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Lifetimes for Radiative Charge Recombination in Donor–Acceptor Molecules

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Abstract: In this paper we demonstrate that the marked solvent dependence of the rates k_{rad} for radiative recombination in some donor (D)–bridge (B)–acceptor (A) molecules, which increase with decreasing solvent polarity (i.e., with increasing peak energy $\langle\nu\rangle$ for charge-transfer fluorescence), can be quantitatively accounted for in terms of a dominating contribution of (DBA)*–D$^+$BA$^-$ mixing, involving intensity borrowing from local (DBA)* electronic excitations. In these DBA molecules, the traditional two-level D$^+$BA$^-$–DBA coupling scheme is inapplicable. The analysis of the $\langle\nu\rangle$ dependence of k_{rad} for a certain DBA in a series of solvents results in the (DBA)*–D$^+$BA$^-$ couplings V^*, which are in good agreement with the V^* parameters extracted from oscillator strengths for charge-transfer absorption. The V^* parameters, which obey the relation $V^* \propto \exp(-\alpha N)$ (where N is the number of bonds in the bridge), determine the rates for nonradiative (DBA)* $\rightarrow$ D$^+$BA$^-$ charge separation and recombination from electronically excited states. The (DBA)*–D$^+$BA$^-$ mixing is maximized for the isolated, solvent-free DBA molecule. For the isolated molecules analyzed herein, the fraction of (DBA)* admixture within the charge-transfer state is ~0.02, being even smaller for the solvated molecules.

I. Prologue

The nonradiative, nonadiabatic multiphonon electron-transfer (ET) theory in its classical[1,2] and quantum mechanical[3–5] versions is widely utilized for the unified description of a wide class of nonradiative ET processes in chemistry, physics, and biology.[6–8] The quantification of ET rates, $k = (2\pi/\hbar)V^2F$, requires theoretical calculations or independent information on the electronic coupling V and the thermally averaged Franck–Condon factor F. A central source of independent experimental information on these electronic and nuclear parameters for ET originates from the general relation between nonradiative and radiative processes in condensed phase[9–11] and in large molecules,[12] with the nonradiative process (induced by V) being analogous to the radiative emission process (induced by the radiative coupling) in the limit of zero frequency. This analogy was explored[5,13–28] for ET processes in solutions, where the optical processes

$$\mathrm{DA} \xrightarrow{h\nu} \mathrm{D^+A^-}$$

for a donor (D)–acceptor (A) complex[21,29–33] and

$$\mathrm{DBA} \xrightarrow{h\nu} \mathrm{D^+BA^-}$$

in a bridged (B) D–A supermolecule[14,15,17–28,34] can serve as

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spectroscopic probes for the determination of the nuclear and electronic parameters, which determine the nonradiative ET rates for charge recombination $D^+A^- \rightarrow DA$ and $D^+BA^- \rightarrow DBA$. Regarding the nuclear Franck–Condon factor, the isomorphism between the (absorption or emission) optical line shape and the free energy relationship for nonradiative ET provides information[5,13,21,24–28,34] on the energetic and the nuclear parameters which determine F, i.e., the (free) energy gap, the medium and intramolecular reorganization energies, the intramolecular nuclear–electronic coupling, and the intramolecular frequencies. Concerning the electronic coupling, researchers have attempted since the landmark work of Mulliken[29] to relate the intensity, i.e., the oscillator strength f, of the optical charge-transfer transition to V. These relations have been independently developed and explored by Hush[14] and by others[15–17,19,26–28] for the determination of V. In view of the fundamental relations between the Einstein absorption and spontaneous emission coefficients, complementary evaluation of V would emerge from the experimental pure radiative lifetimes k_{rad} (i.e., $k_{rad} = k_t Y$, where Y is the fluorescence quantum yield and k_t is the total decay rate of the D^+A^- or D^+BA^- state).[21,24–28] It was hoped that these "experimental" values of V obtained from spectroscopy will provide reliable information on the intermolecular[35,36] and intramolecular[36–39] electronic interactions (i.e., "through space" and "through bonds") responsible for nonradiative charge recombination, for the confrontation with theoretical calculations, and for the determination of distance and orientation dependence of ET rates.[15,16,19,25–28,40–42]

How reliable are these V parameters emerging from the analysis of the oscillator strengths or radiative lifetimes? Most of such information[14,15,16,19,21] rests on the two-states model advanced by Mulliken,[29] which considered the coupling between the ground state DA (or DBA) and the charge-transfer state D^+A^- (or D^+BA^-). Murrel[31] extended the two-states model to incorporate mixing of the charge-transfer state D^+A^- (or D^+BA^-) with locally excited state(s) $(DA)^*$ (or $(DBA)^*$) with the ET optical transition stealing (or borrowing) intensity from the local transition DA (or DBA) $\rightarrow (DA)^*$ (or $(DBA)^*$). Murrel[31] and Mulliken and Parson[30] proposed that this intensity borrowing mechanism may perhaps account for the charge-transfer intensity of weak DA complexes but not for strong complexes with large f values. An early effort to evaluate the importance of this intensity borrowing in exciplexes was presented by De Schryver et al.[43] The intensity borrowing mechanism was invoked by Pasman, Rob, and Verhoeven[25] to account for the (large) intensities of the first charge-transfer band in rigid DBA molecules and by Oevering and Verhoeven[26,27] to account for the intensity of the first and the second charge-transfer absorption bands in a series of DBA molecules (Figure 1), with D = 1,4-dimethoxynaphthalene or dimethoxybenzene, A = 1,1-dicyanovinyl or 1,2-bis(carboxymethyl)ethylene, and B = norbornylogous bridges. Pasman[24] noted a small increase of the radiative rates with decreasing solvent polarity, which was attributed[24,26,27] to an enhanced admixture of locally excited states upon decreasing the solvent stabilization of the D^+BA^- state. Indeed, it was shown[28] that the application of the two-state model for radiative lifetimes of DBA molecules results in marked apparent solvent-dependent V parameters which increase with decreasing the solvent polarity.

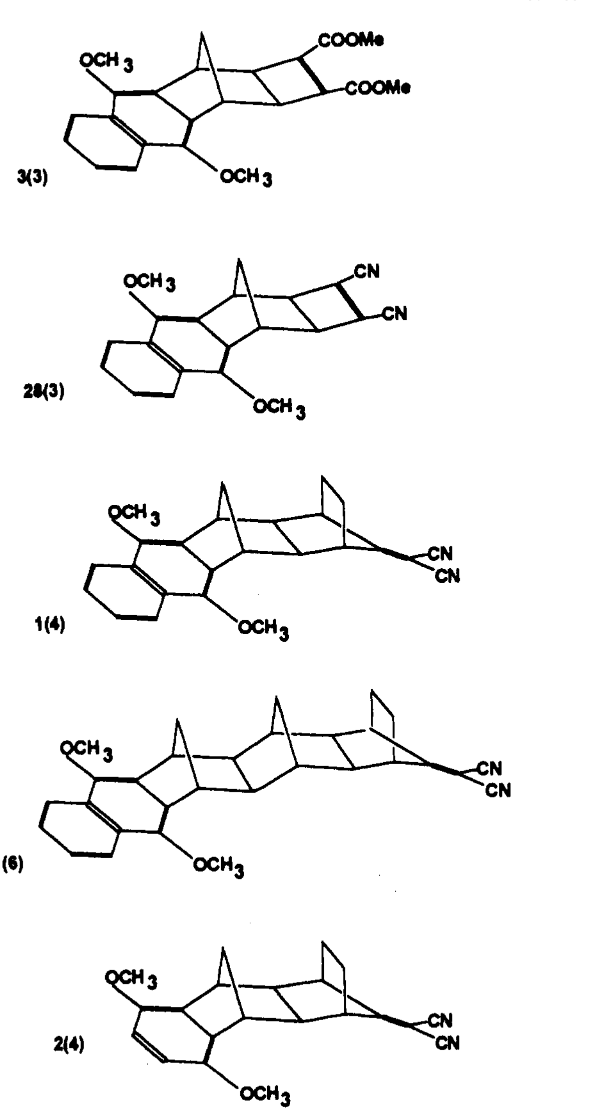

Figure 1. Structures of norbornye-bridged donor–acceptor molecules whose solvent-dependent k_{rad} data[26–28a] are analyzed. The compounds are grouped according to their D–A separation by three, four, and six σ bonds, and the numbers used in original references[26–28a] have been retained.

In this paper we challenge the conventional wisdom[14–16,19,21] regarding the utilization of the f and of k_{rad} data in conjunction with the two-state model for the extraction of the V parameter for charge-transfer recombination. We shall demonstrate that the solvent dependence of the experimental radiative rates k_{rad} for the radiative ET fluorescence $D^+BA^- \rightarrow DBA$[25–28] is inconsistent with the two-state model. We shall show instead that the solvent dependence of k_{rad}, which originates from the solvent shift of the vertical energy gap, can be quantitatively accounted for in terms of the dominating contribution of intensity borrowing from locally excited states, as proposed by Verhoeven et al.[25,26] Our analysis of the energy gap dependence of the radiative lifetimes and of the oscillator strength for charge-transfer excitation results in estimates of the electronic coupling V^* between the local excitation $(DBA)^*$ and the charge-transfer state D^+BA^-. Of course, V^* cannot be utilized to calculate the ET rate for nonradiative charge recombination to the ground DBA state. Such electronic couplings determine the rate of the ET processes for charge separation and recombination from the relevant electronically excited state, i.e., $(DBA)^* \rightleftarrows D^+BA^-$. Such ET reactions are important for the elucidation of photoinduced charge separation, being of prime importance in the primary

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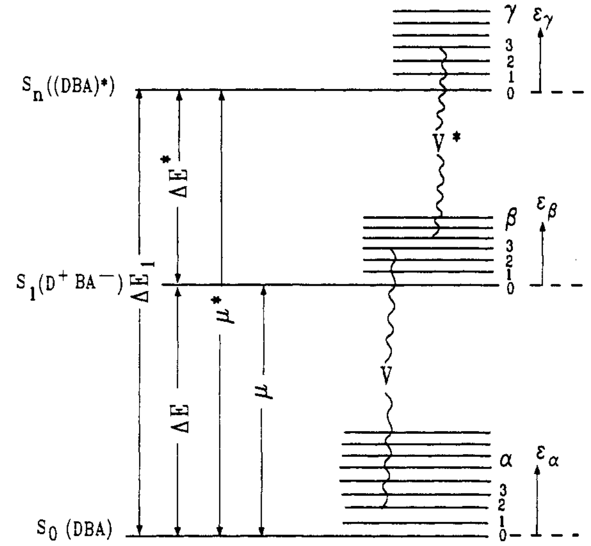

Figure 2. Three-state model consistency of the (zeroth-order) electronic states: ground-state DBA, charge-separated-state D^+BA^-, and localized excitation (DBA). The energies of the vibronic states in the three electronic manifolds are ϵ_α, ϵ_β, and ϵ_γ, respectively. The electronic energy gaps between the electronic origins of D^+BA^- and DBA and between (DBA)* and D^+BA^- are denoted by ΔE and ΔE^*, respectively, with $\Delta E_1 = \Delta E + \Delta E^*$. The electronic couplings are $V = \langle D^+BA^-|\hat{H}|DBA\rangle$ and $V^* = \langle (DBA)^*|\hat{H}|D^+BA^-\rangle$. The electronic transition moments are $\mu = \langle DBA|\hat{\mu}|D^+BA^-\rangle$ and $\mu^* = \langle DBA|\hat{\mu}|DBA)^*\rangle$.

process in photosynthesis, where ET occurs from the electronically excited chlorophyll dimer.

II. Radiative Decay Rate for Charge-Transfer Fluorescence

The radiative decay rate k_{rad} from the electronic origin (or the thermally equilibrated vibronic manifold) of D^+BA^- to the ground electronic state manifold of DBA is given by the sum of rates for individual radiative decay channels $k_{\mathrm{rad}}(\nu)$, each corresponding to the photon energy ν (in cm^{-1}):

$$k_{\mathrm{rad}} = \int \mathrm{d}\nu\, k_{\mathrm{rad}}(\nu) \qquad \text{(II.1)}$$

where

$$k_{\mathrm{rad}}(\nu) = \frac{32\pi^3 n^3}{3\hbar}\nu^3|\mu_{\mathrm{v}}(\nu)|^2 \qquad \text{(II.2)}$$

where n is the refractive index of the medium (n^3 corrects the density of states of the radiation field in the medium), and $\mu_{\mathrm{v}}(\nu)$ is the vibronic transition moment for the photon energy ν, with $|\mu_{\mathrm{v}}(\nu)|^2$ being the vibronic transition moment density per unit energy range (Appendix A).

The calculation of the frequency-dependent vibronic transition moment is based on the three-state model (Figure 2), which constitutes a slight extension of the Murrel scheme[31] to incorporate vibronic effects. The three-state model considers the (symmetry-allowed) mixing of the charge-transfer excitation with the intense, closest lying in energy localized excitation. Of course, other higher localized excitations might mix with the charge-transfer state. We shall follow the traditional approach in molecular physics for interstate mixing (e.g., vibronic coupling in isolated molecules[44] or crystal field mixing in molecular solids[45]), where the mixing of a single localized excitation is considered. The mixed vibronic levels, $|G,v_G>$, of the ground electronic state $|G>$ with a vibrational state $|v_G>$, and $|CT,v_{CT}>$ of the charge-transfer electronic state $|CT>$ with the vibrational state $|v_{CT}>$, are

$$|G,v_G> = |DBA,\bar{\alpha}> + \sum_\beta \frac{V}{\Delta E - \epsilon_{\bar{\alpha}} + \epsilon_\beta}|\beta>\langle\beta|\bar{\alpha}\rangle|D^+BA^-> \qquad \text{(II.3a)}$$

$$\begin{aligned}|CT,v_{CT}> = {} & |D^+BA^-,\bar{\beta}> - \sum_\alpha \frac{V}{\Delta E - \epsilon_\alpha + \epsilon_{\bar{\beta}}}|\alpha>\langle\alpha|\bar{\beta}\rangle|DBA\rangle + \\ & \sum_\gamma \frac{V^*}{\Delta E^* - \epsilon_{\bar{\beta}} + \epsilon_\gamma}|\gamma>\langle\gamma|\bar{\beta}\rangle|(DBA)^*>\end{aligned} \qquad \text{(II.3b)}$$

The zeroth-order electronic states (Figure 2) are $|DBA>$, $|D^+BA^->$, and $|(DBA)^*>$, with the corresponding vibrational levels $|\alpha>$ (with energies ϵ_α), $|\beta>$ (with energies ϵ_β), and $|\gamma>$ (with energies ϵ_γ), respectively. The electronic energy gaps are ΔE for the electronic origin of D^+BA^- above DBA and ΔE^* for the electronic origin of (DBA)* above D^+BA^- (Figure 2). These energy gaps are related by $\Delta E_1 = \Delta E^* + \Delta E$, where ΔE_1 is the energy gap between the energetic origins of (DBA)* and DBA (Figure 2). The vibronic states (II.3a) and (II.3b) have a parentage in the (zeroth-order) states $|DBA,\bar{\alpha}>$ and $|D^+BA^-,\bar{\beta}>$, respectively. The electronic couplings are $V = \langle DBA|\hat{H}|D^+BA^-\rangle$ for the two-level mixing and $V^* = \langle D^+BA^-|\hat{H}|(DBA)^*\rangle$ for the mixing of the local excitation with the charge-transfer state, where $\hat{H}$ is the system's Hamiltonian. The energy gaps in eqs II.3a and II.3b can be expressed in terms of the photon energy ν for the $|CT,v_{CT}> \rightarrow |G,v_G>$ radiative transition, i.e.,

$$\nu = \Delta E + \epsilon_{\bar{\beta}} - \epsilon_{\bar{\alpha}} \qquad \text{(II.4)}$$

The vibronic transition moment for the photon energy ν is

$$\begin{aligned}\langle G,v_G|\hat{\mu}|CT,v_{CT}\rangle = {} & <DBA|\hat{\mu}|D^+BA^-><\bar{\alpha}|\bar{\beta}> + \\ & \left(\frac{V}{\nu}\right)(\Delta\mu)<\bar{\alpha}|\bar{\beta}> + \sum_\gamma \frac{V^*\langle\bar{\alpha}|\gamma\rangle\langle\gamma|\bar{\beta}\rangle}{\Delta E_1 - \nu + \epsilon_\gamma - \epsilon_{\bar{\alpha}}}\mu^*\end{aligned} \qquad \text{(II.5)}$$

where $\hat{\mu}$ is the (electronic) dipole moment operator, $\Delta\mu = \langle D^+BA^-|\hat{\mu}|D^+BA^-\rangle - \langle DBA|\hat{\mu}|DBA\rangle$ is the difference between the permanent dipole moments of D^+BA^- and DBA, and $\mu^* = \langle DBA|\hat{\mu}|(DBA)^*\rangle$ is the electronic transition moment for the localized excitation. The first term on the right-hand side (RHS) of eq II.5, which depends on the intermolecular overlap, is neglected.[29] The third term on the RHS of eq II.5 is approximated by writing $<\bar{\alpha}|\gamma> = \delta_{\bar{\alpha}\gamma}$, assuming a small equilibrium configurational change between (DBA)* and DBA electronic states. Equation II.5 is recast in the form

$$\langle G,v_G|\hat{\mu}|CT,v_{CT}\rangle = \left[\left(\frac{V}{\nu}\right)\Delta\mu + \left(\frac{V^*}{\Delta E_1 - \nu}\right)\mu^*\right]<\bar{\alpha}|\bar{\beta}> \qquad \text{(II.5a)}$$

Following the analysis of Appendix A, we obtain

$$|\mu_{\mathrm{v}}(\nu)|^2 = |V\Delta\mu|^2(F(\nu)/\nu^2) + 2V^*V(\Delta\mu\mu^*)[F(\nu)/\nu(\Delta E_1 - \nu)] + (V^*\mu^*)^2[F(\nu)/(\Delta E_1 - \nu)^2] \qquad \text{(II.6)}$$

where $(\Delta\mu\mu^*)$ is the scalar product between $\Delta\vec{\mu}$ and $\vec{\mu}^*$.

$$F(\nu) = Z^{-1}\sum_{\bar{\alpha}}\sum_{\bar{\beta}} \exp(-\epsilon_{\bar{\beta}}/k_{\mathrm{B}}T)|<\bar{\beta}|\bar{\alpha}>|^2\delta(\Delta E + \epsilon_{\bar{\beta}} - \epsilon_{\bar{\alpha}} - \nu) \qquad \text{(II.7)}$$

where $Z = \sum_{\bar{\beta}}\exp(-\epsilon_{\bar{\beta}}/k_{\mathrm{B}}T)$ is the partition function in the initial charge-transfer manifold. $F(\nu)$, eq II.7, is the thermally averaged Franck–Condon vibrational overlap density per unit energy at

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the energy ν, eq II.4, which can be obtained from the experimental charge-transfer fluorescence line shape.[5,13–28,34]

Armed with eqs II.1, II.2, and II.6, we have an explicit expression for $k_{\rm rad}$. Invoking the approximation $\int d\nu\, F(\nu)g(\nu) = g(\langle\nu\rangle)$, where $g(\nu)$ is some function of ν appearing on the RHS of eq II.6 and $\langle\nu\rangle$ is the peak energy of the charge-transfer fluorescence band, one obtains

$$k_{\rm rad} = \left(\frac{32\pi^3 n^3}{3\hbar}\right)[(V\Delta\mu)^2\langle\nu\rangle + 2V^*V(\Delta\mu\mu^*)\langle\nu\rangle^2/(\Delta E_1 - \langle\nu\rangle) + (V^*\mu^*)^2\langle\nu\rangle^3/(\Delta E_1 - \langle\nu\rangle)^2] \quad \text{(II.8)}$$

Two limiting cases are of interest. (A) The two-state model:

$$k_{\rm rad} = \frac{32\pi^3 n^3}{3\hbar}(V\Delta\mu)^2\langle\nu\rangle \quad \text{(II.9)}$$

This result was previously derived and applied by Oevering et al.,[26,27] by Kroon et al.,[28] and by Gould et al.[21] (B) The mixing of charge-transfer states with a localized excitation. This state of affairs is realized when

$$(V^*/V) > (\Delta\mu/\mu^*)[(\Delta E_1 - \langle\nu\rangle)/\langle\nu\rangle] = (eR_c/\mu^*)[(\Delta E_1 - \langle\nu\rangle)/\langle\nu\rangle] \quad \text{(II.10)}$$

where R_c is the center-to-center D–A separation. Under these conditions,

$$k_{\rm rad} = \frac{32\pi^3 n^3}{3\hbar}(V^*\mu^*)^2\langle\nu\rangle^3/(\Delta E_1 - \langle\nu\rangle)^2 \quad \text{(II.11)}$$

Of course, when both mechanisms A and B contribute, the complete expression, eq II.8, has to be utilized, where the cross term (i.e., the second term on the RHS of eq II.8) can be either positive or negative (due to VV^*) or zero (due to the appearance of the scalar product $(\Delta\mu\mu^*) \equiv (\vec{\Delta\mu}\cdot\vec{\mu}^*)$).

In the foregoing analysis we have adopted a perturbative scheme for the treatment of the mixed vibronic levels which rests on eqs II.3a and II.3b. The validity conditions for this scheme imply, of course, large energy gaps relative to the electronic coupling. For the two-level mixing, one requires that $(V/\langle\nu\rangle)^2 \ll 1$, a condition which seems to be always well satisfied. For the mixing of local excitations with charge-transfer states, the validity condition implies that the fraction g^* of the neutral excitation in the charge-transfer state,

$$g^* \simeq (V^*/(\Delta E_1 - \langle\nu\rangle))^2 \quad \text{(II.12)}$$

is small, (i.e., $g^* \lesssim 0.1$). When heavy vibronic mixing due to near-degeneracy between the low-lying vibronic levels of D^+BA^- (within the thermal energy range k_BT above the electronic origin of D^+BA^-) and the vibronic levels of $(DBA)^*$ prevails, our treatment has to be extended, with the required theoretical scheme being reminiscent of the treatment of the pseudo-Jahn–Teller effect.[44] This problem may be of interest for the exploration of the radiative lifetimes of excited D–A exciplexes.[21] The validity condition, $g^* \ll 1$, is *a posteriori* justified for the analysis of the radiative decay of the DBA donor–acceptor molecules[25–28] considered herein.

III. Analysis of Experimental $k_{\rm rad}$ Data

The experimental data[25–28] for $k_{\rm rad}$ vs $\langle\nu\rangle$ (Figures 3 and 4) reveal a marked solvent dependence of $k_{\rm rad}$ which is considerably higher in nonpolar hydrocarbons than in polar solvents. For the **4c** compound[25] (Figure 3), as well as for the **3(3)**, **1(4)**, **28(3)**, **2(4)**, and **1(6)** compounds[26–28] (Figure 1), the experimental data (Figure 4) definitely cannot be accounted for in terms of a linear $\langle\nu\rangle$ dependence of $k_{\rm rad}$, as implied for the two-state model, eq II.9. The superlinear $\langle\nu\rangle$ dependence of $k_{\rm rad}$ for all these molecules (Figures 3 and 4) is stronger than $k_{\rm rad} \propto \langle\nu\rangle^3$, which would imply that $|\mu_\nu(\nu)|^2$ is independent of ν. The experimental $k_{\rm rad}$ data can be well accounted for in terms of eq II.11, i.e., $k_{\rm rad} \propto \langle\nu\rangle^3/(\Delta E_1 - \langle\nu\rangle)^2$. The ΔE_1 values which are required for this fit (Table 1) are taken from the experimental spectroscopic data for the donor–acceptor molecules, in conjunction with symmetry considerations.[26,27] For compound **4c**, the intense $\pi\pi^*$ excitation at ΔE_1 = 43 900 cm^{-1} was chosen. Symmetry considerations (for point group C_s) imply[26,27] that for compounds **3(3)** and **28(3)** the first charge-transfer excitation mixes effectively with the intense ΔE_1 = 41 000-cm^{-1} excitation (220–240 nm region), while for compounds **1(4)** and **1(6)**, effective mixing will occur with the lower, weaker ΔE_1 = 29 400-cm^{-1} excitation (in the 320–360 nm region). For compounds **2(4)**, we had to fit the data with ΔE_1 = 41 000 cm^{-1}.

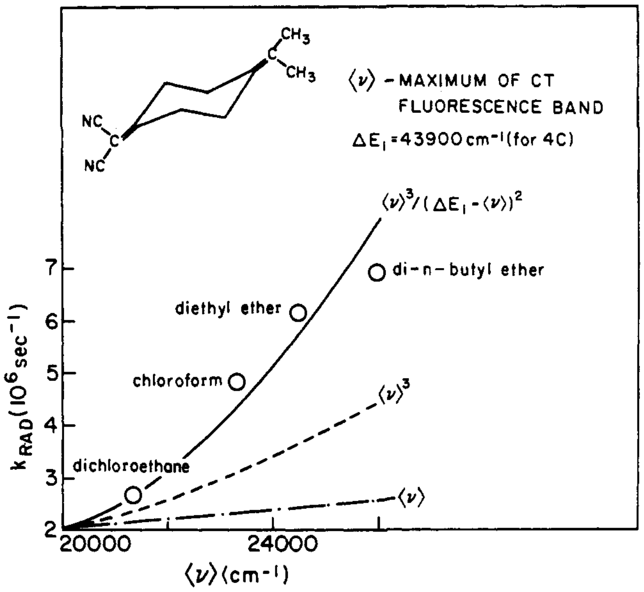

Figure 3. $\langle\nu\rangle$ dependence of $k_{\rm rad}$ for compound **4c** (structure given). Experimental data (○) in the solvents marked on the figure are taken from ref 25. The dependence of $k_{\rm rad}$ on $\langle\nu\rangle$ (–·–), on $\langle\nu\rangle^3$ (- - -), and on $\langle\nu\rangle^3/(\Delta E_1 - \langle\nu\rangle)^2$ (—) with ΔE_1 = 43 900 cm^{-1} [25] is marked.

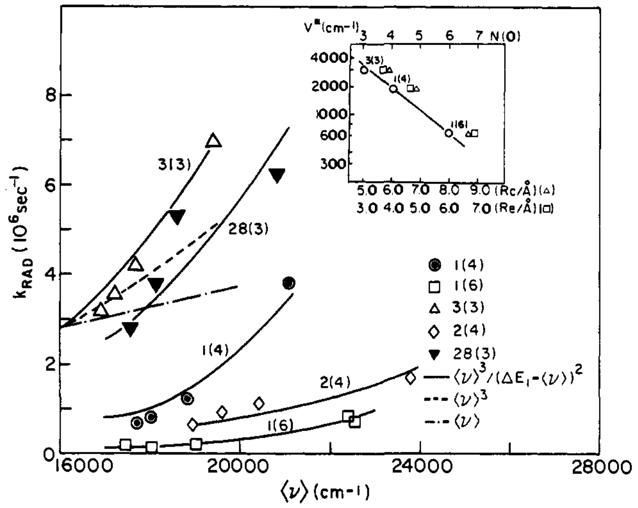

Figure 4. $\langle\nu\rangle$ dependence of $k_{\rm rad}$ for compounds **4(3)**, **28(3)**, **1(4)**, **1(6)**, and **2(4)** (Figure 1) in different solvents. The experimental data (marked on the figure) are taken from refs 26–28a. The solid curves (—) mark the dependence $k_{\rm rad} = a\langle\nu\rangle^3/(\Delta E_1 - \langle\nu\rangle)^2$ for all the compounds with the ΔE_1 data given in Table 1. For compound **3(3)** we also give the dependence of $k_{\rm rad}$ on $\langle\nu\rangle$ (–·–) and on $\langle\nu\rangle^3$ (- - -). The inset portrays the exponential dependencies of V^* on N (number of bonds), on R_c (center-to-center distance), and on R_e (edge-to-edge distance).

Table 1. Evaluation of Charge-Transfer-Localized Excitation Electronic Couplings $V^* = \langle D^+BA^- | \hat{H} | (DBA)^* \rangle$ $(DBA)^*\rangle$ from Radiative Rates k_{rad}

donor–acceptor molecule	geometrical characteristics	ΔE_l (cm^{-1})	a (cm s^{-1})[e]	f^* [f]	V^* (cm^{-1})
4c[a]		43 900	142	0.39	3100
3(3)[b]	$N = 3$ $R_e = 3.7$ Å $R_c = 5.8$ Å	41 000	427	1.23	2990
28(3)[c]	$N = 3$ $R_c = 6.8$ Å	(41 000)[d]	305	(1.2)[d]	(2550)
1(4)[b]	$N = 4$ $R_e = 4.6$ Å $R_c = 6.8$ Å	29 400	25	0.16	1830
1(6)[b]	$N = 6$ $R_e = 6.8$ Å $R_c = 8.7$ Å	29 400	3.2	0.16	660
2(4)[b]	$N = 4$ $R_c = 4.6$ Å $R_c = 6.1$ Å	41 000	40	0.66	1200

[a] Reference 25. [b] References 26 and 27. [c] Reference 28a. [d] ΔE_l and f^* data were taken as equal to those for molecule **3(3)**. [e] Fit of experimental k_{rad} (Figures 2 and 3) with eq III.1. [f] Evaluated from the spectroscopic data of refs 25–28a using eq III.3.

The good account accomplished for the solvent dependence of k_{rad} in terms of (II.11) is inconsistent with the two-state model, eq II.9, and provides strong evidence for the dominance of mixing of charge-transfer and localized excitations. Our conclusion regarding the dominant mixing of charge-transfer and localized excitations in determining k_{rad} (and the oscillator strength) of the charge-transfer transition for the DBA molecules considered herein requires further elaboration. From the analysis of the available experimental data (Appendix B), we conclude that for these DBA molecules one can set an upper limit $V/V^* < 0.1$ for the relative magnitude of the D^+BA^-–DBA coupling.

To evaluate V^*, we shall rewrite eq II.11 in the form

$$k_{rad} = a\langle\nu\rangle^3/(\Delta E_l - \langle\nu\rangle)^2 \qquad \text{(III.1)}$$

where

$$a = \bar{a}n^3 \qquad \text{(III.2a)}$$

and

$$\bar{a} = \frac{32\pi^3}{3\hbar}(V^*\mu^*)^2 \qquad \text{(III.2b)}$$

$\bar{a}$ is a compound-specific parameter. We note in passing that the (solvent-dependent) refractive index was incorporated in eq III.2a; however, as for all the solvents used herein, the refractive indices vary only in the range of 5%, leading to a 10% overall change, and we shall take an average value $n = 1.38$. (In any case, we could have plotted k_{rad}/n^3, but in view of uncertainties in the effects of n on μ, we have refrained from doing so.)

We still require information for the transition moment μ^*, which is obtained from the oscillator strength f^*, for the localized excitation[30]

$$f^* = \frac{4\pi mc}{3\hbar e^2}\langle\nu_A^*\rangle|\mu^*|^2 = 4.70 \times 10^{-7}(\langle\nu_A^*\rangle/\text{cm}^{-1})|\mu^*/\text{D}|^2 \qquad \text{(III.3)}$$

where $\langle\nu_A^*\rangle$ is the peak absorption energy (in cm^{-1}) of the localized excitation (Table 1). f^* is obtained from the lazy man's estimate:[30]

$$f^* \simeq 4.32 \times 10^{-9}\, \epsilon^*_{max}\, \Delta\nu^*_{1/2} \qquad \text{(III.4)}$$

where ϵ^*_{max} and $\Delta\nu^*_{1/2}$ are the peak absorption coefficient and line width (fwhm) of the localized excitation (Table 1).

Table 2. Evaluation of the Excited-State Charge-Transfer Electronic Couplings V^* from the Oscillator Strengths for Charge-Transfer Absorption in Cyclohexane[a,b]

compd	$\langle\nu_A\rangle$ (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	f	f^*	$\langle\nu_A^*\rangle$ (cm^{-1})	V^* (cm^{-1})
1(4)[a]	31 250	800	0.019	0.16	34 000	1080
3(3)[b]	30 000	1100	0.026	1.2	41 000	1890
28(3)[b]	28 990	750	0.018[c]	(1.2)[d]	(41 000)	(1750)

[a] References 26 and 27. [b] Reference 28a. [c] $f = 4.32 \times 10^{-9}(\epsilon_{max}/\text{M}^{-1}\,\text{cm}^{-1})(\Delta\nu_{1/2}/\text{cm}^{-1})$, with the estimate $\Delta\nu_{1/2} = 5500$ cm^{-1}. [d] The parameters for molecule **28(3)** were taken as equal to those for molecule **3(3)**.

The excited-state electronic coupling V is obtained from eqs III.2–III.4 in the final form

$$V^* = [(mc/8\pi^2e^2)(a\langle\nu_A^*\rangle/f^*n^3)]^{1/2} \qquad \text{(III.5)}$$

In Table 1 we summarize the V^* parameters obtained from this analysis. The following features emerge.

(1) The excited-state electronic coupling $V^* = 0.38$ eV for compound **4c**, emerging from the analysis of k_{rad} data, is in a very good agreement with the value $V^* = 0.37$ eV originally obtained by Pasman et al.[25] from the analysis of the oscillator strength of the intense charge-transfer absorption band of compound **4c**.

(2) The oscillator strengths f for the charge-transfer absorption bands at the peak energy $\langle\nu_A\rangle$, absorption band line width $\Delta\nu_{1/2}$, and peak absorption coefficient ϵ_{max} (with $f = 4.32 \times 10^{-9}\epsilon_{max}\Delta\nu_{1/2}$), which are available for compounds **1(4)**, **3(3)**,[26,27] and **28(3)**,[28a] can be utilized for an independent estimate of V^* using the relation

$$f/f^* = (\langle\nu_A\rangle/\langle\nu_A^*\rangle)|V^*|^2/(\langle\nu_A^*\rangle - \langle\nu_A\rangle)^2$$

The V^* data emerging from this independent analysis (Table 2) are in reasonable agreement (within 40%) with the excited-state electronic couplings obtained from k_{rad} (Table 1). The agreement between V^* obtained from k_{rad} and f^* data provides further support for the dominance of the mixing of the local excitation in determining the spectroscopic observables for radiative ET.

(3) The V^* couplings provide spectroscopic rulers for the distance dependence of nonradiative ET from the relevant localized states. We note (insert in Figure 4) that the V^* parameters obey the exponential relations $V^* \propto \exp(-\alpha N) \propto \exp(-\beta R_e)$, and $\propto \exp(-\gamma R_c)$ (where N is the number of bonds and R_e and R_c are the edge-to-edge (e) and center-to-center (c) distances), as expected.

Although the radiative decay characteristics of the charge-transfer state are dominated by the mixing of the neutral $(DBA)^*$ excitation, the extent of this mixing is rather small. Making use of eq II.12, together with the V^* and ΔE_l data (Table 1), the estimates of the D^+BA^-–DBA mixing are straightforward. The largest fractions g^* of the neutral excitation in the charge-transfer state for a given molecule (which is characterized by the smallest value of $(\Delta E_l - \langle\nu\rangle)$) will arise for the nonpolar hydrocarbon solvents. For n-hexane as solvent, we estimate $g^* = 0.02$ for **3(3)**, $g^* = 0.02$ for **28(3)**, $g^* = 0.05$ for **1(4)**, $g^* = 0.01$ for **1(6)**, and $g^* = 0.005$ for **2(4)**. These values represent the upper limit of g^* for each solvated molecule. Accordingly, the $(DBA)^*$–D^+BA^- mixing is rather weak, and the lowest (spin-allowed) excited electron charge-transfer state is of a predominantly D^+BA^- character. However, this small $(DBA)^*$–D^+BA^- mixing dominates the lifetime for radiative charge recombination in these DBA molecules. We also note in passing that the small values of g^* justify the utilization of our perturbative treatment (section II).

IV. Concluding Remarks

(A) The radiative decay rates exhibit a marked solvent dependence. This is surprising, as the conventional two-state model would imply the weak solvent dependence $k_{rad} \propto \langle \nu \rangle$.[21,26-28] The solvent dependence of k_{rad} for the donor–acceptor molecules studied herein is inconsistent with the traditional description of D^+BA^-–DBA coupling and is quantitatively accounted for in terms of the dominant mixing of neutral excitations.

(B) The solvent dependence of the radiative rates, manifested by eq III.1, corresponds to an algebraic function of the adiabatic energy gap ΔE, which is related to $\langle \nu \rangle$ by[5,13,21-23,34] $\Delta E = (\langle \nu \rangle + \lambda_s + \lambda)$, where λ_s is the solvent reorganization energy and λ is the intramolecular reorganization energy.

(C) Both the radiative decay rate studied herein and the nonradiative ET rate from the D^+BA^- charge-transfer state exhibit solvent dependence, which can be quantified in terms of the $\langle \nu \rangle$ dependence of the rates for a certain DBA molecule in a series of solvents. The radiative rate is of the form $k_{rad} \propto \langle \nu \rangle^3/(\Delta E_1 - \langle \nu \rangle)^2$. On the other hand, the nonradiative decay rate exhibits the exponential energy gap law,[12,46-49] which for the isolated molecule is[48,49] $k_{ET} \propto \exp(-\gamma \Delta E)$, while for the solvated molecule,[46,47,49] $k_{ET} \propto \exp[-\gamma(\Delta E - \lambda_S)]$, where λ_s is the solvent reorganization energy. This result for the solvated molecule can be recast in the form[49] $k_{ET} \propto \exp(-\gamma \langle \nu \rangle)$. Accordingly, with increasing $\langle \nu \rangle$ (i.e., for nonpolar solvents), we expect k_{rad} to increase (as an algebraic function (III.1)) and k_{ET} to decrease (exponentially).

(D) The donor–acceptor molecules studied herein are characterized by a relatively not-too-large distance of donor–acceptor separation (R_c = 5.8–8.7 Å, see Table 1). From a cursory examination of the validity condition for the dominance of the mixing of a neutral excitation, eq II.10, it appears that such a situation will be realized for not-too-large values of eR_c/μ^*, while for larger R_c values, the contribution of V to the transition, eq II.9, will be manifested. The dominance of the mixing of neutral excitations demonstrated for the DBA molecules studied herein is not universal, being (DBA or DA) system and solvent dependent. A recent analysis by Gould et al.[50] of the radiative lifetimes of DA complexes in a series of solvents reveals a joint contribution of D^+A^-–DA and D^+A^-–DA* mixing, with an enhanced mixing of DA* excitations for weaker complexes.

(E) The radiative ET in isolated solvent-free molecules is of interest. The fluorescence spectra of the molecules **3(3)**[26,27] and **28(3)**[28] were recorded in the gas phase. The large values of $\langle \nu \rangle$ (21 270 cm^{-1} for **3(3)** and 23 260 cm^{-1} for **28(3)**) in the gas phase imply that for the isolated molecules, the large radiative rates ($k_{rad} \simeq 1.1 \times 10^7$ s^{-1} for **3(3)** and $k_{rad} = 1.2 \times 10^7$ s^{-1} for **28(3)** as extrapolated from the data of Figure 3 with eq III.1) manifest the maximization of the charge-transfer-localized excitation mixing in the isolated donor–acceptor molecules. In these solvent-free DBA molecules, the fraction of the mixing of the localized excitation into the charge-transfer state, eq II.12, is still low, being $g^* \simeq 0.023$ for **3(3)** and $g^* = 0.017$ for **28(3)**. This small (DA)*–D^+A^- mixing goes a long way in determining the lifetime and oscillator strength of the charge-transfer excitations in these molecules.

From the point of view of general methodology, we have adopted the traditional approach in molecular physics,[44,45] considering the mixing of a single localized excitation within the D^+BA^- state. There are two aspects of the (DBA)*–D^+BA^- coupling which facilitate (but thus definitely do not prove) the significant contribution from the single localized state, i.e., the contribution of the energy denominator and the symmetry consideration. Indeed, for the exclusive single localized excitation (DBA)* considered by us, the relevant energetics (ΔE_1) and transition moment (μ^*) are in accord with the spectroscopic data. There are some uniform features of the traditional two-state model (D^+BA^-–DBA mixing) which are modified in the three-state model (which incorporates important (DBA)*–D^+BA^- mixing). The sum rule for the total oscillator strength implies a uniform reduction of all the intensities of the localized excitations for the two-state model. For the three-state model, there will be a selective reduction of the intensity of the localized transition(s), which effectively mix in the charge-transfer state.

Appendix A. Radiative Lifetimes from a Thermally Equilibrated Manifold

We consider the radiative decay from the vibronic charge-transfer manifold $\{|CT,v_{CT}>\}$, (eq II.3a), with energies ϵ_{CT} (above the origin) to the final manifold $\{|G,v_G\}$, eq (II.3b), with energies ϵ_G. The radiative rate for the emission of a photon at energy ν from the thermally equilibrated vibronic charge-transfer manifold is

$$k_{rad}(\nu) = \frac{32\pi^3 n^3 \nu^3}{3\hbar Z} \sum_G \sum_{CT} \exp(-\epsilon_{CT}/k_B T) |<G,v_G|\hat{\mu}|CT,v_{CT}>|^2 \delta(\Delta E + \epsilon_{CT} - \epsilon_G - \nu) \quad (A.1)$$

where $Z = \sum_{CT} \exp(-\epsilon_{CT}/k_B T)$ is the partition function, and the sums are taken over the vibronic states in the two vibronic manifolds. From eqs A.1 and II.2, we define the vibronic transition moment density per unit energy in the form

$$|\mu_v(\nu)|^2 = \frac{1}{Z} \sum_G \sum_{CT} \exp(-\epsilon_{CT}/k_B T) |<G,v_G|\hat{\mu}|CT,v_{CT}>|^2 \delta(\Delta E - \epsilon_{CT} - \epsilon_G - \nu) \quad (A.2)$$

Identifying the parentage of the mixed states, setting $|v_{CT}> \simeq |\bar{\beta}>$ with $\epsilon_{CT} \simeq \epsilon_{\bar{\beta}}$ and $|v_G> \simeq |\bar{\alpha}>$ with $\epsilon_G \simeq \epsilon_{\bar{\alpha}}$, we get from eqs A.2 and II.5a

$$|\mu_v(\nu)|^2 = [|V\Delta\mu|^2/\nu^2 + 2V^* V(\Delta\mu\mu)/\nu(\Delta E_1 - \nu) + (V^*\mu^*)^2/(\Delta E_1 - \nu)^2] \sum_{\bar{\alpha}} \sum_{\bar{\beta}} \frac{1}{Z} \exp(-\epsilon_{\bar{\beta}}/k_B T) |<\bar{\alpha}|\bar{\beta}>|^2 \delta(\Delta E + \epsilon_{\bar{\beta}} - \epsilon_{\bar{\alpha}} - \nu) \quad (A.3)$$

where $Z = \sum_{\bar{\beta}} \exp(-\epsilon_{\bar{\beta}}/k_B T)$. Equation A.3 results in eqs II.6 and II.7.

Appendix B. Estimates of an Upper Limit for V/V^*

It is instructive to estimate an upper limit for the relative contribution of the D^+A^-–DA two-level mixing. For a DBA molecule characterized by perpendicular directions of $\Delta\vec{\mu}$ and $\vec{\mu}^*$, eq II.8 gives

$$\frac{k_{rad}}{b\langle \nu \rangle} = (V\Delta\mu)^2 + (V^*\mu^*)^2 X^2 \quad (B1)$$

where $b = 32\pi 3n^3/3\hbar$ (with a weakly varying n) and $X = \langle \nu \rangle/(\Delta E_1 - \langle \nu \rangle)$. For parallel directions of $\Delta\vec{\mu}$ and $\nu = \vec{\mu}^*$, eq II.8 gives

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$$\frac{k_{\mathrm{rad}}}{b\langle\nu\rangle} = (V\Delta\mu)^2 + 2V^*V\Delta\mu\mu^*X + (V^*\mu^*)^2X^2 \quad \text{(B2)}$$

which for $(V^*\mu^*)/V\Delta\mu \gg 1$ and $X \sim 1$ is

$$\frac{k_{\mathrm{rad}}}{b\langle\nu\rangle X} \simeq 2V^*V\Delta\mu\mu^* + (V^*\mu^*)^2X \quad \text{(B3)}$$

In view of the limited experimental information (i.e., four data points for each system) and incomplete spectroscopic information regarding the polarization of the (DBA)* excitation, we utilized both eqs B1 and B3 to estimate the residual contribution to $k_{\mathrm{rad}}/\langle\nu\rangle$ and to $k_{\mathrm{rad}}/\langle\nu\rangle X$ in the limit $X \rightarrow 0$. This residual contribution is given by $\rho = I/S$, where I and S are the intercept and the slope, respectively, of the plots of $k_{\mathrm{rad}}/\langle\nu\rangle$ vs X or of $k_{\mathrm{rad}}/\langle\nu\rangle X$ vs X. For (B1) we get $\rho = (V\Delta\mu/V^*\mu^*)^2$, while for (B3) we obtain $\rho = 2V\Delta\mu/V^*\mu^*$. Rough estimates for the **4c**, **3(3)**, and **4(1)** molecules yield $\rho = 0 \pm 0.10$ for both cases. We thus evaluate an upper limit $\rho < 0.1$. Relation B1 then gives $V/V^* < \rho^{1/2}(\mu^*/\Delta\mu)$, while relation B3 yields $V/V^* < \rho(\mu^*/\Delta\mu)$. We use typical values of $(\mu^*/\Delta\mu) = 0.15$–0.30 (where $\Delta\mu$ is inferred from the geometry and μ^* is estimated from the oscillator strength of the localized excitation) to evaluate V/V^*. We thus obtain $V/V^* < 0.03$ for $\vec{\mu}^* \| \Delta\vec{\mu}$ and $V/V^* < 0.1$ for $\vec{\mu}^* \perp \Delta\vec{\mu}$ in these DBA molecules. Thus $V/V^* < 0.1$ constitutes the upper limit for the relative value of the ground-state electronic coupling.