Band-Shape Analysis of the Charge-Transfer Fluorescence in Barrelene-Based Electron Donor-Acceptor Compounds

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In this paper we analyze the band shapes of the stationary fluorescence spectra for the radiative charge transfer recombination $D^+-A^- \rightarrow D-A + h\nu$ in a series of barrelene-based organic bridged donor (D)-acceptor (A) molecules D-A, exploring solvent polarity and temperature effects on the band shape. Free energy changes for charge recombination, medium reorganization energies, and intramolecular reorganization energies (for high- and medium-frequency vibrational modes) were evaluated from the band maximum energies and the full widths at half-maximum and from the fits of standard Franck-Condon factors to the entire fluorescence band shape. Utilization of a single high-frequency intramolecular model ($\hbar\omega_i = 1300 \text{ cm}^{-1}$) in conjunction with solvent modes provided a satisfactory fit of the band shape; however, such an analysis results in unphysically large medium reorganization energies for nonpolar solvents (0.30-0.45 eV) and their large temperature dependence. The inclusion of medium-frequency ($\hbar\omega \simeq 500 \text{ cm}^{-1}$) intramolecular modes in the band-shape analysis is important for the proper distinction between solvent and intramolecular reorganization.

1. Introduction

Organic and organometallic donor-acceptor compounds which exhibit direct charge-transfer (CT) emission or absorption have attracted enormous attention in recent years. Part of the interest stems from the application of such systems as molecular probes for static^{1,2} and dynamic solvent properties,³ part from their potential as test cases for photoinduced electron-transfer (ET) processes⁴⁻¹² which promise to allow a fairly detailed determination of the relevant solvent and intramolecular parameters. A particular challenge in ET studies has always been the independent determination of the quantities relevant for the reaction,¹³ e.g., the (free) energy change ΔG , the solvent and intramolecular reorganization energies λ_s and λ_i , respectively, intramolecular mode-specific reorganization energies, the frequencies of the vibronic states coupled to the ET, etc. Since the pioneering work of Marcus¹⁴ the solvent dependencies of the free energy change and of the solvent reorganization energy were treated by dielectric continuum theory and some of its extensions, e.g., the mean spherical approximation.^{15,16} Approximate calculations of the solvent parameters together with estimates of the intramolecular parameters at different levels of sophistication can be utilized for the calculation of ET rates, which can be confronted with experimental kinetic data.7-12,16,17

An alternative approach for the independent estimation of medium and intramolecular parameters, which govern ET, rests on the close analogy between radiative and radiationless processes in condensed media¹⁸ and in large molecules,¹⁹ with the nonradiative process corresponding to a radiative emission process in the limit of zero optical frequency. In particular, optical CT absorption and emission spectra between S₀(DA) and S₁(D⁺A⁻) contain essentially the same information as the bell-shaped (distorted parabola) free energy relation for the nonradiative ET rates.²⁰ Several workers have explored⁴⁻¹² the radiative CT band shapes to extract information on the energetic and nuclear parameters which determine the Franck–Condon factor for the nonradiative ET.



Figure 1. Structures of the barrelene-based donor-acceptor compounds 1-6.

In this paper we present an analysis of the band shapes for the CT emission spectra of a series of bridged organic donor-acceptor molecules in different nonpolar and polar solvents with an attempt to derive the nuclear medium and intramolecular parameters relevant for the characterization of nonradiative and optical ET. The donor acceptor molecules 1-6 in Figure 1 used in this study can be derived from dibenzobarrelene. Formal substitution of the two hydrogen atoms at the ethylene bridge by dicarboxy ester residues introduces an electron-acceptor compounds have been investigated before. CT absorption has been described in dibenzobarrelenes containing p-benzoquinones²¹ or tetracyano-quinodimethane^{21c,d} as the electron-accepting group. We shall explore the bandshapes of the CT emission of compounds 1-6 which are amenable to a theoretical analysis for the following

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reasons: (1) Charge separation and recombination can be observed for a broad range of nonpolar and polar solvents; (2) the charge recombination spectra in both polar and nonpolar solutions constitute the lowest energy fluorescence which does not overlap with fluorescence from the individual donor or acceptor constituents; (3) the molecules are simple enough to make them amenable to detailed MQ calculations.²² A comprehensive comparison between the electronic structure calculations within the INDO/S-CI model and the absorption and fluorescence spectra for three of the donor-acceptor compounds utilized in the present study has already been undertaken.^{22a}

The physical information emerging from the optical CT emission band shape pertains to the (free) energy changes, medium reorganization energies of nonpolar and polar solvents, and modespecific intramolecular reorganization energies as well as the temperature dependence of these parameters.

2. Experimental Procedures

a. Synthesis of the Compounds. The donor-acceptor molecules were synthesized²³ by refluxing anthracene, tetracene, benzanthracene, dibenzanthracene, pentacene, or naphthopyrene with an excess of acetylene-dicarboxymethyl ester in *p*-xylene solution in the dark under a nitrogen atmosphere. The progress of the reaction was checked by thin-layer chromatography. The Diels-Alder products were purified by column chromatography (silica gel/toluene), recrystallization in methanol and subsequent sublimation in vacuo (yield 30-70%).

b. Absorption and Fluorescence Spectra. Absorption and fluorescence spectra were recorded on a Varian 2300 UV-Vis-NIR spectrophotometer and a Spex Fluorolog F212E spectrofluorometer, operating in the single-photon-counting mode. For fluorescence emission spectra the excitation wavelength was 280 nm (1), 275 nm (2), 290 nm (3), 277 nm (4), 302 nm (5), and 348 nm (6) for the given donor-acceptor molecules. Emission spectra were recorded with a slit width of 1 mm resulting in a spectrometer bandwidth of 1.7 nm. Fluorescence spectra were corrected for instrumental throughput and detector sensitivity by means of a correction file supplied by the manufacturer. For these spectra Rayleigh and Raman scattered light in second order of interference was suppressed by suitable cutoff filters. A sharp drop of the sensitivity of the detector limited the spectral range to below 750 nm. The temperature was kept constant within ± 0.5 °C by means of a commercial cryostat. Sample concentrations were 10-4 M. Solvents were of spectroscopic grade and were used as supplied.

c. Photochemical Stability. The photolysis of benzobarrelenes and naphthobarrelenes has been extensively investigated²⁴ as an example of the di- π -methane rearrangement. However, with the exception of compound 5 no change of the fluorescence intensity or of the spectral features has been observed in samples of our compounds even after several hours of irradiation in the fluorescence spectrometer.

d. Band-Shape Analysis. Experimental fluorescence spectra were recorded as a function of the wavelength but were later analyzed as functions of the wavenumber. To this aim wavelengthdependent spectra were multiplied by λ^2 in order to convert counts per wavelength into counts per wavenumber. Furthermore, the proportionality of the emission intensity I(v) to v^3 in the Einstein coefficient was eliminated by further multiplication with λ^3 . Afterward, the abscissa was transformed from a wavelength to a wavenumber scale. The resulting reduced intensity L(v) = $I(\nu)/\nu^3$ as a function of the wavenumber is the relevant quantity for the band-shape analysis. The band-shape analysis was performed by means of a nonlinear least-squares fit routine based on the Marquardt algorithm. As the criterion for the quality of a fit, we take the sum χ^2 of the weighted residuals. It should be kept in mind, however, that in the fluorescence spectra reported here, the signal height does not reflect the actual count rate but includes the correction factor for detector sensitivity and instrumental throughput. This factor varies by up to 2 orders of magnitude across the experimental spectrum and leads to systematic errors significantly exceeding the scatter due to the statistics of the photons.

3. Results

3.1. Fluorescence Emission Spectra. The emission spectra for the donor-acceptor compounds 1-6 in several solvents are presented in Figure 2 together with the absorption spectra in hexane. It was already shown^{22a} that the shoulder at 290 nm in the absorption spectrum of compound 1 representing the lowest vertical excitation must be assigned to a direct CT transition. The lowest vertical excitations of the other compounds are dominated by π,π^* transitions localized on the arenes.²² Any CT absorption bands in the other systems lie above the first local excitation and are probably obscured by strong $\pi.\pi^*$ excitations of the donor chromophore in this region. Nevertheless, evidence that the relaxed CT state represents the first excited state in all the molecules in solution is provided by the observation of a broad and structureless emission band in all the systems. The assignment of this emission to charge recombination fluorescence for the compounds 1-3 was already discussed.^{22a} The arguments which support this interpretation pertain to the other compounds as well: (1) Most conspicuous is a pronounced sensitivity of the position of the maximum of this fluorescence band on the polarity of the solvent indicative of CT emission. The solvatochromic shifts between n-hexane and acetonitrile correspond to energy differences of 0.4-0.7 eV. (2) The fluorescence excitation spectra of the broad bands closely follow the UV absorption spectra, i.e., being independent of the initially excited state, with the molecules undergoing an efficient radiationless transition to the CT state. Quantum yield estimates and preliminary time-resolved fluorescence measurements indicate a characteristic time scale of 1-3 ps. (3) Further evidence for the CT character of the emission is provided by the large Stokes shifts as will be shown below.

Following Lippert,²⁵ Mataga,²⁶ and others^{1,2,27} it has become common practice to relate solvatochromic shifts of CT bands to the vertical transition energy of a point dipole in a continuum dielectric characterized by the static and optical dielectric constants ϵ and n^2 , respectively. On the assumption that the ground-state dipole moment μ_g of the donor-acceptor molecule is negligible compared to that of the excited state μ_e , the following approximate linear relationship is obtained between the position $h\nu_{max}$ of the fluorescence maximum of the CT band and the solvent polarity functions $f(\epsilon)$ and $f(n^2)$:

$$h\nu_{\max} = \text{constant} - \frac{2\mu_e^2}{a_0^3} \left(f(\epsilon) - \frac{1}{2} f(n^2) \right)$$
(1)

where f(x) = (x - 1)/(2x + 1) and a_0 is the effective spherical radius of the respective donor-acceptor molecule. The linear correlation of the experimental data according to eq 1 as is shown in Figure 3 is satisfactory. A crude estimate of the magnitude of the excited-state dipole moment in solution μ_e can be obtained from the slopes in Figure 3. The effective spherical radius a_0 is estimated from $a_0 = (3M/4\pi\rho N)^{1/3}$ with the density ρ ($\simeq 1$ g cm⁻¹) of the respective donor-acceptor compound, its molar mass M and Avogadro's number N. The respective data are collected in Table 1. The excited-state dipole moments of 12–17 D correspond to a CT distance of about 3 Å, which roughly agrees with the center-to-center distance between the acceptor and donor moieties of the molecules.

3.2. Temperature Dependence of the Band Maximum and of the Spectral Bandwidth. The effect of the temperature on the charge recombination emission spectra was investigated for the compounds 2, 3, and 6 in hexane and CH_2Cl_2 solution where the quality of the experimental spectra is best. As a representative example the spectra for compound 3 are shown in Figure 4.



Figure 2. UV absorption spectra in *n*-hexane solution and fluorescence emission spectra of the donor-acceptor compounds 1-6 at room temperature in the following solvents: (1) *n*-hexane, (2) tetrachloroethylene (C_2Cl_4), (3) tetrachloromethane (CCl_4), (4) trichloroethylene (C_2HCl_3), (5) butyl acetate (BuOAc), (6) methylene chloride (CH_2Cl_2), (7) acetonitrile (MeCN).

TABLE 1. Solvatochromic Slopes $2(\mu_e^2)/a_0^3$ (in cm⁻¹), Effective Radii a_0 (in angstroms) Estimated from Effective Molecular Volumes for a Density of $\rho = 1.0$ g cm⁻³ and Experimental Excited-State Dipole Moments in Solution μ_e (in debye)

compound	$2\mu_{e}^{2}/a_{0}^{3}$	a_0	μ_{e}
1	10 800	5.0	12
2	18 300	5.3	16
3	13 800	5.3	14
4	18 100	5.5	17
5	13 600	5.5	15
6	16 800	5.6	17

The maximum of the fluorescence intensity is blue-shifted with increasing temperature. The extent of this blue-shift is well represented by a linear temperature dependence (Figure 5a):

$$h\nu_{\rm max} = A + BT \tag{2}$$

where the temperature coefficient $B = (\partial h \nu_{max} / \partial T)$ is considerably higher in the polar solvent relative to the nonpolar one studied by us.

In addition to the temperature-dependent shift of the spectra an increase of the bandwidth (full width at half-maximum, fwhm) $\Delta \nu_{1/2}$ by about 200-400 cm⁻¹ is observed between 180 and 300 K. In view of the discussion in section 4.1 this temperature dependence of $\Delta \nu_{1/2}$ is displayed in Figure 5b in the form

$$(\Delta \nu_{1/2})^2 = C + DT$$
 (3)

However, with an estimated uncertainty of $\Delta v_{1/2}$ of ± 100 cm⁻¹ the experimental slopes D represent no more than first estimates.

TABLE 2. Intercepts A (in cm⁻¹) and Temperature Coefficients $B = \partial (b\nu_{max})/\partial T$ of the Maximum of the Fluorescence Intensity (in cm⁻¹/K), as Defined in Eq 2, Intercepts C (in cm⁻²) and Temperature Coefficients D (in cm⁻² K⁻¹) of $(\Delta \nu_{1/2})^2$ as Defined in Eq 3 for the Given Systems

	compound						
	2		3		6		
solvent	Α	В	A	В	Α	В	
hexane	22 930	1.1	20 250	1.4	18 660	3.9	
CH ₂ Cl ₂	15 090	13.3	14 470	9.7	12 030	11.3	
solvent	С	D	С	D	С	D	
hexane	2.1×10^{7}	28 600	2.3×10^{7}	14 600	2.3×10^{7}	9200	
CH_2Cl_2	2.2×10^{7}	23 900	2.4×10^{7}	15 600			

Nonetheless, the data in Figure 5b reveal a qualitative agreement with eq 3 whereby the intercept C seems to be independent of the solvent (Table 2).

4. Analysis

The intensity $I(\nu)$ of the CT emission as a function of the emission frequency ν is given by the expression²⁰

$$I(\nu) = \frac{32\pi^3}{3\hbar c^3} n^3 \nu^3 |M|^2 FC(\nu)$$
(4)

with the transition dipole moment M and the Franck-Condon factor FC(ν). In the following we shall ignore prefactors and instead focus on the shape of the emission band $L(\nu)$ which is given by the (properly normalized) reduced intensity $L(\nu) = I(\nu)/\nu^3$ (see Appendix).



Figure 3. Solvatochromic shift of the maximum of the fluorescence intensity $h\nu_{\text{max}}$ for the compounds 1-6 as a function of the solvent parameter $\Delta f = ((\epsilon - 1)/(2\epsilon + 1) - 1/2(n^2 - 1)/(2n^2 + 1))$.



Figure 4. Temperature-dependent fluorescence emission spectra (normalized reduced intensity $L(\nu) = I(\nu)/\nu^3$) of the compound 3 in (a, top) hexane between 180 and 320 K and (b, bottom) methylene chloride solution between 180 and 300 K in steps of 20 K.

4.1. Analysis of the Band Maximum and the Full Width at Half-Maximum. From a theoretical point of view, a convenient analysis of optical band shapes²⁸ is undertaken in terms of the moments M_n of the spectrum:

$$M_{n} = \frac{\int L(\nu)\nu^{n} \,\mathrm{d}\nu}{\int L(\nu) \,\mathrm{d}\nu}$$
(5)

The first two moments M_1 and M_2 are approximately given by



Figure 5. (a, top) Thermochromic shift of the band maximum $h\nu_{max}$ (taken from the reduced intensity $L(\nu) = I(\nu)/\nu^3$) and (b, bottom) temperature dependence of the squared full width at half-maximum $(\Delta\nu_{1/2})^2$ of the charge-recombination spectra of the compounds 2, 3, and 6 in hexane (---) and methylene chloride solution (--).

the frequency ν_{max} at the band maximum

$$M_1 \simeq \nu_{\rm max}$$
 (6a)

and the full width at half-maximum (fwhm) $\Delta v_{1/2}$ of the band

$$(M_2 - M_1^2) \simeq (\Delta \nu_{1/2})^2 / 8 \ln 2$$
 (6b)

For experimental reasons, though, we have been unable to measure fluorescence spectra over a range of wavelengths which is wide enough to allow the direct calculation of the moments in eq 5 with sufficient accuracy. Therefore, our first considerations will instead focus directly on ν_{max} and $\Delta \nu_{1/2}$.

Utilizing the approximate relations 6a and 6b, the following expressions can be derived from a moment analysis within a harmonic description of the potential energy surfaces:^{18,20,28-31}

$$h\nu_{\max} \simeq -(\Delta G + \lambda_s + \lambda_i)$$
 (7)

 $(h\Delta\nu_{1/2})^2\simeq$

$$8(\ln 2)\left(2k_{\rm B}T\lambda_{\rm s}+\frac{1}{2}\sum_{\alpha}(\hbar\omega_{i\alpha})^2\Delta_{\alpha}^{-2}\coth\left(\frac{\hbar\omega_{i\alpha}}{2k_{\rm B}T}\right)\right) (8)$$

where ΔG is the free energy change, i.e., $\Delta G = \Delta E - T\Delta S$, with ΔE being the adiabatic energy gap (between the quantum electronic origins of the final and the initial electronic states) and ΔS is the (solvent) entropy difference between the two electronic states. λ_s is the medium reorganization energy and $\lambda_i = \sum_{\alpha} 1/2\hbar \omega_{i\alpha} \Delta_{\alpha}^2$ is the intramolecular reorganization energy. $\omega_{i\alpha}$ ($\alpha = 1, 2, ...$) denote the angular frequencies of the intramolecular modes, which are characterized by the reduced displacements Δ_{α} ($\alpha = 1, 2, ...$).

The appearance of the (solvent) free energy change in eq 7 has been based on rather heuristic arguments.⁵ Recently, a quantum mechanical treatment of the optical CT band shape by Hupp et al.³⁰ and by Bixon and Jortner³¹ considered a system of two displaced harmonic potential surfaces with different frequencies.³² The application of Kubo and Toyozawa's generating functions¹⁸ and Lax's method of moments²⁸ provided an explicit expression

TABLE 3

(a) 0–0 Transition Energies E_{00} of the Lowest Energy Neutral Excitation and Results of the Band-Shape Analysis for the Free Energy Change ΔG

	compound						
E ₀₀ [eV] solvent	1 4.45 ΔG [eV]	2 3.85 ΔG [eV]	3 3.78 ΔG [eV]	4 3.81 Δ <i>G</i> [eV]	5 3.43 ΔG [eV]	6 3.26 Δ <i>G</i> [eV]	
n-hexane C ₂ Cl ₄		-3.66	-3.32 -3.19	-3.72	-3.10 -3.04	-3.10 -2.98	
CCl4	-3.59	-3.46	-3.21	-3.56	-2.99		
C ₂ HCl ₃	-3.50	-3.33	-3.08	-3.39	-2.93	-2.83	
BuOAc	-3.60	-3.43	-3.14	-3.50	-3.06	-2.90	
CH ₂ Cl ₂	-3.48	-3.22	-2.93	-3.20	-2.86	-2.72	
MeCN	-3.55	-3.19	-2.98	-3.17	-2.78	-2.65	

(b) Fit Results for the Reorganization Energies λ_i and λ_s Using the Single-Mode Approximation of Eq 9

	compound						
λ _i [eV] solvent	1 0.45 λ, [eV]	2 0.40 λ, [eV]	3 0.34 λ, [eV]	4 0.39 λ, [eV]	5 0.36 λ, [eV]	6 0.36 λ, [eV]	
<i>n</i> -hexane C ₂ Cl ₄		0.40	0.47 0.41	0.51	0.37 0.38	0.33 0.31	
CCL	0.31	0.32	0.46	0.42	0.36		
C ₂ CHCl ₃	0.33	0.38	0.47	0.43	0.45	0.38	
BuOAc	0.44	0.57	0.54	0.65	0.54	0.46	
CH ₂ Cl ₂	0.49	0.50	0.48	0.49	0.53	0.50	
MeCN	0.66	0.67	0.67	0.66	0.52	0.56	

for the first moment^{18,28-31} $h\nu_{\rm max} \simeq M_1 = \Delta E + k_{\rm B} T \sum_j (\Delta \omega_{\rm sj}) / \omega_{\rm sj}$ + λ_s + λ_i where { ω_{si} } are the solvent frequencies in the initial state and $\{\Delta \omega_{ij}\}$ are the frequency differences between the final and initial states. The contribution of the frequency changes to the second moment, eq 8, is of the second order and can be neglected.²⁹ On the condition that the relative frequency changes $\Delta \omega_{si}/\omega_{si}$ of the individual vibrations are small, the medium (vibrational) entropy change is^{30,31} $\Delta S \simeq -k_{\rm B} \sum_{i} (\Delta \omega_{si}) / \omega_{si}$. The contribution of intramolecular modes is generally expected to be much smaller, although it could be substantial in reactions involving metal complexes.³³ These considerations result in eq 7 with ΔG containing the medium vibrational entropy change. It is still an open question to what extent arbitrary frequency changes as well as (solvent) degrees of freedom which cannot properly be described as harmonic oscillators can be incorporated in an entropy contribution.^{30,31} Thus, the precise meaning of the parameter ΔG in the band shape and its relation to the ordinary thermodynamic driving force (free energy change) of the corresponding thermal ET are not yet known. In practical cases this distinction is usually ignored.

From the first moment, eq 7, we infer that the temperature coefficient of the band maximum, eq 2, is $B = -(\partial \Delta G/\partial T + \partial \lambda_s/\partial T) = \Delta S - \partial \lambda_s/\partial T$. The experimental B data (Table 2) reflect the cumulative contribution of the entropy and the temperature dependence of λ_s .

Next we consider the temperature dependence of the fwhm $\Delta \nu_{1/2}$, eq 8. Provided that the intramolecular frequencies are sufficiently high, i.e., $\hbar \omega_{i\alpha} \gg k_B T$ (an assumption which is not always justified), eq 8 can be simplified to

$$(\hbar\Delta\nu_{1/2})^2 \simeq 8(\ln 2)(2k_{\rm B}T\lambda_{\rm s} + \lambda_i\hbar\langle\omega_i\rangle) \qquad (8a)$$

where $\hbar \langle \omega_i \rangle = \sum_{\alpha} (\hbar \omega_{\alpha})^2 (\Delta_{\alpha}^2/2) / \lambda_i$ is an average intramolecular frequency. Equation 8a is in accord with the experimental relation, eq 3, and Figure 5b. As a first approximation we take an average (temperature independent) value of λ_s over the relevant temperature domain and identify the parameters C and D in Table 2 with $C = 8(\ln 2)\lambda_i \hbar \langle \omega_i \rangle$ and $D = 16(\ln 2)k_B\lambda_s$.³⁴ Adopting $\hbar \langle \omega_i \rangle = 1300 \text{ cm}^{-1}$ (a value which will be justified later) the experimental values of C (Table 2) result in $\lambda_i = 0.36-0.41 \text{ eV}$ for all the compounds. Yet, the solvent reorganization energies estimated from the slopes D (Table 2) result in a large scatter of the λ_s data (e.g., 0.15 and 0.46 eV for compounds 2 and 6 in hexane, respectively). As the solvent contribution $2k_BT\lambda_s$ represents only a small ($\leq 20\%$) contribution to the bandwidth, its determination is much more sensitive to experimental errors than the larger intramolecular term in $\Delta \nu_{1/2}$.

4.2. A Single High-Frequency Mode. We shall first adopt the common approximation in the theory of ET rates and CT band shapes, considering a system of medium modes and a single high-frequency intramolecular vibration ($\hbar\omega_l > 1000 \text{ cm}^{-1}$).³⁵ The (unnormalized) emission band shape is then given by

$$L(\nu) = e^{-S} \sum_{n=0}^{\infty} \frac{S^n}{n!} \exp\left(-\frac{(\Delta G + h\nu + n\hbar\omega_i + \lambda_s)^2}{4\lambda_s k_B T}\right)$$
(9)

 $(S = \lambda_i/\hbar\omega_i)$. The appearance of the free energy change in eq 9 was discussed⁵ and can be shown to originate from the vibrational entropy contributions of solvent modes with frequency changes.³¹

In a first attempt, all the parameters ΔG , ω_i , λ_a , and λ_i were varied as free fit parameters. Not unexpectedly, some of these parameters, e.g., ω_i and λ_i , as well as ΔG and λ_a turn out to be highly correlated, a point which has also been discussed in some detail by Zeng and Zimmt.¹¹ This instability of the fits leads to a numerical uncertainty of λ_i , λ_a , and ΔG which we estimate at ± 0.05 eV each. Nevertheless, a large number of such fits gave an average value of $\hbar \omega_i \simeq 0.16$ eV ($\simeq 1300$ cm⁻¹) for the highfrequency mode which, therefore, was kept constant in later fits. With ω_i fixed, ΔG , λ_a , and λ_i were fitted (Table 3). As is shown in Figure 6, eq 9 in general reproduces measured fluorescence spectra within the experimental accuracy.

The average values of the intramolecular reorganization energy λ_i , which for the different compounds fall in the range $\lambda_i = 0.34$ -0.45 eV (Table 3) are in reasonable agreement with the results of the temperature dependence of the bandwidths (section 4.1).

The Stokes shift of the fluorescence band given by

$$S_{\rm s} = 2(\lambda_{\rm s} + \lambda_i) \tag{10a}$$

spans a range of 1.34–2.14 eV from nonpolar to polar solution. Such large values support the interpretation of the fluorescence emission as a transition with significant CT character. Consistency with eq 7 requires that the fitted values of λ_i , λ_s , and ΔG also fulfill the alternative definition

$$S_{\rm s} \simeq -2(\Delta G + h\nu_{\rm max})$$
 (10b)

Experimentally, the energy at the band maximum $h\nu_{max}$ exceeds the right-hand side of eq 7 by about 0.05 eV which is within the experimental and numerical uncertainty of the spectra and the fit parameters, resulting in a mismatch of 0.1 eV between the two estimates of S_s .

The free energy changes $(-\Delta G)$ obtained from this analysis (Table 3) decrease with increasing solvent polarity, as expected. A continuum dielectric model of the solvation of a giant dipole in a dielectric results in

$$\Delta G(\epsilon) = \Delta G^{\circ} + \frac{\mu_{e}^{2}}{a_{0}^{3}} f(\epsilon)$$
(11)

where the parameters were defined in section 3.1. This dependence of ΔG on $f(\epsilon)$ is exemplarily shown for compound 6 in Figure 7a. A crude linear correlation is indeed obtained. The slope in Figure 7a results in $\mu_e^2/a_0^3 \simeq 12\ 000\ \text{cm}^{-1}$ being somewhat larger than expected from the solvatochromic shift $(1/2, 16800\ \text{cm}^{-1})$ in Table 1. Similar results are obtained for the other compounds. On the same level of approximation the solvent reorganization energy λ_e



Figure 6. Representative examples of experimental fluorescence spectra, showing the reduced intensity $L(\nu) = I(\nu)/\nu^3$ (in arbitrary units), and the corresponding numerical fits using eq 9. (a, top) Compound 2 in butyl acetate, (b, middle) compound 4 in methylene chloride, (c, bottom) compound 6 in tetrachloroethylene; all measurements at room temperature.

is given by

$$\lambda_{s}(\epsilon, n) = \frac{\mu_{e}^{2}}{a_{0}^{3}}(f(\epsilon) - f(n^{2}))$$
(12)

The respective data for compound 6 are shown in Figure 7b. The slope according to eq 12 is about 6000 cm⁻¹, being lower than the value $\mu_e^2/a_0^3 \simeq 8400$ cm⁻¹ obtained from the solvatochromic shift and lower by a factor of 2 than obtained from the analysis of ΔG (Figure 7a). This crude analysis, which rests on the continuum model, is just indicative and not expected to result in quantitative correlations.

The continuum model completely fails to account for the λ_s data in nonpolar solvents, where $\epsilon \simeq n^2$ and eq 12 predicts that $\lambda_s \simeq 0$, in striking contrast to the large values of λ_s in hexane, CCl₄ and C₂Cl₄ (Table 3). Of course, the continuum model is inapplicable in nonpolar solvents, as documented in earlier experimental studies.^{9b,11,12b} The finite medium reorganization energy in nonpolar solvents may originate from short-range interactions with bond dipoles and/or from local CT from the donor-acceptor molecule to the solvent. Thus, finite values of λ_s in nonpolar solvents are physically plausible. What is troubling are the large reorganization energies in nonpolar solvents in the



Figure 7. Correlation between (a, top) fitted free energies of charge recombination ΔG and (b, bottom) solvent reorganization energies λ_{ϵ} and the solvent parameters $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$ and $f(\epsilon) - f(n^2) = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$ for compound 6 in the one-mode (1m) and two-mode (2m) approximations of eqs 9 and 15, respectively.

TABLE 4. Temperature Dependence of the Reaction Free Energy ΔG and the Solvent Reorganization Energy λ_{0} as Determined from Band Shape Fits in the One-Mode Approximation of Eq 9

T [K]	compound							
	3 in hexane		3 in CH ₂ Cl ₂		6 in hexane			
	ΔG [eV]	$\lambda_{s} [eV]$	$\Delta G [eV]$	λ, [eV]	$\Delta G [eV]$	λ_{s} [eV]		
320	-3.28	0.42			-3.10	0.32		
300	-3.31	0.46	-2.98	0.54	-3.09	0.32		
280	-3.30	0.46	-2.96	0.54	-3.08	0.33		
260	-3.31	0.47	-2.95	0.56	-3.08	0.34		
240	-3.33	0.49	2.96	0.60	-3.08	0.35		
220	-3.34	0.51	-2.95	0.61	-3.09	0.37		
200	-3.37	0.56	-2.97	0.65	-3.11	0.39		
180			-2.99	0.70	-3.12	0.42		

range $\lambda_s \simeq 0.3$ -0.45 eV at 300 K emerging from the band-shape analysis (Table 3). These values are considerably higher than reorganization energies $\lambda_s \simeq 0.15$ eV derived from kinetic free energy relationships for ET in nonpolar hydrocarbons^{17a} and from the band-shape analysis of intermolecular contact ion pairs.^{10b}

Additional information is obtained from the analysis of the temperature-dependent spectra. Free fits of ΔG and λ_s from spectra at different temperatures usually yielded a stronger temperature dependence of the solvent reorganization energy λ_s than that of the free energy change ΔG . Simple estimates based on the temperature dependence of the solvent parameters ϵ and n in eqs 11 and 12 as well as the temperature dependence of the effective dipole radius within the mean spherical approximation^{15e} would rather suggest otherwise. Extreme care must be exerted in assessing the reliability of the fits of ΔG and λ_s at different temperatures, due to the insufficient dynamical range of the fluorescence spectra. Therefore, fit results are given in Table 4 only for the compounds 3 and 6 in hexane and 3 in CH₂Cl₂ for which the quality of the data is best. The analysis of these spectra resulted in a surprisingly large temperature dependence of λ_s .

Thus, the analysis of the band shape, which rests on the single high-frequency mode description, resulted in two unphysical results for nonpolar solvents, which involve the high values of the medium reorganization energies and their pronounced temperature dependence.

4.3. A Semiclassical Approximation for a System with Two Intramolecular Modes. Experimental and theoretical evidence is accumulating that the simple high-frequency one-mode description of intramolecular vibrations requires modifications. Raman³⁶ and resonance Raman³⁷ investigations in particular suggest that vibrations in the range 400-600 cm⁻¹ make a sizable contribution to the overall intramolecular rearrangement. Such frequencies are also known to be important for an understanding of CT emission spectra in organometallic complexes.⁷⁰⁻⁸ Furthermore, the occurrence of photoinduced intramolecular ET from a locally excited electronic state to a CT state even in solvent-free, isolated molecules³⁸ implies the participation of intramolecular vibration modes with low ($\hbar \omega \leq 200 \text{ cm}^{-1}$) or intermediate ($\hbar \omega$ $\simeq 400-600 \,\mathrm{cm}^{-1}$) frequencies. In the barrelene-based compounds studied here, one possible source of an intermediate frequency vibration strongly coupled to the CT could be a rotation of the carbonyl groups of the esters relative to the ethylene bridge entailed by the reduction of the acceptor as was shown by means of AM1 calculations.¹¹ Alternatively, intermediate intramolecular modes coupled to the ET may originate from skeletal vibrations of the barrelene bridge.

Following these guidelines, we shall now consider two intramolecular modes, a high-frequency mode $\omega_{\rm H}$ with a reorganization energy $\lambda_{\rm H}$ and an intermediate frequency mode $\omega_{\rm L}$ with a reorganization energy $\lambda_{\rm L}$. For simplicity we retain the value $\hbar\omega_{\rm H} = \hbar\omega_i = 1300 \,{\rm cm}^{-1}$ in this section. The intermediate frequency is expected to fall into the range $\hbar\omega_{\rm L} = 400-600 \,{\rm cm}^{-1}$. Provided that $\lambda_{\rm L}/\hbar\omega_{\rm L} \gg 1$ a semiclassical approximation³⁹ can be adopted for the intermediate-frequency mode. With a quantum treatment for the high-frequency mode the (unnormalized) band shape is

$$L(\nu) = e^{-S} \sum_{n=0}^{\infty} \frac{S^n}{n!} \exp\left(-\frac{\left(\Delta G_{\rm scl} + h\nu + n\hbar\omega_i + \lambda_{\rm s,scl} + \lambda_{\rm L}\right)^2}{2\left(2\lambda_{\rm s,scl}k_{\rm B}T + \lambda_{\rm L}\hbar\omega_{\rm L}\coth(\hbar\omega_{\rm L}/2k_{\rm B}T)\right)}\right)$$
(13)

where $S = \lambda_{\rm H}/\hbar\omega_{\rm H}$. (For better distinction we add scl to the index in $\lambda_{\rm s,scl}$ and $\Delta G_{\rm scl}$ in the semiclassical approximation.) The functional dependence of the band shape on the frequency ν of the CT emission is the same as in the single-mode approximation but contains more parameters. Thus, the application of eq 13 does not require a new fit but a simple reinterpretation of the solvent reorganization energy $\lambda_{\rm s}$ in eq 9:

$$\lambda_{s} \rightarrow \lambda_{s,scl} + \lambda_{L} \frac{\hbar \omega_{L}}{2k_{B}T} \coth \frac{\hbar \omega_{L}}{2k_{B}T}$$
$$\Delta G \rightarrow \Delta G_{scl} - \lambda_{L} \left(\frac{\hbar \omega_{L}}{2k_{B}T} \coth \frac{\hbar \omega_{L}}{2k_{B}T} - 1 \right)$$
(14)

To extract $\lambda_{s,scl}$, λ_L , and ω_L , λ_s is written as a linear equation in $X = \hbar \omega_L/2k_BT \coth(\hbar \omega_L/2k_BT)$. Furthermore, we assume $\lambda_{s,scl}$ to be temperature-independent. For fixed ω_L , linear regression then should yield $\lambda_{s,scl}$ and λ_L . The results are exemplified in Figure 8a for compound 3 in hexane and CH₂Cl₂ and for compound 6 in hexane. It turns out that the quality of the linear correlation is practically independent of the choice of ω_L . Yet $\omega_L < 400 \text{ cm}^{-1}$ usually gives unrealistically high values for λ_L and a solvent reorganization energy $\lambda_{s,scl} < 0$ eV in hexane, i.e., it leads to unphysical results (see Figure 8b). Reasonable values of the parameters corresponded to $\omega_L = 500-600 \text{ cm}^{-1}$ consistent with resonance Raman data in CT complexes. The corresponding λ_L is very sensitive to the choice of ω_L . For $\omega_L = 500 \text{ cm}^{-1}$ the following values are obtained from Figure 8: for compound 3 λ_L



Figure 8. (a, top) Dependence of the apparent solvent reorganization energy on the temperature-dependent parameter $X(T) = \hbar \omega_L/2k_B T$ oth- $(\hbar \omega_L/2k_B T)$ in the semiclassical approximation according to eq 14 for the compounds 3 and 6 in hexane (3(1) and 6(1)) and methylene chloride solution (3(6) and 6(6), respectively). The intermediate frequency was fixed at $\omega_L = 500 \text{ cm}^{-1}$; for the resulting $\lambda_{s,scl}$ and λ_L see the text. (b, bottom) Dependence of the solvent reorganization energy $\lambda_{s,scl}$ and the reorganization energy λ_L on the intermediate-frequency vibration ω_L of compound 3 in hexane (...) and methylene chloride solution (—) in the semiclassical approximation.

= 0.22 eV, $\lambda_s = 0.12$ eV in hexane and $\lambda_L = 0.26$ eV, $\lambda_s = 0.16$ eV in CH₂Cl₂; for compound 6 in hexane $\lambda_L = 0.15$ eV and $\lambda_s = 0.11$ eV. With $\lambda_L/\hbar\omega_L > 3$ the criterion for the applicability of the semiclassical approximation is fulfilled.

Despite some arbitrariness in these parameters several qualitative conclusions can be drawn from the foregoing interpretation of the data. First, the inclusion of a mode of intermediate frequency drastically reduces the apparent solvent reorganization energy λ_s . Second, thermal activation of this mode can easily account for a strong temperature dependence of the apparent solvent reorganization energy of the single-mode model. Yet, by keeping $\lambda_{s,cl}$ constant, the entire temperature dependence of the band maximum is attributed to the free energy change ΔG alone, a simplification which may not always be justified.

4.4. A Quantum-Mechanical Treatment of a System with Two Intramolecular Modes. General expressions for the fully quantummechanical multimode Franck-Condon factor for arbitrary frequencies have been derived.^{20,40,41} For the special case of one high-frequency mode and one mode of intermediate frequency these expressions reduce to

$$L(\nu) = e^{-S_{\rm H} - S_{\rm L} \coth(\hbar\omega_{\rm L}/2k_{\rm B}T)} \sum_{l_{\rm H}} \sum_{l_{\rm L}} \sum_{k_{\rm L}} \frac{S_{\rm H}^{l_{\rm H}}}{l_{\rm H}!} \frac{S_{\rm L}^{l_{\rm L}+k_{\rm L}}}{l_{\rm L}! \cdot k_{\rm L}!} \langle n_{\rm L} \rangle^{k_{\rm L}} (1 + \langle n_{\rm L} \rangle)^{l_{\rm L}} \exp\left(-\frac{(\Delta G + h\nu + l_{\rm H}\hbar\omega_{\rm H} + (l_{\rm L} - k_{\rm L})\hbar\omega_{\rm L} + \lambda_{\rm s})^{2}}{4\lambda_{\rm s}k_{\rm B}T}\right)$$

(15)

with $\langle n_L \rangle = (\exp(\hbar \omega_L/k_BT) - 1)^{-1}$. Since the one-mode approximation with eq 9 already gives a satisfactory agreement with experimental spectra the additional parameters λ_L and ω_L

TABLE 5. Temperature Dependence of the Reaction Free Energy ΔG and the Solvent Reorganization Energy λ_S for Compound 3 in Methylene Chloride and Hexane and Compound 6 in Hexane Solution in the Two-Mode Approximation of Eq 15^a

T [K]	compound							
	3 in hexane		3 in CH ₂ Cl ₂		6 in hexane			
	ΔG [eV]	λ _s [eV]	ΔG [eV]	λ, [eV]	$\Delta G [eV]$	λ, [eV]		
320	-3.26	0.19			-3.11	0.14		
300	-3.28	0.22	-2.96	0.30	-3.09	0.13		
280	-3.27	0.21	-2.92	0.29	-3.09	0.14		
260	-3.26	0.20	-2.91	0.30	-3.08	0.14		
240	-3.27	0.21	-2.91	0.34	-3.07	0.14		
220	-3.26	0.21	-2.88	0.32	-3.07	0.15		
200	-3.27	0.23	-2.89	0.35	-3.07	0.16		
180			-2.87	0.37	-3.07	0.17		

^a For simplicity all the spectra were fitted with the same parameters $\omega_L = 400 \text{ cm}^{-1}$, $\lambda_L = 0.26 \text{ eV}$, $\omega_H = 1400 \text{ cm}^{-1}$, and $\lambda_H = 0.31 \text{ eV}$.

do not follow from a free fit. Therefore, the two intramolecular frequencies had to be fixed. We have chosen $\hbar\omega_{\rm L} = 400$ cm⁻¹ and $\hbar\omega_{\rm H} = 1400$ cm⁻¹. A somewhat larger value $\omega_{\rm H}$ as compared to ω_i and $\omega_{\rm H}$ in section 4.3 was taken in order to account for the observation that in a one-mode approximation an additional intermediate frequency lowers the effective frequency ω_i . The other parameters were fitted to a series of spectra of compound 6 for which the quality of the spectra was best, measured in hexane solution between 180 and 320 K. Average values of $\lambda_{\rm L} \simeq 0.26$ eV and $\lambda_{\rm H} \simeq 0.31$ eV were obtained and were kept constant in a second run of fits. For simplicity the parameters were used for the other compounds as well.

In Table 5 we present the results of the two-mode analysis for temperature-dependent spectra of the same systems as in section 4.3. The solvent dependencies of ΔG and λ_s for compound 6 are displayed in Figure 7 together with the data from the one-mode approximation. Analogous results are obtained in the other systems as well. They can be summarized as follows:

(1) The free energy change ΔG is practically the same within ± 0.05 eV as for the one-mode band-shape function (Figure 7a).

(2) The solvent reorganization energy λ_s in hexane is considerably reduced to (0.15 ± 0.02) eV which is consistent with the analysis of ET rates in hydrocarbon solvents.^{10b,17a} Analogously, the reorganization energies λ_s in other solvents differ by about 0.2 eV from the results of the one-mode fit in Table 3. Thus, the dependence of λ_s on the solvent polarity function $(f(\epsilon) - f(n^2))$ in Figure 7b is essentially retained, whereas the intercept for $\epsilon \rightarrow n^2$ is reduced to considerably lower values of 0.1–0.2 eV.

(3) For the limited data set considered, both ΔG and λ_s exhibit a temperature dependence with a total variation of $\Delta \lambda_s \simeq \Delta |\Delta G|$ $\leq 0.04 \text{ eV}$ in hexane solution and $\Delta \lambda_s \simeq \Delta |\Delta G| = 0.08-0.09 \text{ eV}$ in CH₂Cl₂ solution between 180 and 320 K (Table 5). The increase of the driving force $(-\Delta G)$ with the temperature for the charge recombination corresponds to a positive reaction entropy, as expected. Yet, in view of the (estimated) stability of the fits within $\pm 0.05 \text{ eV}$ this effective partitioning of the total temperature dependence of the band maximum must still be considered tentative. It should be noted in passing that the relation $-(\Delta G$ $+ \lambda_s + \lambda_H + \lambda_L) \simeq \hbar \nu_{max}$ (eq 7) remains fulfilled, as required.

5. Discussion

The different methods of the band-shape analysis result in the following information concerning the physical parameters, which determine CT radiative (and nonradiative) processes:

(1) Intramolecular Reorganization Energies. The single high-frequency mode description resulted in $\lambda_i = 0.36-0.45$ eV while the two intramolecular modes analysis led to $\lambda_L = 0.26$ eV and $\lambda_H = 0.31$ eV. The mode-specific intramolecular reorganization energy for the high-frequency mode is similar within the framework of the two methods. Its precise value depends on the

choice of the corresponding frequencies ω_i and $\omega_{\rm H}$. An intramolecular reorganization energy of $\lambda_i \simeq 0.39-0.43$ eV has also been described¹¹ for a related donor-acceptor system containing a dimethoxyanthracene and the same ethylenedicarboxy dimethyl ester as is used here.

(2) Free Energy Changes ΔG . The band-shape analysis yields free energy changes as a function of the solvent parameters (with an accuracy of <0.1 eV), which are very close for the single high-frequency and for the two intramolecular modes descriptions. However, an accurate estimate of the temperature dependence of ΔG has not been achieved yet.

(3) Medium Reorganization Energies λ_s . The situation is less satisfactory with respect to the solvent reorganization energy λ_s . The most serious shortcoming stems from our general ignorance of the modes which couple to the ET. In this context frequencies of $\hbar \omega = 200-600 \text{ cm}^{-1}$ are particularly important. Unless such vibrations are explicitely accounted for, unrealistically high values of λ_s and a spurious temperature dependence result. In the absence of independent molecular information this intramolecular coupling has to be included by a somewhat arbitrary averaged intermediatefrequency vibration. Low-frequency ($\hbar \omega < 200 \text{ cm}^{-1}$) intramolecular vibrations of the donor-acceptor molecules may contribute to the (effective) λ_s values, in particular for nonpolar solvents.

(4) Dependence of ΔG and λ_s on Solvent Polarity. An inspection of Table 3 and a comparison of the respective slopes in Figure 7 reveal that the free energy change ΔG exhibits a significantly stronger dependence than λ_s on the polarity of the solvent. Within the dielectric continuum approximation the slopes in Figure 7 should be identical. It should be noted, however, that the near equality of the solvent dependencies of ΔG and λ_s is not limited to the continuum model but applies to more refined descriptions of the solvent as well, e.g., the mean spherical approximation.^{15,16} From the charge recombination emission of intermolecular contact ion pairs of tetracyanobenzene and hexamethylbenzene Gould et al.^{10b} deduce a change of ΔG by 0.14 eV, whereas λ_s increases by as much as 0.39 eV upon a change of the solvent from the nonpolar cyclohexane to the polar solvent dichloroethane. It must be left to further studies whether these findings indicate a deficiency of current theories of the solvent dependence of λ_s and ΔG or simply indicate a general inability of the band-shape analysis to yield reliable estimates of both quantities as functions of the solvent polarity and even more so of the temperature.

Part of the inconclusiveness of the physical parameters emerging from the band-shape analysis can be readily traced to the rather unspecific and unstructured shape of the CT fluorescence spectrum. The maximum of the fluorescence intensity is approximatley given by eq 7, i.e., the sum of ΔG , λ_s , and λ_i . The width of the band is essentially determined by eq 8, i.e., the product of $\hbar \langle \omega_i \rangle$ and λ_i , whereas the solvent reorganization term contributes only little to the entire bandwidth. Thus, the bandshape analysis fixes the sum of the two solvent-dependent and temperature-dependent parameters ΔG and λ_s but does not sufficiently discriminate between them.

6. Concluding Remarks

In this paper we focus on the determination of free energy changes and solvent and intramolecular reorganization energies of the photoinduced charge recombination in a series of organic donor-acceptor compounds from stationary luminescence spectra. An attempt was made to explore the dependence of these quantities on the solvent polarity and on the temperature. The explicit shape of the fluorescence band was analyzed by fitting model band-shape functions to the experimental spectra. Fairly consistent estimates of the high-frequency intramolecular reorganization energy as well as of the reaction free energy as a function of the solvent can be obtained. However, the estimate of the solvent reorganization energy is fraught with considerable uncertainty. This uncertainty is rooted in our ignorance of the

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nature of the intramolecular modes which couple to the CT. Unphysically high values of λ_s for nonpolar solvents and their marked temperature dependence in the simple single-mode approximation strongly suggest the need for the incorporation of intramolecular vibrations of intermediate frequency ($\hbar \omega \simeq 400-500 \text{ cm}^{-1}$). Yet the CT emission spectra are too unspecific to provide sufficient information about the individual mode-specific intramolecular reorganization energies. Instead, the corresponding frequencies must be known from other experiments, such as resonance Raman data. The inclusion of such intramolecular vibrations results in a reasonable description of the medium reorganization energy.

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Appendix. Reduced Emission Spectra

The emission intensity $I(\nu)$ per unit frequency (ν) is given, according to eq 4, by

$$I(\nu) \propto \nu^3 |M(\nu)|^2 FC(\nu)$$
 (A1)

where $M(\nu)$ is the transition moment at frequency ν and $FC(\nu)$ is the Franck–Condon factor, which is of interest to us. Standard CT theory⁴² considers mixing between three electronic states: the ground state DA, the CT state D⁺A⁻, and a neutral excitation (DA)^{*}, resulting in

$$M(\nu) = \frac{V\Delta\mu}{\nu} + \frac{V^*\mu^*}{\Delta E_1 - \Delta E}$$
(A2)

where $V = \langle DA | H | D^+A^- \rangle$, $V^* = \langle D^+A^- | H | (DA)^* \rangle$, with H being the Hamiltonian of the system. $\Delta \mu = \mu_{D^+A^-} - \mu_{DA}$ is the difference between the permanent dipole moments of D^+A^- and of DA, respectively. $\mu^* = \langle DA | \mu | (DA)^* \rangle$ is the transition dipole for the direct $DA \rightarrow (DA)^*$ electronic transition. ΔE is the energy gap between the electronic origins of D^+A^- and DA, while ΔE_1 is the energy gap between the electronic origins of (DA)* and of DA. Equations A1 and A2 result in

$$I(\nu) \propto [a\nu + b\nu^2 + c\nu^3] FC(\nu)$$
 (A3)

where $a = (V\Delta\mu)^2$ is the contribution of the direct D⁺A⁻-DA coupling, $c = (V^* \mu^* / (\Delta E_1 - \Delta E))^2$ is the contribution of intensity borrowing from neutral excitations, while $b = \sqrt{ac}$ is a mixed term. Several recent studies^{10b-d} have set c = b = 0 in eq A3. Mulliken and his colleagues have proposed⁴² that the contribution of intensity borrowing in donor-acceptor complexes can be substantial while Verhoeven et al.43 suggest that this mechanism is important for the intensity and the radiative lifetimes of CT states in bridged donor-acceptor molecules, although it is rather difficult to establish which is the dominant contribution to $|M(v)|^2$ in eq A3. In view of this difficulty, we have chosen to describe the reduced intensity in terms of $L(\nu) \propto FC(\nu) = I(\nu)/\nu^3$. It should be noted, however, that $h\nu_{\max}$, $\Delta\nu_{1/2}$, and the values of λ_i , λ_s , and ΔG resulting from the band shape fit depend to some extent on this choice. Typically, the band maximum hv_{max} for c = b = 0 is blue-shifted by 300-500 cm⁻¹; the bandwidth $\Delta v_{1/2}$

decreases by 250-400 cm⁻¹. In the single-mode approximation (eq 9) these differences result in a reduction of λ_i by 20%. Similarly, $-\Delta G$ and λ_s decrease by 0.05 eV, which is in the range of the uncertainty of the parameters.

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