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Analysis of Charge-Transfer Absorption and Emission Spectra on an Absolute Scale: Evaluation of Free Energies, Matrix Elements, and Reorganization Energies

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The relationship between the absorption and emission spectra of the charge-transfer complexes formed between a series of methyl-substituted benzene donors with 1,2,4,5-tetracyanobenzene as acceptor in 1,2-dichloroethane was examined in detail. The association constants for charge-transfer complex formation and the emission quantum yields for these complexes were used to place the experimental absorption and emission spectra on absolute scales. The simultaneous analysis of these spectra is valid only when the Mulliken two-state model is justified. For several of the complexes included in this study the electron-transfer parameters, including the electronic coupling matrix elements, obtained from the analysis of the individual absorption and emission spectra are in close agreement. The simultaneous analysis of the combined absorption and emission spectra leads to a well-defined set of electron-transfer parameters for these complexes. In other complexes, where the two-state model does not apply because of the influence of localized excited states on the absorption spectrum, analysis of the absorption and emission spectra led to significantly different sets of electron-transfer parameters. It is demonstrated that the electronic coupling matrix elements are a very sensitive indicator of the influence of localized excited states on these spectra.

Introduction

The last three decades have seen tremendous advances in the understanding of electron-transfer (ET) processes. Numerous examples of inverted region behavior, proposed initially by Marcus,[1] have been reported and the measurements of ET free energies, electronic coupling matrix elements, and reorganization energies for ion pairs are now common.[2−17] The application of the Fermi golden rule expression[8,18] to nonadiabatic electronic transitions has also been established firmly in the descriptions of many of the spectroscopic and dynamic processes related to ET within geminate ion pairs.[8−11,19−22] Because of the broad applicability of the golden rule expression, many processes associated with weakly coupled electronic transitions can be described once the ET parameters for a different, albeit related, process have been determined. Examples showing the correlations among ET rate constants, radiative rate constants, the shapes and magnitudes of charge-transfer (CT) emission and absorption spectra, and Raman scattering intensities have all been reported.[8−10,23−27]

The golden rule expression for nonadiabatic electron transfer gives the electron-transfer rate constant, k_{ET}, as a product of the square of the electronic coupling matrix element (V) and a Franck−Condon weighted density of states (FCWD) as shown in eq 1:[8]

$$k_{\mathrm{ET}} = \frac{4\pi^2}{h}(V)^2(\mathrm{FCWD}(g)) \tag{1}$$

Here, FCWD(g) is given by

$$\mathrm{FCWD}(g) = \sum_{j=0}^{\infty} F_j(4\pi\lambda_{\mathrm{S}}k_{\mathrm{B}}T)^{-1/2}\exp\left[-\frac{(g + jh\nu_{\mathrm{V}}(V) + \lambda_{\mathrm{S}})^2}{4\lambda_{\mathrm{S}}k_{\mathrm{B}}T}\right] \tag{2}$$

with

$$F_j = \frac{(\lambda_{\mathrm{V}})^j}{(h\nu_{\mathrm{V}})^j j!}\exp\left(-\frac{\lambda_{\mathrm{V}}}{h\nu_{\mathrm{V}}}\right) \tag{3}$$

and

$$g = \Delta G_{\mathrm{ET}} \tag{4}$$

In this expression, ΔG_{ET} is the driving force for the electron transfer, λ_{V} is the vibrational reorganization energy associated with a single average high-frequency mode of frequency ν_{V}, and λ_{S} is the reorganization energy of the low-frequency modes usually attributed to solvent redistribution. The calculation of FCWD includes a numerical summation over the j quanta of the average high-frequency mode active in the ET process.

CT absorption can also be viewed as an electron-transfer process that can be evaluated according to eq 5.[8]

$$\epsilon\nu = \frac{8N\pi^3}{3000h^2c\ln 10}n(V)^2\Delta\mu^2(\mathrm{FCWD}(g')) \tag{5}$$

Equations 2 and 3 still apply except that g' is now given by

$$g' = \Delta G_{\mathrm{ET}} - h\nu \tag{6}$$

The quantity $\epsilon\nu$ is the product of the extinction coefficient for the absorption at frequency ν multiplied by this frequency, which is called the reduced absorption, $\Delta\mu$ is the change in dipole

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moment due to the transfer of the electron, and n is the solvent refractive index.

An analogous expression for the reduced emission intensity, I/ν, which is the emission intensity at frequency ν divided by that frequency, is given in eq 7,[8]

$$\frac{I_f}{\nu} = \frac{64\pi^4}{3h^3c^3} n^3 (V)^2 \Delta\mu^2 (\mathrm{FCWD}(g'')) \tag{7}$$

where g'' is given by

$$g'' = \Delta G_{\mathrm{ET}} + h\nu \tag{8}$$

At first glance the frequency dependence of the reduced absorption and emission spectra as given by eqs 5 and 7 may seem unusual and indeed the dependence presented here differs somewhat from that described initially by Marcus.[1c] We have chosen to use the frequency dependence given by eqs 5 and 7 because the reduced spectra, once plotted, should be exact mirror images of each other. Thus, visual conformation of the applicability of the relationships is possible. The derivation of these relationships and a discussion of the frequency dependence is available elsewhere.[8d]

The electronic coupling matrix element that appears in eqs 1, 5, and 7 can also be related to the radiative rate constant, k_F, through eq 9,[8]

$$k_{\mathrm{F}} = \frac{64\pi^4}{3h^3c^3} n^3 \nu_{\mathrm{av}} (V)^2 \Delta\mu^2 \tag{9}$$

where ν_{av} is the average frequency of the reduced emission spectrum.

One approach to determining the reorganization parameters plots k_{ET} versus ΔG_{ET} for a series of related reaction partners and models the observed behavior according to eq 1.[12−17] Values of V, λ_V, λ_S, and ν_V can be determined as adjustable parameters from the fitting procedure. The range of driving forces available for these studies is usually limited and the anticipated bell-shaped curves are rarely defined adequately. Large uncertainties in the determined ET parameters are common. Furthermore, this type of analysis assumes that the reorganization energies for the individual partners remain constant within the series of acceptors and donors studied. In practice, the variation in reorganization energy can be significant, even for a closely related series of donor/acceptor pairs.[8] Such variation in reorganization energy leads to systematic errors in the determined ET parameters; the matrix elements are usually underestimated and the total reorganization energies are overestimated.

A different approach has been to analyze the reduced emission spectra obtained after direct excitation of CT complexes.[8−10] In these cases only the spectral range collected limits the range of driving forces studied and a significant fraction of the bell-shaped Marcus curve is usually observed. Because these spectra are generally broad and featureless, significant uncertainty in the ET parameters obtained from the fitting procedure is still common. The quantity $\Delta G_{\mathrm{ET}} + \lambda$ can be well-defined, but separation of this sum into its components ΔG_{ET} and λ, let alone the separation of λ into meaningful values of λ_V and λ_S, remains a challenge.

Attempts to determine a unified set of ET parameters have combined the analysis of spectroscopic information collected using several techniques. Perhaps the most widely studied ET system to date is the hexamethylbenzene/tetracyanoethylene CT complex where CT absorption, contact radical ion pair (CRIP) emission, and resonance Raman spectra were all modeled simultaneously.[9,24,25] Yet, even for this intensely studied system it is still unclear whether a unified set of ET parameters can be determined with accuracy. Of particular concern is the wavelength dependence of the CRIP emission spectrum of the tetracyanoethylene complex.[9] Emission from nonequilibrated states or reactive intermediates would present a significant problem in the analysis of these spectra. The success, or failure, of the combined analysis hinges on whether the two-state model is strictly valid and that the same pair of states is probed by all of the spectroscopic techniques employed.

This report focuses on the combined analyses of the absorption and emission spectra of the CT complexes formed between 1,2,4,5-tetracyanobenzene (TCNB) as acceptor and three methyl-substituted benzene donors: hexamethylbenzene (HMB), pentamethylbenzene (PMB), and durene (DUR) in 1,2-dichloroethane (DCLE) solvent. These complexes were chosen specifically because the Mulliken two-state model[28,29] has been shown to be valid in these cases.[30−34] The CT absorption spectra for these complexes are well characterized.[35] While there are multiple CT absorption bands in each complex, the relative positions of these bands can be predicted with accuracy. The CRIP produced by direct excitation of the CT complexes are relatively long-lived and the emission spectra do not exhibit excitation wavelength dependence. Collectively, these attributes make these CT complexes ideal candidates for an attempt to determine a unified set of electron-transfer parameters using the combined analyses of the CT absorption and emission spectra.

To achieve this goal the association constants for CT complex formation and CRIP emission quantum yields were used to place the observed CT absorption and CRIP emission spectra on absolute scales. The relationship between the shapes and magnitudes of the reduced absorption and emission spectra of the CT complexes and the measured return electron-transfer rate constants was evaluated. The results obtained are contrasted with those of the mesitylene (MES)/TCNB complex, where the two-state model does not apply, and the influence of LE states on the absorption spectrum disrupts the direct relationship between the CT absorption and emission spectra.

Experimental Section

Methods. For all spectroscopic measurements, solutions of TCNB and appropriate donor, both approximately 10^{-2} M in DCLE, were placed in 1 cm quartz cuvettes at 25 ± 1 °C. Ground-state absorption spectra were recorded using a Beckman DU 640 UV−vis spectrometer. Steady-state emission spectra were measured using an Edinburgh FLS920 fluorescence spectrometer equipped with a liquid nitrogen cooled PMT (Hamamatsu R5509). The correction factors for the emission spectra were determined by comparison with standard spectra.[36] CT emission quantum yields were measured relative to optically matched solutions of tris-2,2′-bipyridylruthenium(II) chloride (Ru[bpy]$_3$Cl$_2$) in H$_2$O ($\Phi_f = 0.042 \pm 0.002$)[37] and 2-(p-dimethylaminostyryl)pyridylmethyl iodide (2-DASPI) in methanol ($\Phi_f = 0.0040 \pm 0.0005$)[38] as secondary fluorescence standards. Average values of quantum yield determinations using both standards were reported.

Materials. TCNB was purchased from Aldrich Chemical Co. and was purified by passing it through silica gel twice with methylene chloride as the eluting solvent, followed by recrystallization from chloroform. HMB, PMB, and DUR were purchased from Aldrich and purified by passing them through alumina with methylene chloride as the eluting solvent, followed

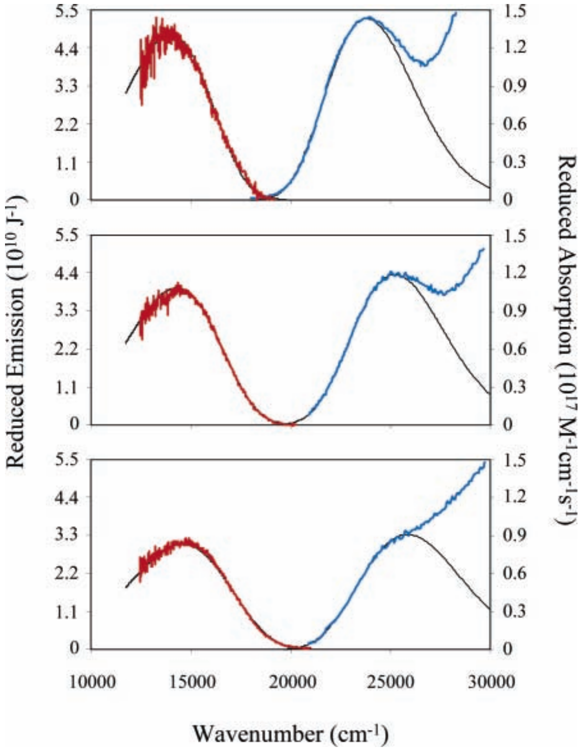

Figure 1. Absolute reduced absorption and emission spectra of the HMB, PMB, and DUR complexes with TCNB in DCLE. Also shown are the best simultaneous fits of the spectra according to eqs 5 and 7, using the parameters given in Table 2.

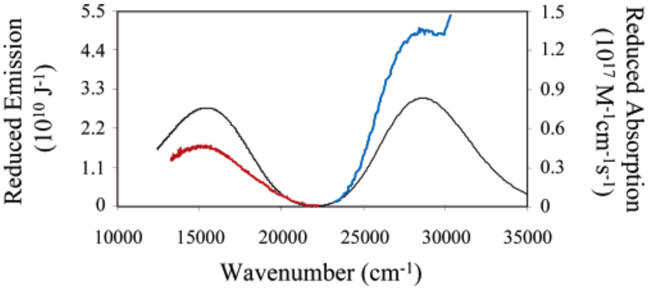

Figure 2. Absolute reduced absorption and emission spectra of the MES/TCNB complex in DCLE. Also shown is the best simultaneous fit of the spectra according to eqs 5 and 7, using the parameters given in Table 2.

by recrystallization from ethanol. MES was purchased from Aldrich, purified by fractional distillation, and passed twice through alumina. HPLC-grade DCLE was purchased from VWR and was used as received.

Results

The reduced absorption and emission spectra of the HMB, PMB, and DUR complexes with TCNB in DCLE on absolute scales are presented in Figure 1. The reduced absorption and emission spectra for the MES/TCNB complex in DCLE are shown in Figure 2. The emission spectra were obtained by direct excitation of the CT complex at 380 nm. At this wavelength the individual acceptor and donors do not absorb. The emission quantum yields (Φ_F) and radiative rate constants for each complex are given in Table 1. The radiative rate constants were determined using the measured emission quantum yields and the CRIP decay constants published previously.[39] The k_F values were used to place the reduced emission spectra in absolute units (J^{-1}). The maximum reduced emission intensities for each complex are also included in Table 1. Knowledge of the extinction coefficient of the CT complex is required to place the reduced absorption spectrum on an absolute scale (with units of M^{-1} cm^{-1} s^{-1}). Our methods of determining the association constants and extinction coefficients of weakly bound CT complexes have been described[40,41] and the reported values for the HMB, PMB, DUR, and MES complexes in DCLE[41] were used to scale the reduced absorption spectra in Figures 1 and 2. The maximum reduced absorption values for each complex obtained are collected in Table 1.

TABLE 1: Absolute Scales of Reduced Absorption and Emission Spectra of 1,2,4,5-Tetracyanobenzene Complexes with Methyl-Substituted Benzene Donors in 1,2-Dichloroethane

donor	ϕ_f[a]	k_f[b]	$(I_f/\nu)_{max}$[c]	ϵ_{max}[d]	$\epsilon\nu_{max}$[e]
HMB	2.7×10^{-4}	2.1×10^{6}	4.7×10^{10}	202	1.4×10^{17}
PMB	3.0×10^{-4}	1.9×10^{6}	3.9×10^{10}	164	1.2×10^{17}
DUR	3.3×10^{-4}	1.6×10^{6}	3.1×10^{10}	109	8.6×10^{16}
MES	11.6×10^{-4}	1.0×10^{6}	1.7×10^{10}	168	1.4×10^{17}

[a] ±10%. [b] ±15%. [c] In J^{-1}, ±15%. [d] In M^{-1} cm^{-1}, from ref 35. [e] In M^{-1} cm^{-1} s^{-1}, ±15%.

Discussion

The spectral data collected for the HMB, PMB, and DUR complexes with TCNB in DCLE were analyzed three different ways. In each case, ΔG_{ET}, λ_V, and λ_S were used to determine the position, width, and asymmetry of the absorption and emission spectra according to eqs 5 and 7, respectively. The matrix element, V, was used to scale the magnitude of the predicted spectra to obtain agreement with the measured spectra. A value of $\nu_V = 1400$ cm^{-1} was assumed in all cases as a typical value for aromatic donor/acceptor pairs.[42] The consequences of this assumption will be described in due course.

The first procedure calculated the reduced absorption spectra according to eq 5. The values ΔG_{ET}, V, λ_V, and λ_S that resulted in the minimization of the square of the difference between the calculated and experimental spectra were obtained. The region of the absorption spectrum analyzed included only those wavelengths where the lowest energy absorption band contributed greater than 95% of the total absorbance based on the published analyses of these spectra.[30,35] For each complex the fitting region spanned the red edge of the absorption band and included several data points past the observed absorption maximum. Shorter wavelengths could not be included because the lowest energy CT band overlaps significantly with additional CT absorptions and eventually with the LE absorption band of TCNB. The parameters ΔG_{ET}, V, λ_V, and λ_S obtained from the reduced absorption spectrum of each complex are collected in Table 2 along with the estimated confidence intervals in these values.

The second procedure required the reduced emission spectra for each complex to be calculated according to eq 7. The calculated and observed emission spectra were compared and the set of ET parameters that resulted in the least-squares minimization of residuals was again obtained. The entire available range of each emission spectrum shown in Figure 1 was used in the fitting procedure and the resulting parameters ΔG_{ET}, V, λ_V, and λ_S were collected (Table 2). Confidence intervals for the fitting parameters are also included in the table.

The third fitting procedure assumed that the absorption and emission spectra for each complex could be analyzed simultaneously according to eqs 5 and 7 and a single unified set of ET parameters determined. The least-squares summations for the individual traces were normalized and then weighted based on

TABLE 2: Electron-Transfer Parameters Obtained from the Reduced Absorption and Emission Spectra of 1,2,4,5-Tetracyanobenzene Complexes with Methyl-Substituted Benzene Donors in 1,2-Dichloroethane[a]

	absorption[b]				emission[c]				simultaneous[d]			
donor	V	λ_V	λ_S	ΔG_{ET}	V	λ_V	λ_S	ΔG_{ET}	V	λ_V	λ_S	ΔG_{ET}
HMB	870	0.33	0.35	2.35	863	0.31	0.46	2.45	869	0.36	0.33	2.35
PMB	816	0.40	0.35	2.45	806	0.40	0.29	2.40	810	0.40	0.35	2.46
DUR	728	0.47	0.30	2.50	741	0.45	0.34	2.54	733	0.47	0.30	2.51
MES	924	0.48	0.25	2.87	561	0.31	1.36	3.52	713	0.53	0.36	2.74

[a] Electronic coupling matrix elements (V) given in cm^{-1} (±10%). Reorganization energies (λ_V and λ_S) and free energy (ΔG_{ET}) given in eV. Error limits based on 25% increase in χ^2. [b] $\lambda_V = \pm 0.08$, $\lambda_S = \pm 0.15$, $\Delta G_{ET} = \pm 0.10$, $\Delta G_{ET} + \lambda = \pm 0.02$, $\lambda = \pm\ 0.08$. [c] $\lambda_V = \pm 0.10$, $\lambda_S = \pm 0.20$, $\Delta G_{ET} = \pm 0.15$, $\Delta G_{ET} + \lambda = \pm 0.03$, $\lambda = \pm 0.10$. [d] $\lambda_V = \pm 0.03$, $\lambda_S = \pm 0.03$, $\Delta G_{ET} = \pm 0.01$, $\Delta G_{ET} + \lambda = \pm 0.01$, $\lambda = \pm 0.02$.

the number of data points analyzed in each spectrum. The analysis included the same spectral regions used in the previous analyses as described above. The values of ΔG_{ET}, V, λ_V, and λ_S that minimized the residuals were determined and these values are collected in Table 2 along with the confidence intervals in these parameters. The calculated spectra based on the results of the simultaneous fitting procedure are shown in Figure 1.

Examination of the values collected in Table 2 shows that when the absorption or emission spectra were analyzed individually, the sum $\Delta G_{ET} + \lambda$ was well defined within a narrow range of acceptable values. Uncertainties of only ±0.03 eV on this sum were observed. However, the individual values of ΔG_{ET} and λ were poorly defined; uncertainties in the individual values were 5 times larger than those observed for their sum. Clearly, the values of ΔG_{ET} and λ are strongly correlated. Furthermore, the partitioning of λ into its components λ_V and λ_S leads to uncertainties that are so large as to render the estimates of these parameters of little value. It has been a common practice to fix one of these values (usually λ_V) and allow only λ_S to change.[8] The use of this restriction assumes that all of the variation in the total reorganization energy is due to changes in λ_S. The validity of this practice has been a matter of debate,[43] and as will be seen below, is unnecessary in certain cases.

Combined analyses, as described above, are physically meaningful only if the two-state model applies for a particular complex under investigation. When the two-state model is valid, the reduced absorption and emission spectra should correspond to transitions between identical pairs of states and both spectra may be characterized by a common set of ET parameters. The parameters obtained from the simultaneous analysis of HMB, PMB, and DUR spectra are comparable to those obtained from the individual spectra, albeit with significantly lower uncertainties, and are consistent with values reported for similar systems.[8] The validity of the simultaneous analysis can be tested further by comparing the χ^2 value of the simultaneous fit with the sum of χ^2 values of the individual fits. The ratios of the χ^2 values, given by $R\chi^2 = \chi^2_{sim}/(\chi^2_{abs} + \chi^2_{em})$, were 1.16, 1.16, and 1.20 for the HMB, PMB, and DUR complexes, respectively. The accuracy of the fitting procedure decreases by no more than 20% when each pair of absorption and emission spectra are forced to share a single set of parameters: a 2-fold reduction in the number of degrees of freedom. Such minor increases in $R\chi^2$ are sufficiently small to justify the use of the simultaneous fitting procedure.

The fact that single sets of ET parameters, including the matrix elements, are obtained from the analysis of the absorption and emission spectra has two important implications. First, the two-state model is likely to be valid for the HMB, PMB, and DUR complexes with TCNB in DCLE. This conclusion has been reached previously based on the analysis of the absorption spectra and the observed transition moment vector directions.[31−34] Second, and perhaps more importantly, the analytical determinations of the emission quantum yields and absorption extinction coefficients must both be accurate. The difficulties associated with using Benesi−Hildebrand[44] or related methods[45−47] to determine the association constants required to establish the extinction coefficients are well documented.[29] We have developed an alternative method that was used to determine the association constants and extinction coefficients of the CT complexes of interest herein.[40,41] The agreement between absolute scales of the absorption and emission spectra observed in this report confirms that our alternative method of determining the association constants is significantly more accurate than methods used previously for weakly bound CT complexes.

TABLE 3: Electron-Transfer Parameters Obtained from the Reduced Absorption, Reduced Emission, and Return Electron-Transfer Rate Constants of 1,2,4,5-Tetracyanobenzene Complexes with Methyl-Substituted Benzene Donors in 1,2-Dichloroethane[a]

donor	$k_{-ET,CP}$[b]	ΔG_{ET}[c]	V[d]	λ[e]	λ_V[e]	λ_S[e]
HMB	7.7×10^9	2.35	886	0.70	0.40	0.30
PMB	5.6×10^9	2.45	818	0.75	0.41	0.34
DUR	4.0×10^9	2.51	727	0.76	0.45	0.31

[a] Return electron-transfer rate constants were treated as constraints on the ET parameters according to eq 1. All parameters were obtained with ν_V fixed at 1400 cm^{-1}. [b] From refs 8d and 39b, $\pm 0.2 \times 10^9$ s^{-1}. [c] ±0.01 eV. [d] ±10%. [e] ±0.02 eV, $\lambda = \pm 0.01$ eV.

When the absorption and emission spectra of these CT complexes are analyzed simultaneously, not only is the sum $\Delta G_{ET} + \lambda$ well defined but also their individual values are now determined precisely; ΔG_{ET} is defined by the intersection of the reduced spectra and λ is related to the separation of the spectral maxima. The partitioning of the reorganization energy into its components λ_V and λ_S is still a problem. The partitioning of λ defines the asymmetry of the spectra about their respective maxima. Unfortunately, the individual parameters obtained from the simultaneous analysis still reflect significant uncertainty as shown by the error limits reported for these values (Table 2). The available spectral range for the reduced absorption and emission spectra cover the Marcus normal region and the inverted region is poorly represented in both spectra.

The ET parameters collected in Table 2 can be used to calculate the CRIP return electron-transfer rate constants ($k_{-ET,CP}$) for the HMB, PMB, and DUR complexes with TCNB in DCLE according to eq 1. Values of $k_{-ET,CP} = 5.2 \times 10^9$, 4.7×10^9, and 5.1×10^9 s^{-1} were predicted for each of these complexes, respectively, with uncertainties of approximately $\pm 3 \times 10^9$ s^{-1}. Although these calculated rate constants are in agreement with the published values given in Table 3, the uncertainties in the predicted $k_{-ET,CP}$ values are quite large. This fact arises because small uncertainties in the partitioning of λ into λ_V and λ_S lead to large uncertainties when extrapolated deep into the inverted region to determine $k_{-ET,CP}$. Accordingly, the experimental return ET rate constants can be used to place a restriction on the ET parameter set through eq 1. By using the measured rate constants as additional constraints on the ET parameter sets, precise values of the ET parameters were obtained, including the partitioning of the reorganization energy into its components λ_V and λ_S. The final sets of ET parameters for the HMB, PMB, and DUR/TCNB complexes, which include the simultaneous analysis of the reduced spectra and the return electron-transfer rate constant as a restriction, are collected in Table 3. The incorporation of the return ET rates into the combined analysis reduces the allowed values of λ_V and λ_S as depicted by the greatly reduced error limits on these values. The return ET rate constants for the complexes used in this study are complimentary to the spectra because the rate constants describe processes that occur deep in the inverted region, which is exactly the region that is poorly represented in both of the spectra.

Before discussing the values of the determined ET parameters in more detail, first consider the reduced absorption and emission spectra of the MES/TCNB complex in DCLE shown in Figure 2. The reduced absorption and emission spectra do not conform to the mirror image relationship expected if the two-state model were applicable.[30] When these spectra are analyzed independently, two significantly different parameter sets are obtained (Table 2). The emission spectrum appears to be broader than the absorption spectrum as confirmed by comparing the values of λ obtained from the individual fits collected in Table 2. The ΔG_{ET} values predicted from the individual spectra also differ by more than 0.65 eV and the electronic coupling matrix elements differ by a factor of 2. These differences suggest that the two-state model does not apply for this complex. Additionally, the matrix element predicted for the absorption of the MES/TCNB complex is larger than the matrix element observed for the HMB/TCNB complex (Table 2). This finding is inconsistent with what would be expected based on the two-state model and suggests that intensity borrowing plays a significant role in the absorption process of the MES/TCNB complex. When the absorption and emission spectra of the MES/TCNB complex are fit simultaneously to a single set of ET parameters, the predicted spectra deviate significantly from the measured spectra, as shown in Figure 2. The value of χ^2 obtained from the simultaneous fit is more than 100 times greater than the sum of χ^2 values of the individual fits.

Just as it was concluded that the two-state model applies to the HMB, PMB, and DUR complexes with TCNB in DCLE because the reduced absorption and emission spectra produce common sets of ET parameters, it must be concluded that the two-state model does not apply for the MES/TCNB complex in DCLE because this complex fails this test. We conclude that excitation of the MES/TCNB complex leads to a state with considerable LE character; as much as 20% of the oscillator strength is due to intensity borrowed from LE based on time-resolved linear dichroism measurements.[34] The parameters determined from the analysis of the absorption spectrum do not describe the transition from the ground state to the CRIP, but rather a transition from the ground state to a mixed CRIP-LE exciplex. The steady-state emission observed from the MES/TCNB complex in DCLE has contributions from the initial CRIP-LE exciplex, which is electronically distinct from the relaxed CRIP[30] and is therefore a combination of spectra from two distinctly different species. This spectrum should not be subjected to direct analysis according to eq 7. Parameters obtained from such an analysis would be meaningless.

Turning attention to the parameter sets determined using the combined analysis (Table 3) it is observed that the ΔG_{ET} values are consistent with the trend predicted by the Weller equation:

$$\Delta G_{ET} = E_{ox}(D) - E_{red}(A) + \Delta_{RIP} \tag{10}$$

where $E_{ox}(D)$ and $E_{red}(A)$ are the oxidation and reduction potentials of the donor and acceptor, respectively, and Δ_{RIP} is a solvent-dependent term that accounts for the Coulombic stabilization of the ion pair. Given the donor oxidation potentials (versus SCE) of 1.59 (HMB), 1.71 (PMB), and 1.78 eV (DUR) and $E_{red}(TCNB) = -0.64$ eV, a value $\Delta_{RIP} = 100 \pm 20$ meV results, which is consistent with values reported previously in DCLE.[48]

The electronic coupling matrix elements of the HMB, PMB, and DUR complexes with TCNB in DCLE are comparable to values determined for related systems.[8,49] The decrease in V with increasing ET driving force has also been reported for methyl-substituted benzene/TCNB complexes in chloroform based on the analysis of CRIP emission spectra.[8] The magnitude of the total reorganization energy observed in the present systems is consistent with previous observations in chlorinated solvents and the increase in λ upon decreasing the methyl substitution of electron donors has been noted.[8,50] Because V and λ change systematically with ΔG_{ET}, analysis of a plot of $k_{-ET,CP}$ versus ET driving force according to eq 1 will not give a valid set of ET parameters for the present series of CT complexes.

It is tempting to compare the precisely determined reorganization parameters λ_V and λ_S, but a discussion of how the choice of $\nu_V = 1400$ cm^{-1} influences the values of the ET parameters is in order. A brief survey of the literature reveals that values of ν_V between 1400 and 1500 cm^{-1} are common for aromatic donor/acceptor pairs.[42] Indeed, in this study it was found that assumed values of ν_V of as low as 1300 cm^{-1} and as high as 1800 cm^{-1} allowed reasonable fits to the data to be achieved. If the reduced spectra and the return ET rate constant are analyzed assuming a value of $\nu_V = 1500$ cm^{-1} the values of ΔG_{ET}, V, and λ are not affected, but the partitioning of λ into λ_V and λ_S changes significantly. For the DUR/TCNB complex, λ_V decreases from 0.45 to 0.40 eV and λ_S increases from 0.31 to 0.36 eV when ν_V is changed from 1400 to 1500 cm^{-1}. Resonance Raman studies have shown that there may be several vibrational modes that contribute significantly to the reorganization of the CRIP and the use of a single average frequency may not be uniformly applicable in all cases.[9,24,25] While the reorganization parameters may be precisely determined using the combined analysis as described above, the accuracy of these determinations will remain questionable until a more rigorous approach to determining the form of ν_V is found. Given the sensitivity of the values of λ_V and λ_S to the assumed value of ν_V, coupled with the expectation that ν_V may be different for each of the complexes studied, it seems unreasonable to critically evaluate even the trends in the individual components of the total reorganization energy at this time.

Before concluding this report it is appropriate to comment on the potential utility of this combined analysis approach to the spectroscopy of CT complexes in general. The question of whether the absorption and emission spectra can be analyzed simultaneously amounts to determining if the Mulliken two-state model is applicable to the complex of interest. It has been shown that the degree of LE intensity borrowing depends on the energy difference between the CT transition maximum and the closest LE transition.[34] For transitions that are well separated in energy the degree of intensity borrowing will be negligible and the two-state model is likely to apply. Unfortunately, the CRIP energies in many of these systems are relatively low and nonradiative return ET will be rapid. Therefore, the limitation of the combined analysis is not finding complexes in which the two-state model is applicable, but finding two-state complexes where the CRIP is sufficiently long-lived so that the emission spectrum can be observed.

Conclusions

It has been demonstrated that when the Mulliken two-state model applies, the reduced absorption and emission spectra of a CT complex yield self-consistent sets of electron-transfer parameters, ΔG_{ET}, V, λ_V, and λ_S, when analyzed according to the golden rule expressions for nonadiabatic ET. Because CT spectra typically define the normal region of the Marcus curve, small uncertainties in λ_V and λ_S can lead to large uncertainties in the calculated return ET rate constants that occur deep in the inverted region. When the experimental return ET rate constant is treated as a constraint on the ET parameter set, further refinement of the partitioning between λ_V and λ_S is achieved. At this point, accurate definition of the individual reorganization energies is limited mainly by the uncertainty in the average mode frequency, ν_V.

The simultaneous analysis of CT absorption and emission spectra is a sensitive test of the applicability of the Mulliken two-state model. The ability to measure a CT absorption spectrum on an absolute scale and then predict the return ET rate constant of the CRIP becomes increasingly important in polar solvents and strongly coupled donor/acceptor systems where the emission spectrum is difficult to observe. To date, the relationship between the spectroscopy and dynamics of such systems has received relatively little attention. By carefully selecting donor/acceptor combinations that strictly obey the two-state model, the analysis of CT absorption spectra can lead to a better understanding of ET processes that approach the time scale of solvent polarization and/or occur near the nonadiabatic/adiabatic limit.

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