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 (\nu) 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 (\nu) dependence of k_{rad} for a certain DBA in a series of solvents results in the (DBA)^*—D^*BA^- couplings \nu^*, which are in good agreement with the \nu^* parameters extracted from oscillator strengths for charge-transfer absorption. The \nu^* parameters, which obey the relation \nu^* = \exp(-aN) (where N is the number of bonds in the bridge), determine the rates for nonradiative (DBA)^* — 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 \sim 0.02, being even smaller for the solvated molecules.

DA \rightarrow \text{D}^\ast A^- \\

DA \rightarrow \text{D}^\ast \text{BA}^- 

for a donor (D)—acceptor (A) complex\textsuperscript{21,28—33} and

\textbf{I. Prologue}

The nonradiative, nonadiabatic multiphonon electron-transfer (ET) theory in its classical\textsuperscript{1,2} and quantum mechanical\textsuperscript{3} versions is widely utilized for the unified description of a wide class of nonadiabatic ET processes in chemistry, physics, and biology.\textsuperscript{6—8} The quantification of ET rates, k = (2\pi/\hbar)^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 phases\textsuperscript{9—11} and in large molecules,\textsuperscript{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\textsuperscript{12,13} for ET processes in solutions, where the optical processes...
spectroscopic probes for the determination of the nuclear and electronic parameters, which determine the nonradiative ET rates for charge recombination D\(^+\)A\(-\) DA and D\(^+\)BA\(-\) 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\(^{5,13,21,24-28}\) 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 \(\kappa_{\text{rad}}\) (i.e., \(\kappa_{\text{rad}} = k_i Y\), where \(Y\) is the fluorescence quantum yield and \(k_i\) 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\(^{26-29}\) 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\(-\)). Murrell\(^{31}\) 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\(^*\)). Murrell\(^{31}\) and Mulliken and Parsons\(^{30}\) 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\(^ {25,26}\) to account for the (large) intensities of the first charge-transfer bands 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 = norbornyllogous bridges. Pasman\(^ {24}\) noted a small increase of the radiative rates with decreasing solvent polarity, which was attributed 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...
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where \( n \) is the refractive index of the medium (\( n_3 \) corrects the density of states of the radiation field in the medium), and \( C(Y(Y) \) is the vibronic transition moment for the photon energy \( Y \), with \( I_c(Y(Y) \) 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\(^{3,12} \) 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\(^{4,5} \) or crystal field mixing in molecular solids\(^{6,7} \)), where the mixing of a single localized excitation is considered. The mixed vibronic levels, \( | G, \nu_0 \rangle \), of the ground electronic state \( G \) with a vibrational state \( | \nu_0 \rangle \), and \( | C_T, \nu_C \rangle \) of the charge-transfer electronic state \( C_T \) with the vibrational state \( | \nu_C \rangle \), are

\[
| G, \nu_0 \rangle = | D_BA, \bar{\nu} \rangle + \sum_{\beta} \frac{V}{\Delta E - \epsilon_\alpha + \epsilon_\beta} | \beta (\bar{\alpha}) \rangle | D^*BA \rangle 
\]

\[
| C_T, \nu_C \rangle = \frac{V}{\Delta E - \epsilon_\gamma + \epsilon_\gamma} | (\gamma (\bar{\gamma})) \rangle | (D^*BA) \rangle 
\]

The vibronic transition moment for the photon energy \( \nu \) is

\[
\langle G, \nu_0 | \mu | C_T, \nu_C \rangle = \langle D_BA | \mu | D^*BA \rangle + \langle D_BA | \mu | D^*BA \rangle + \sum_{\gamma} \langle (\gamma (\bar{\gamma})) \rangle | D^*BA \rangle 
\]

\[
\psi = \Delta E + \epsilon_\beta - \epsilon_\alpha 
\]

Following the analysis of Appendix A, we obtain

\[
| G, \nu_0 \rangle = | D_BA, \bar{\nu} \rangle + \sum_{\beta} \frac{V}{\Delta E - \epsilon_\alpha + \epsilon_\beta} | \beta (\bar{\alpha}) \rangle | D^*BA \rangle 
\]

\[
| C_T, \nu_C \rangle = \frac{V}{\Delta E - \epsilon_\gamma + \epsilon_\gamma} | (\gamma (\bar{\gamma})) \rangle | (D^*BA) \rangle 
\]

The vibronic transition moment for the photon energy \( \nu \) is

\[
\langle G, \nu_0 | \mu | C_T, \nu_C \rangle = \left[ \frac{V}{\nu} \Delta \mu + \frac{V^*}{\Delta E_1 - \nu} \mu^* \right] | (\gamma (\bar{\gamma})) \rangle 
\]

\[
F(\nu) = Z^{-1} \sum_{\beta} \sum_{\beta} \exp(-\epsilon_\beta/k_B T) | \beta (\bar{\alpha}) \rangle | (\Delta E + \epsilon_\beta - \epsilon_\alpha - \nu) 
\]
the radiative lifetimes of excited D-A exciplexes.21 The validity of this treatment has to be extended, with the required theoretical scheme being reminiscent of the treatment of the pseudo-Jahn-Teller effect. This problem may be of interest for the exploration of the near-degeneracy between the low-lying vibronic levels of D+BA- (within the thermal energy range $k_B T$ 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 considered herein.

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

The experimental data25-28 for $k_{rad}$ vs $\nu$ (Figures 3 and 4) reveal a marked solvent dependence of $k_{rad}$ which is considerably higher in nonpolar hydrocarbons than in polar solvents. For the 4c compound25 (Figure 3), as well as for the 3(3), 1(4), 1(6), 2(4), and 1(6) compounds26-28 (Figure 1), the experimental data (Figure 4) definitely cannot be accounted for in terms of a linear $\nu$ dependence of $k_{rad}$, as implied for the two-state model, eq 11.11.

![Figure 3](image-url) **Figure 3.** $\nu$ dependence of $k_{rad}$ for compound 4c (structure given). Experimental data (O) in the solvents marked on the figure are taken from ref 25. The dependence of $k_{rad}$ on $\nu$ (---), on $\nu^2$ (- - -), and on $\nu^3/\Delta E_1$ (---) is stronger than $\nu$ (---). The inset portrays the exponential dependence of $V^m$ on $N$ (number of bonds), on $R_0$ (center-to-center distance), and on $R_n$ (edge-to-edge distance).

![Figure 4](image-url) **Figure 4.** $\nu$ dependence of $k_{rad}$ for compounds 3(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 of $k_{rad}$ on $\nu$ (---), on $\nu^2$ (- - -), and on $\nu^3/\Delta E_1$ (---). The inset portrays the exponential dependence of $V^m$ on $N$ (number of bonds), on $R_0$ (center-to-center distance), and on $R_n$ (edge-to-edge distance).
Table 1. Evaluation of Charge-Transfer-Localized Excitation Electronic Couplings \( V = (D^*BA)^*f[(DBA)^*]^{-1}(DBA)^* \) from Radiative Rates \( k_{rad} \)

<table>
<thead>
<tr>
<th>donor-acceptor molecule</th>
<th>geometrical characteristics</th>
<th>( \Delta E_1 ) (cm(^{-1}))</th>
<th>( \alpha ) (cm(^{-1}))</th>
<th>( f^* ) (cm(^{-1}))</th>
<th>( V^* ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3(3)b</td>
<td>( N = 3 )</td>
<td>43 900</td>
<td>142</td>
<td>0.39</td>
<td>3100</td>
</tr>
<tr>
<td>28(3)c</td>
<td>( N = 3 )</td>
<td>(41 000)(^c)</td>
<td>305</td>
<td>(1.2)(^d)</td>
<td>(2550)</td>
</tr>
<tr>
<td>1(4)b</td>
<td>( N = 4 )</td>
<td>29 400</td>
<td>25</td>
<td>0.16</td>
<td>1830</td>
</tr>
<tr>
<td>1(6)b</td>
<td>( N = 6 )</td>
<td>29 400</td>
<td>3.2</td>
<td>0.16</td>
<td>660</td>
</tr>
<tr>
<td>2(4)b</td>
<td>( N = 4 )</td>
<td>41 000</td>
<td>40</td>
<td>0.66</td>
<td>1200</td>
</tr>
</tbody>
</table>

\( ^a \) Reference 25. \( ^b \) Reference 26 and 27. \( ^c \) Reference 28a. \( ^d \) \( \Delta E_1 \) and \( f^* \) data were taken as equal to those for molecule 3(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

\[
k_{rad} = \alpha (\nu)^2 / (\Delta E_1 - \nu)^2 \quad (III.1)
\]

where

\[
\alpha = \bar{a} \tilde{n}^3 \quad (III.2a)
\]

and

\[
\bar{a} = \frac{32 \pi^3}{3h} \left( \frac{V^* \mu^*}{2} \right)^2 \quad (III.2b)
\]

\( \bar{a} \) 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 \( \bar{n} = 1.38 \). (In any case, we could have plotted \( k_{rad}/\bar{n}^2 \), but in view of uncertainties in the effects of \( n \) on \( \mu \), we have refrained from doing so.)

We still require information for the transition moment \( \mu^* \), which is obtained from the oscillator strength \( f^* \), for the localized excitation\(^20\)

\[
f^* = \frac{4mc}{3h \varepsilon_0^2} (\nu_A^*)^2 / (\nu_A^*)^2 = 4.70 \times 10^{-7} \left( \frac{\nu_A^*}{\text{cm}^{-1}} \right) \mu^* / D^2 \quad (III.3)
\]

where \( (\nu_A^*)^2 \) is the peak absorption energy (in cm\(^{-1}\)) of the localized excitation (Table 1). \( f^* \) is obtained from the lazy man’s estimate\(^30\)

\[
f^* \approx 4.32 \times 10^{-9} \varepsilon_{max} \Delta \nu_{1/2} \quad (III.4)
\]

Table 2. Evaluation of the Excited-State Charge-Transfer Electronic Couplings \( V \) from the Oscillator Strengths for Charge-Transfer Absorption in Cyclohexane

<table>
<thead>
<tr>
<th>compd</th>
<th>( \nu_A ) (cm(^{-1}))</th>
<th>( \varepsilon_{max} ) (M(^{-1}) cm(^{-1}))</th>
<th>( f )</th>
<th>( f^* ) (cm(^{-1}))</th>
<th>( V ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(4)a</td>
<td>31 250</td>
<td>800</td>
<td>0.19</td>
<td>0.16</td>
<td>34 000</td>
</tr>
<tr>
<td>3(3)b</td>
<td>30 000</td>
<td>1100</td>
<td>0.026</td>
<td>1.2</td>
<td>41 000</td>
</tr>
<tr>
<td>28(3)b</td>
<td>28 990</td>
<td>750</td>
<td>0.018</td>
<td>(1.2)d</td>
<td>(41 000)</td>
</tr>
</tbody>
</table>

\( ^a \) References 26 and 27. \( ^b \) Reference 28a. \( \varepsilon_{max} = 4.32 \times 10^{-9} \left( \frac{\varepsilon_{max}}{\text{M}^{-1} \text{cm}^{-1}} \right)^2 (\Delta \nu_{1/2}/\text{cm}^{-1}) \), with the estimate \( \Delta \nu_{1/2} = 5500 \text{ cm}^{-1} \). The parameters for molecule 28(3) were taken as equal to those for molecule 3(3).

where \( \varepsilon_{max} \) and \( \Delta \nu_{1/2} \) are the peak absorption coefficient and line width (fwhm) of the localized excitation (Table 1).

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

\[
V = \left( \frac{mc}{8 \pi^2 \varepsilon_0^2} \left( \frac{\nu_A^*}{\text{cm}^{-1}} \right) \mu^* \right)^{1/2} \quad (III.5)
\]

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 4e, emerging from the analysis of \( k_{rad} \) data, is in 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 \( \nu_A \), absorption band line width \( \Delta \nu_{1/2} \), and peak absorption coefficient \( \varepsilon_{max} \) (with \( f = 4.32 \times 10^{-9} \varepsilon_{max} \text{ M}^{-1} \text{cm}^{-1} \), 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

\[
f/f^* = \left[ (\nu_A^*)^2 \right] / (\nu_A^* - \nu_A^*) \quad (III.6)
\]

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 localized 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 \( V^* \propto \exp(-\alpha N) \propto \exp(-\gamma R_a) \) and \( \exp(-\beta R_c) \) (where \( N \) is the number of bonds and \( R_a \) 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 \( \Delta E_1 \) 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 \( \Delta E_1 - \nu_A \)) 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).
excitation into the charge-transfer state, the traditional approach in molecular physics, is typically considered in the gas phase. The large values of the radiative decay rate in the gas phase indicate that the mixing of the localized and charge-transfer states, with an enhanced mixing of the neutral excited states, is a significant factor in determining the lifetime of the excited state.

There are two aspects of the (DBA)-D+BA- coupling which are of interest. The fluorescence spectra of the molecules 3 and 28 were recorded in the gas phase. The large values of the radiative decay rate in the gas phase imply that for the isolated molecule, the radiative rate is: 

\[ k_{\text{rad}}(v) = \frac{32\pi^2\hbar^3}{3hZ} \sum_{G,C,T} \exp\left(-\frac{\epsilon_{CT}}{k_B T}\right) |G,\psi_G| \langle CT,\psi_{CT}\rangle |^2 \delta(\Delta E + \epsilon_{CT} - \epsilon_0 - v) \]  

where \( Z = \sum_{G,C,T} \exp(-\epsilon_{CT}/k_B T) \) 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 

\[ |\mu_v(v)|^2 = \frac{1}{Z} \sum_{G,C,T} \exp\left(-\frac{\epsilon_{CT}}{k_B T}\right) |G,\psi_G| \langle CT,\psi_{CT}\rangle |^2 \delta(\Delta E + \epsilon_{CT} - \epsilon_0 - v) \]  

Identifying the parentage of the mixed states, we get from eqs A.2 and II.5a 

\[ |\mu_v(v)|^2 = \frac{(|V\Delta\mu|^2 + 2V^*\Delta\mu)v(\Delta E_1 - v) + (V^*\mu*)^2}{(\Delta E_1 - v)^2} \sum_{\alpha} \frac{1}{Z} \sum_{\beta} \exp(-\epsilon_\beta/k_B T) |\alpha\beta| |^2 \delta(\Delta E + \epsilon_\beta - \epsilon_0 - v) \]  

where \( Z = \sum_{\beta} \exp(-\epsilon_\beta/k_B T) \) is the partition function. 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 \( \Delta\mu \) and \( \mu^* \), eq II.8 gives 

\[ k_{\text{rad}}(v) = \frac{V(\Delta\mu)^2 + (V^*\mu^*)^2}{b(v)} \]  

where \( b = 32\pi^2n^2/3\hbar \) (with a weakly varying \( n \) and \( \chi = \langle v \rangle / (\Delta E_1 - \langle v \rangle) \)). For parallel directions of \( \Delta\mu \) and \( v = \mu^* \), eq II.8 gives 

\[ k_{\text{rad}}(v) = \frac{V(\Delta\mu)^2 + (V^*\mu^*)^2}{b(v)} \]  

where \( b = 32\pi^2n^2/3\hbar \) (with a weakly varying \( n \) and \( \chi = \langle v \rangle / (\Delta E_1 - \langle v \rangle) \)). For parallel directions of \( \Delta\mu \) and \( v = \mu^* \), eq II.8 gives 

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\[ k_{\text{rad}}(v) = \frac{V(\Delta\mu)^2 + (V^*\mu^*)^2}{b(v)} \]
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\[
\frac{k_{\text{red}}}{b(\nu)} = (V^2 \Delta \mu)^2 + 2V^* V \Delta \mu^* X + (V^* \mu^*)^2 X^2 \tag{B2}
\]

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

\[
\frac{k_{\text{red}}}{b(\nu) X} \simeq 2V^* V \Delta \mu^* + (V^* \mu^*)^2 X \tag{B3}
\]

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 \(k_{\text{red}}/\langle \nu \rangle\) and to \(k_{\text{rad}}/\langle \nu \rangle\) \(X\) in the limit \(X \to 0\). This residual contribution is given by \(\rho = I/S\), where \(I\) and \(S\) are the intercept and the slope, respectively, of the plots of \(k_{\text{rad}}/\langle \nu \rangle\) vs \(X\) or of \(k_{\text{red}}/\langle \nu \rangle X\) 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 \(\rho^{1/2} (\mu^*/\Delta \mu) = 0.15-0.30\) (where \(\Delta \mu\) is inferred from the geometry and \(\mu^*\) is estimated from the oscillator strength of the localized excitation) to evaluate \(V/V^*\). We thus obtain \(V/V^* < 0.03\) for \(\mu^*/\Delta \mu\) and \(V/V^* < 0.1\) for \(\mu^* \perp \Delta \mu\) in these DBA molecules. Thus \(V/V^* < 0.1\) constitutes the upper limit for the relative value of the ground-state electronic coupling.