the Ex is essentially a pure locally excited state (A^*D) whose transition moment, M_{A^*}, corresponds to a fairly strong intramolecular transition and is therefore relatively large. At the other limit, where $f_{CT} \approx 1$, the Ex is equivalent to a contact radical–ion pair ($A^{\bullet-}D^{\bullet+}$), and the transition moment, $M_{A^-D^+}$, is smaller because it corresponds to an intermolecular electron-transfer process.

In principle, the evaluation of M as a function of ν_{av} involves a three-state eigenvalue problem. However, the ground and Ex states can be approximated by Ψ_0 and $c_1\Psi_1 + c_2\Psi_2$, with c_1 and c_2 evaluated as a two-state problem. To a very good approxi-

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(1) See, for example: (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(2) See, for example: (a) *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

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(6) The radiative rate constants are determined as (Φ_f/τ), where Φ_f and τ are the Ex emission quantum yield and lifetime, respectively. The Ex studied here are formed with unit efficiency in the $A^* + D$ reaction.[6b] (b) Gould, I. R.; Mueller, L.; Farid, S. *Z. Phys. Chem.* (*Munich*) **1991**, *170*, 143.

(7) (a) The ν_{av} values for the Ex species are determined as described in ref 5b. The ν_{av} values for TCA*/solvent only systems, where the fractional charge transfer is small, are determined as described in ref 7b. (b) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

(8) (a) We have used $f(n) = n[(n^2 + 2)/3]^2$, which has a better theoretical foundation[8b–d] than the often used $f(n) = n^3$. (b) Chako, N. Q. *J. Chem. Phys.* **1934**, *2*, 644. (c) Hirayama, S.; Phillips, D. *J. Photochem.* **1980**, *12*, 139. (d) Knoester, J.; Mukamel, S. *Phys. Rev. A* **1989**, *40*, 7065.

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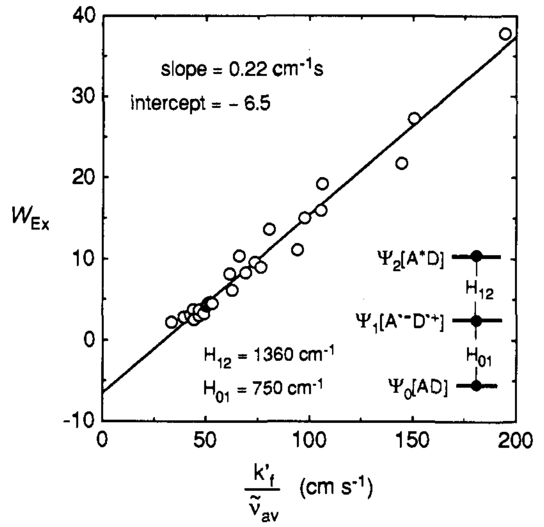

Figure 2. Plot of the quantity W_{Ex} (eq 6a) vs $k'_f/\tilde{\nu}_{av}$ for the TCA Ex systems given in Figure 1 (○), excluding the two Ex points with the highest $\tilde{\nu}_{av}$.

mation, the coupling of these approximate states by H_{01} can then be treated by perturbation theory. The result is given in eqs 3–5, where H_{01}, H_{12}, and ν_{av} are in wavenumbers:[9]

$$M^2 = f_{CT}M^2_{A^-D^+} + (1 - f_{CT})M^2_{A^\bullet} \tag{3}$$

$$M_{A^-D^+} = \frac{\Delta\mu H_{01}}{\tilde{\nu}_{av}} \tag{4}$$

$$f_{CT} = \left[1 + \left(\frac{H_{12}}{\tilde{\nu}_{A^\bullet} - \tilde{\nu}_{av}}\right)^2\right]^{-1} \tag{5}$$

The difference between the static dipole moments of the $A^{\bullet -}D^{\bullet +}$ and AD states, $\Delta\mu$, contributes to M^2 *via* $M_{A^-D^+}$, because H_{01} introduces some ionic character into the ground state.[1b,10] Equations 3–5 are correct for the case where $\Delta\mu$ and $M_{A^\bullet}$ are at right angles, which will be the case if $M_{A^\bullet}$ is polarized in the plane and $\Delta\mu$ is perpendicular to the plane of the anthracene. $M_{A^\bullet}$ can be determined (using eq 2) from the average emission frequency, $\nu_{A^\bullet}$, and radiative rate constant, $(k'_f)_{A^\bullet}$, of TCA* in the nondonating solvents.[11] Thus, from eqs 2–5, the dependence of k'_f on $\tilde{\nu}_{av}$ can be calculated in terms of measurable quantities, with only two adjustable parameters, $(\Delta\mu H_{01})$ and H_{12}. A good fit to the experimental data is obtained in this way (solid curve in Figure 1)[12] with 1350 cm-1 for H_{12} and 9800 D·cm-1 for $(\Delta\mu H_{01})$.[13]

A simple data analysis method results from rearrangement of eqs 2–5 to give eq 6. According to eq 6, a plot of the quantity

$$W_{Ex} \equiv \left(1 - \frac{\tilde{\nu}_{A^\bullet}{}^3}{(k'_f)_{A^\bullet}}\frac{k'_f}{\tilde{\nu}_{av}{}^3}\right)\left(\frac{\tilde{\nu}_{A^\bullet}}{\tilde{\nu}_{av}} - 1\right)^{-2}$$

$$= a + b\left(\frac{k'_f}{\tilde{\nu}_{av}}\right) \tag{6a}$$

$$a = -\left(\frac{H_{01}\Delta\mu}{H_{12}M_{A^\bullet}}\right)^2 \qquad b = \frac{\tilde{\nu}_{A^\bullet}{}^3}{(k'_f)_{A^\bullet}}\frac{1}{H_{12}{}^2} \tag{6b}$$

W_{Ex} vs $k'_f/\tilde{\nu}_{av}$ should be linear, with H_{12} and $(\Delta\mu H_{01})$ determined readily from the slope and the intercept (eq 6b). Such a plot is shown in Figure 2. Data points with $\tilde{\nu}_{av}$ close to $\tilde{\nu}_{A^\bullet}$ (two in this case) are not included because with increasing $\tilde{\nu}_{av}$, W_{Ex} becomes large and very sensitive to small errors in $\tilde{\nu}_{av}$. The slope, *b*, and intercept, *a*, (Figure 2), give 1360 cm-1 and 9700 D·cm-1 for H_{12} and $(\Delta\mu H_{01})$, in very good agreement with the values obtained from fitting k'_f vs $\tilde{\nu}_{av}$ (Figure 1).

For the TCA Ex, a value for $\Delta\mu$ of 13 D can be estimated from the slope of a plot of emission frequency vs a conventional solvent function.[14] Thus, H_{01} is determined from $(\Delta\mu H_{01})$ to be 750 cm-1, which is within the range estimated for this parameter from studies of nonradiative return-electron-transfer reactions in closely related contact radical–ion pairs.[15] It is interesting that H_{12} is significantly larger than H_{01}. This observation may have consequences for comparisons of the rate constants of A*D (or AD*) → $A^{\bullet -}D^{\bullet +}$ reactions with those of $A^{\bullet -}D^{\bullet +}$ → AD.

With 1360 cm-1 for H_{12}, f_{CT} can be determined as a function of $\tilde{\nu}_{av}$ using eq 5. The percentage charge transfer (f_{CT} × 100) increases with decreasing k'_f and $\tilde{\nu}_{av}$ (dashed curve in Figure 1). For the present systems, $M_{A^\bullet}$ is ca. 4 times larger than $M_{A^-D^+}$. Therefore, for Ex with 90% and 99% CT character, M is larger than $M_{A^-D^+}$ by factors of ca. 1.6 and 1.07, respectively (eq 3). If these Ex were assumed to be pure ion pairs ($f_{CT} \approx 1$), i.e., $M_{A^-D^+}$ were identified with M, then the calculated $(\Delta\mu H_{01})$ would be too high by the same factors. This clearly illustrates the importance of taking into account contributions from locally excited states in interpreting Ex radiative rate constants.

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Supplementary Material Available: Theoretical model for mixing of the neutral, pure ion pair, and locally excited states, and the derivation of equations 3–5 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[9] (a) Derivations of eqs 3–5 are given in the supplementary material. The treatment of the mixing of neutral, pure ion pair and locally excited states is similar to others described previously[3a–c] but differs in the manner in which the electronic polarization of the solvent is treated (see, for example, ref 9b). (b) Young, R. H. *J. Chem. Phys.* **1992**, *97*, 8261.

[10] Cannon, R. D. *Electron Transfer Reactions*; Butterworths: Boston, 1980; Section 8.3.

[11] The average values of $\tilde{\nu}_{A^\bullet}$ and $(k'_f)_{A^\bullet}$ for TCA in carbon tetrachloride, dichloromethane, and acetonitrile are 21.6 × 10³ cm-1 and 2.47 × 10⁷ s-1, respectively; hence, $M_{A^\bullet}$ = 2.80 D.

[12] The data were actually fitted as $\log(k'_f)$ vs $\tilde{\nu}_{av}$ to expand the lower part of the curve.

[13] When the difference between $\nu_{A^\bullet}$ and ν_{av} is comparable to H_{12}, coupling among vibronic sublevels should probably be considered, and the simple three-electronic state theory may be inaccurate. Nevertheless, the present theory reproduces the data in this regime, i.e., the points for TCA* in the donor solvents (open squares, Figure 1).

[14] (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.

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