J|A|C|S
A R T I C L E S

The Nature of the Rapid Relaxation of Excited Charge-Transfer Complexes

D. Levy and B. R. Arnold*

*Contribution from the Department of Chemistry and Biochemistry, University of Maryland
Baltimore County, Baltimore, Maryland 21250*

Received February 3, 2004; E-mail: barnold@umbc.edu

Abstract: Examples of contact radical-ion-pair (CRIP) formation from excited charge-transfer (CT) complexes are described. The reduced absorption and emission spectra of the CT complexes formed between hexamethylbenzene, pentamethylbenzene, and durene donors and 1,2,4,5-tetracyanobenzene (TCNB) in 1,2-dichloroethane (DCLE) exhibit a mirror image relationship, suggesting that each set of spectra describes transitions between the same two states. It was concluded that a CRIP is produced immediately upon excitation of the CT complex and that relaxation of the CRIP includes only minor geometry changes and changes in solvent polarization. In contrast to these results, the reduced absorption and emission spectra of the mesitylene (MES)/TCNB CT complex in DCLE are distinctly different and do not display a mirror image relationship. Time-resolved emission decay traces reveal the presence of an initial intermediate species that contributes approximately 10% of the total steady-state emission. The emission spectrum of this initial species mirrors the absorption spectrum of the MES/TCNB complex. In the MES/TCNB complex, excitation does not lead directly to the CRIP, and the relaxation of the excited complex must include an electronic component in addition to changes in geometry and solvation. The implications of these results on the applicability of golden-rule expressions of electron transfer are discussed.

Introduction

The spectroscopy and photophysics of charge-transfer (CT) complexes continue to be of significant interest more than half a century after they were first described.[1-5] These non-covalently bonded complexes are characterized by the appearance of weak electronic absorptions that are not present in the spectra of the individual reaction partners. Mulliken proposed the currently accepted theory used to describe CT complex formation and their spectroscopy, in which the ground state of the complex was depicted as a mixture of multielectron wave functions for nonbonded interactions and of the ion-pair.[6-10] According to this two-state model, the absorption of a photon by a weakly bound complex should result in the direct transfer of an electron from the donor to the acceptor.

It has been proposed that localized excited states of the acceptor or donor may also play a significant role in the description of these complexes; in such cases, an expansion of the simple two-state model was required. Our studies of the CT complexes formed between 1,2,4,5-tetracyanobenzene (TCNB) as acceptor and methyl-substituted benzene donors have shown conclusively that the two-state model is not uniformly applicable to all CT complexes.[11-14] Significant intensity borrowing from the localized excitation (LE) band of the acceptor was proven for several TCNB complexes and has been postulated for many other classes of CT complexes.[1-3]

One motivation for the continued study of CT complexes stems from the fact that rapid electron-transfer (ET) reactions, and processes initiated by these reactions, may be examined in the absence of relatively slow diffusional quenching processes by direct excitation of the CT complex. Unfortunately, this method of ion-pair formation has been shown to be more complex than was initially hoped. Rapid relaxations of excited CT complexes have been observed (Scheme 1).[15-21] In the following report, the generic term initial species (IS) refers to the species produced upon direct excitation of the CT complex.

(1) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1969.
(2) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.
(3) Raber, D. J.; Harris, J. M.; Schleyer, P. R. In *Ions and Ion Pairs in Organic Reactions*; Swartz, M., Ed.; Wiley: New York, 1974.
(4) Chanon, M.; Hawley, M. D.; Fox, M. A. Introduction. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988.
(5) Gould, I. R.; Young, R. H.; Farid, S. In *Photochemical Progress in Organized Molecular Systems*; Honda, K., Ed.; Elsevier: Amsterdam, 1991.
(6) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600.
(7) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4493.
(8) Mulliken, R. S. *J. Chem. Phys.* **1951**, *19*, 514.
(9) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811.
(10) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 397.
(11) Arnold, B. R.; Zaini, R. Y.; Euler, A. *Spectrosc. Lett.* **2000**, *33*, 595.
(12) Arnold, B. R.; Schill, A. W.; Poliakov, P. V. *J. Phys. Chem. A* **2001**, *105*, 537.
(13) Arnold, B. R.; Euler, A.; Poliakov, P. V.; Schill, A. W. *J. Phys. Chem. A* **2001**, *105*, 10404.
(14) Levy, D.; Arnold, B. R. *Can. J. Chem.* **2003**, *81*, 567.
(15) Mataga, M.; Murata, Y. *J. Am. Chem. Soc.* **1969**, *91*, 3144.
(16) Kobayashi, T.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2603.
(17) Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 3380.
(18) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147.
(19) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 5843.
(20) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1991**, *95*, 1956.
(21) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

Scheme 1
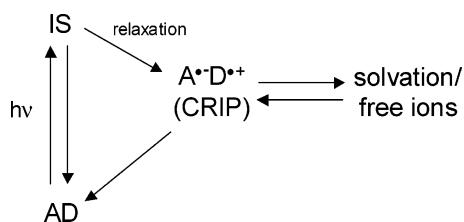
The IS may decay by radiative and nonradiative return to the ground state or by relaxation to the contact radical-ion-pair (CRIP). The decay pathways of the CRIP have been the subject of numerous investigations.[22-28]

The relaxation of the IS has been described as a delay in the formation of the charge-separated state[15-20] and as a relaxation from an initial to a relaxed CRIP.[21] The difference between these two descriptions is more than semantic. In the first description, the relaxation process and ET occur simultaneously, while in the second, ET must precede relaxation. These interpretations, and the ramifications of either interpretation, have yet to be tested fully. An understanding of the relaxation process is required before it will be possible to describe how the IS is related to the CRIP.

The past 30 years have seen tremendous advances in the understanding of ET reactivity. Numerous examples of inverted region behavior, initially proposed by Marcus,[29] have now been reported and the associated measurements of the ET parameters for contact ion-pairs are common.[21,30-36] The application of the golden-rule expression to non-adiabatic electronic transitions has also been firmly established in conjunction with many of the processes related to electron transfer.[21,33-38] Because of the versatility of this expression, which contains the product of a Franck–Condon weighted density of states and the appropriate electronic coupling matrix element, many processes associated with weakly coupled electronic transitions can be described once the parameters for a different, albeit related, process have been determined. Examples showing the relationships between ET rate constants, radiative rate constants, shapes of CRIP emission and CT absorption spectra, and Raman scattering intensities have all been reported.[21,33-36,39-44]

Analyses of the CT absorption and the resulting CRIP emission spectra should reveal details about the nature of the relaxation process. A unified picture of the ET processes would be expected, provided that the absorption and emission correspond to transitions between the same two electronic states. Assuming the two-state model is valid, the relaxation process should include only minor geometric and solvent reorganization processes. In this case, the analysis of the absorption and emission spectra should result in a single set of ET parameters. In contrast, for complexes in which the two-state model is not valid, the absorption and emission spectra may involve different sets of electronic states, and different ET parameters should be observed. It is essential, therefore, to understand how the relaxation processes of excited CT complexes alter the relationship between CT absorption and CRIP emission spectra.

The following report details our studies of the relaxation processes of the CT complexes formed between several methylated benzene derivatives as electron donors, specifically hexamethylbenzene (HMB), pentamethylbenzene (PMB), durene (DUR), and mesitylene (MES), with TCNB as the electron acceptor in 1,2-dichloroethane (DCLE) solvent. The analyses of CT absorption and CRIP emission spectra of these systems are described. These specific complexes were chosen because the LE does not contribute to the CT absorptions for the HMB/TCNB and PMB/TCNB complexes in DCLE, while the CT transitions of the MES/TCNB complex have been shown to include a significant LE contribution.[11-13] The DUR/TCNB is an intermediate case where LE intensity borrowing does occur, but only in higher energy CT transitions, and the lowest CT excited state does not include a significant contribution of the LE.[45] Comparisons among the spectra of these complexes allow the influence of LE intensity borrowing on the nature of the relaxation process to be described.

Experimental Section

Methods. Solutions of TCNB and the appropriate donor, both approximately 10^{-2} M in DCLE solvent, were placed in 1 cm quartz cuvettes. 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). Corrected emission spectra were determined by comparison with standardized spectra.[46] All spectral measurements were performed at 25 °C.

Time-resolved emission decay traces were obtained by the method of time-correlated single-photon counting (SPC). The SPC apparatus used was an Edinburgh LifeSpec-ps system equipped with a thermoelectrically cooled microchannel plate (MCP)–PMT detector (Hamamatsu R3809). Discrimination and TAC parameters were controlled within the Edinburgh TCC900 electronics module using the associated software. All SPC experiments were run in reverse acquisition mode. Stop-trigger pulses were obtained by sampling a small fraction of the fundamental output of a mode-locked Ti:sapphire laser system (Spectra

(22) Weller, A. Z. *Phys. Chem. (Wiesbaden)* **1982**, *133*, 93.
(23) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.
(24) Peters, K. S.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 3643.
(25) Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401.
(26) Arnold, B. R.; Noukakis, D.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1995**, *117*, 4399.
(27) Arnold, B. R.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482.
(28) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.
(29) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
(30) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
(31) Irvine, M. P.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* **1986**, *104*, 315.
(32) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.
(33) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
(34) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 3830.
(35) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Goodman, J. L.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4405.
(36) Vauthey, E. *J. Phys. Chem. A* **2001**, *105*, 340.
(37) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
(38) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078.
(39) Boldrini, B.; Cavalli, E.; Painelli, A.; Terenziani, F. *J. Phys. Chem. A* **2002**, *106*, 6286.
(40) Markel, F.; Ferris, N. S.; Gould, I. R.; Myers, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 6208.
(41) Kulinowski, K.; Gould, I. R.; Myers, A. B. *J. Phys. Chem.* **1995**, *99*, 9017.
(42) Britt, B. M.; McHale, J. L.; Friedrich, D. M. *J. Phys. Chem.* **1995**, *99*, 6347.
(43) Zong, Y.; McHale, J. L. *J. Chem. Phys.* **1997**, *107*, 2920.
(44) Kelley, A. M. *J. Phys. Chem. A* **1999**, *103*, 6891.
(45) It has been reported that the CT absorptions of the DUR/TCNB complex in DCLE do contain LE contributions (refs 11, 13). The excitation wavelength dependence of the time-resolved linear dichroism indicates that the lowest energy CT transition does not include significant intensity borrowing (D. Levy and B. R. Arnold, in press).
(46) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer/Plenum: New York, 1999.

Physics Millenia V/Tsunami). The remaining fundamental (1 W, 80 MHz, 780 nm) was doubled to 390 nm (4 mW, 8 MHz) using a Spectra Physics model 3980 pulse picker/frequency-doubling unit. The output of the pulse picker was polarized vertically with respect to the laboratory frame and was used to excite the sample. Emission spectra were collected in a 90° horizontal configuration with respect to the excitation pulses and were observed through a polarizer oriented at the magic angle with respect to the excitation. Instrument response functions were determined at emission wavelengths between 500 and 700 nm by reference convolution of a sample of 2-(*p*-dimethylaminostyryl)-pyridylmethyl iodide (2-DASPI) in methanol.[47] The measured instrument response of the SPC system was typically 40 ps.

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 column chromatography on alumina with methylene chloride as the eluting solvent, followed by recrystallization from methanol. MES was purchased from Aldrich, purified by fractional distillation, and passed twice through alumina. HPLC-grade DCLE was purchased from VWR and used as received. The dye samples of 2-DASPI were purchased from Exciton and were used without additional purification.
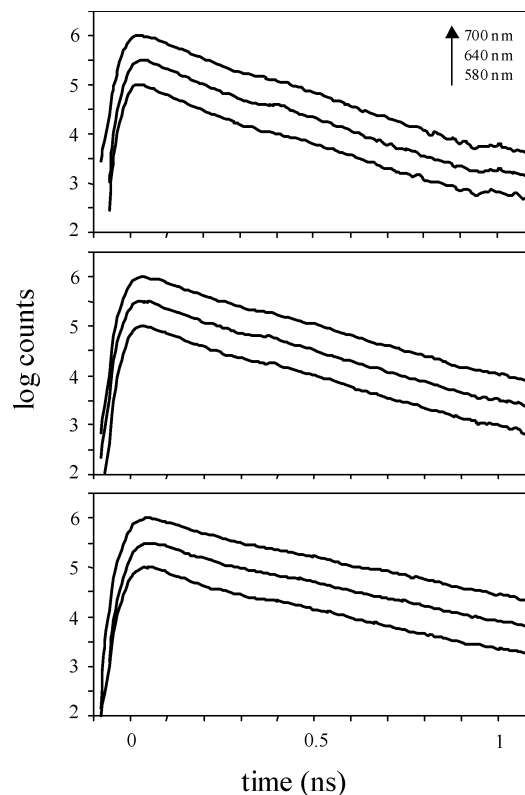
Results

The CT absorption and CRIP emission spectra of the HMB, PMB, and DUR/TCNB complexes in DCLE are shown in Figure 1. Time-resolved emission traces were recorded at several wavelengths in each case. The traces obtained at 580, 640, and 700 nm after 390-nm excitation are shown in Figure 2 for each complex. The absorption and emission spectra for the MES/TCNB complex in DCLE are shown in Figure 3. Time-resolved emission traces were also recorded at several emission wavelengths in this case. The traces obtained at 500, 600, and 700 nm after 390-nm excitation of the MES/TCNB complex are shown in Figure 4.

Discussion

Several time-resolved emission traces are shown in Figure 2 for the direct excitation of the CT complexes between HMB, PMB, and DUR donors with TCNB. These traces were collected at different emission wavelengths across the CRIP emission band from the blue edge to the maximum of the emission. The normalized decay traces for each complex are identical, regardless of the observation wavelength, as can be seen in Figure 2. There are several reports of rapid relaxation processes in the emission and absorption decays of related TCNB complexes in various solvents.[17−21] The lifetime of the relaxation process reported in these cases has been between 30 and 60 ps in chlorinated solvents for several complexes, including the complexes studied here. The relaxation of these complexes has also been reported to be between 5 and 10 ps in acetonitrile on the basis of transient absorption measurements. It is not clear that the reported absorption and emission decay components are due to the same processes because of the significant differences in their lifetimes. The time-resolved emission traces shown in Figure 2 show no evidence of a 30−60 ps decay component at any of the observed emission wavelengths. Reasons for the apparent differences between the reported emission dynamics and those described in the present work are not clear at this time. A ca. 5 ps relaxation process of the IS

(47) Janssens, L. D.; Boens, N.; Ameloot, M.; DeSchreyver, F. C. *J. Phys. Chem.* **1990**, *94*, 3564.
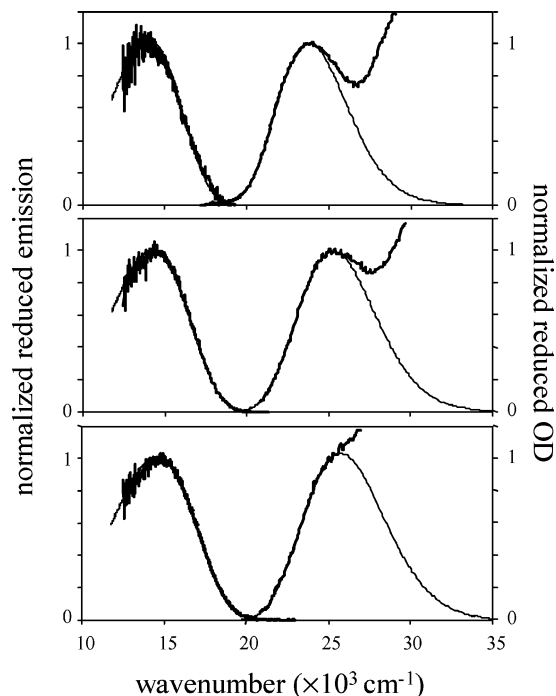
Figure 1. Normalized reduced absorption and emission spectra of the HMB/TCNB (top), PMB/TCNB (center), and DUR/TCNB (bottom) CT complexes in DCLE. The best fits of the absorption spectra according to eq 1 and the emission spectra predicted using the absorption parameters (eq 5) are included (solid lines).

Figure 2. Time-resolved emission decay traces of the HMB/TCNB (top), PMB/TCNB (center), and DUR/TCNB (bottom) complexes in DCLE at 580, 640, and 700 nm, following excitation of the complexes at 390 nm. The traces are offset by one-half log unit for clarity.

would still be possible but undetected in these experiments; the time resolution of our instrument would not allow such a rapid decay to be resolved.

Normalized reduced absorption and emission spectra of the HMB, PMB, and DUR/TCNB complexes in DCLE are shown in Figure 1. The mirror image relationship between the absorption and emission spectra within each set is immediately apparent. This observation is supported by the comparison of the difference between the energy at the band maximum and the energy at half-maximum ($\Delta E = E_{MAX} - E_{1/2MAX}$) of the reduced absorption and emission spectra. For these CT complexes in DCLE, the estimated differences in ΔE for the absorption and emission bands were less than 100 cm^{-1} in each case.

Detailed analysis of the absorption spectra provides the product of the square of the matrix element (V) and the Franck−Condon weighted density of states (FCWD) according to eq 1.[21,38]

$$\epsilon \nu = \frac{8N\pi^3}{3000h^2c \ln 10} n(V)^2 \Delta\mu^2 (\text{FCWD}(g')) \qquad (1)$$

where the FCWD is given by

$$\text{FCWD}(g') = \sum_{j=0}^{\infty} F_j (4\pi\lambda_S k_B T)^{-1/2} \exp\left[-\frac{(g' + jh\nu_V + \lambda_S)^2}{4\lambda_S k_B T}\right] \qquad (2)$$

and

$$F_j = \frac{(\lambda_V)^j}{(h\nu_V)^j j!} \exp\left(-\frac{\lambda_V}{h\nu_V}\right) \qquad (3)$$

with

$$g' = \Delta G_{ET} - h\nu \qquad (4)$$

where $\epsilon\nu$ is the extinction coefficient for the absorption times the frequency ν at which it is observed, called the reduced absorption. 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 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. ΔG_{ET} is the driving force, and $\Delta\mu$ is the change in dipole moment due to the transfer of the electron.

Equation 1 was used to fit all of the CT absorption spectra shown in Figure 1. In each case, the region used for fitting included the red edge of the absorption band, where the lowest energy CT transition contributes >95% to the total absorbance based on the published analysis of these complexes.[11] At higher energies, the lowest energy absorption band overlaps with a second CT band and subsequently with the LE absorption. For the HMB and PMB complexes, the fitted region included a few data points past the respective absorption maxima. For the DUR/TCNB complex, the CT absorption spectrum does not have a clear maximum due to severely overlapping CT transitions. In this case, the fitting was stopped just short of the inflection in the absorption band, where the second CT band starts to contribute significantly to the observed oscillator strength. At this point in the absorption spectrum, the lowest energy band contributes more than 95% of the observed oscillator strength.[11]

The best fit of the absorption bands according to eq 1 obtained by least-squares minimization of the residuals is included in Figure 1.

The values of the reorganization parameters that resulted from the best fit of the HMB/TCNB complex absorption spectrum, assuming a value of $\nu_V = 1400$ cm^{-1}, were $\lambda_V = 0.33$ eV, $\lambda_S = 0.35$ eV, and $\Delta G_{ET} = 2.35$ eV. These reorganization parameters are comparable to those reported for the CRIP emission spectrum of this complex.[34] With these reorganization parameters in hand, the emission spectrum can be predicted using eq 5.[21,38]

$$\frac{I_f}{\nu} = \frac{64\pi^4}{3h^3c^3} n^3(V)^2 \Delta\mu^2 (\text{FCWD}(g'')) \qquad (5)$$

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

$$g'' = \Delta G_{ET} + h\nu \qquad (6)$$

The term I_f/ν is the emission intensity at frequency ν divided by that frequency, called the reduced emission intensity. The emission spectrum calculated according to eq 5 using the reorganization parameters obtained from the CT absorption spectrum is also included in Figure 1. The calculated spectrum is in excellent agreement with the observed emission. Fitting the emission spectrum independently or fitting the emission and absorption spectra simultaneously results in similar reorganization parameters. It appears that the two-state model can be applied to this complex and that any relaxation observed must occur within a single electronic state. The IS and the CRIP are both described as ion-pairs, and the relaxation process includes only minor geometry changes and solvent polarization.

The best fit of the PMB/TCNB absorption spectrum according to eq 1 yields the reorganization parameters $\lambda_V = 0.40$ eV, $\lambda_S = 0.35$ eV, and $\Delta G_{ET} = 2.45$ eV, and the analysis of the DUR/TCNB absorption spectrum gives $\lambda_V = 0.47$ eV, $\lambda_S = 0.30$ eV, and $\Delta G_{ET} = 2.51$ eV. These values are also comparable to those reported previously for similar systems.[34] Using these sets of ET parameters, the CT emission spectra of the PMB/TCNB and DUR/TCNB complexes in DCLE were predicted using eq 5. As was the case with the HMB/TCNB complex, the predicted emission spectra for the PMB and DUR/TCNB CRIP are also in excellent agreement with the measured emission spectra of these complexes. Here, again, it can be concluded that the two-state model can be applied to these complexes.

The situation is different for the MES/TCNB complex. The normalized reduced absorption and emission spectra of the MES/TCNB complex in DCLE are shown in Figure 3. These spectra do not display the mirror image relationship observed in the three previous examples. This statement is again justified by evaluating the $\Delta E = E_{MAX} - E_{1/2MAX}$ values for the reduced absorption and emission spectra. Values of ΔE estimated from the spectra in Figure 3 are 2720 cm^{-1} for the absorption and 3150 cm^{-1} for the emission band. The difference between these two values indicates an increase in the emission band half-width of more than 400 cm^{-1}. Fitting of the absorption spectrum according to eq 1 gives the following parameters: $\lambda_V = 0.48$ eV, $\lambda_S = 0.25$ eV, and $\Delta G_{ET} = 2.87$ eV. The emission spectrum predicted using these parameters is considerably blue-shifted and much narrower than the observed emission spectrum, as can be seen in Figure 3. Attempts to fit both spectra to a single
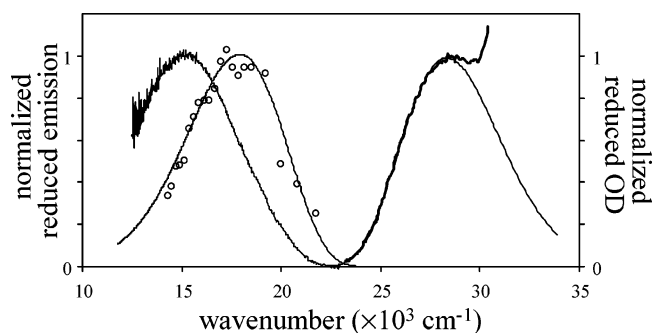
Figure 3. Normalized reduced absorption and emission spectra of the MES/TCNB CT complex in DCLE. The best fit of the absorption spectrum according to eq 1 and the emission spectrum predicted using the absorption parameters (eq 5) are included. The open circles represent the spectrum of the fast emission component calculated from the time-resolved emission decays.

Figure 4. Time-resolved emission decay traces of the MES/TCNB complex in DCLE at 500, 600, and 700 nm, after excitation of the complex at 390 nm. An example of the typical instrument response function is included (gray circles).

set of reorganization parameters fail. The standard error obtained by fitting both spectra simultaneously is several times larger than the sum of the errors observed when both spectra are fit individually. It must be concluded that the absorption and emission spectra cannot be described by a single set of reorganization parameters. This finding suggests that the emission and absorption do not occur within the same set of electronic states for the MES/TCNB complex and the relaxation of the IS must include an electronic component in addition to geometry changes and solvent polarization.

Clearly, the Mulliken two-state model does not apply to all CT complexes described herein. This conclusion has been reached previously on the basis of the analysis of the CT absorption spectra[11] and subsequently on the analysis of time-resolved linear dichroism data.[12–14] It has been shown that intensity borrowing from the LE of TCNB does not occur in the lowest CT absorptions of the HMB, PMB, and DUR/TCNB complexes, in which case the two-state model should apply. On the other hand, it was also shown that the lowest energy CT absorption band of the MES/TCNB complex does include a significant contribution due to borrowed LE intensity. In the case of the MES/TCNB complex, the two-state model does not apply and the IS must be distinctly different from the CRIP.

Additional information concerning the IS can be obtained from the time-resolved emission decays of the MES/TCNB complex in DCLE shown in Figure 4. These traces must be analyzed as a sum of three exponential decays. The two slowest time constants are assigned to decay of geminate ion-pairs where feedback from the solvent separated radical-ion-pair to repopulate the CRIP must occur ($\tau_1 = 510 \pm 60$ ps and $\tau_2 = 1240 \pm 80$ ps). The fastest time constant ($\tau = 50 \pm 10$ ps) must then describe the relaxation of the IS to produce the CRIP. This assignment was supported by the observation that the relative contribution of the fastest decay to the overall emission changes as the emission wavelength increases, as seen in Figure 4. The contribution of the fastest component to the observed steady-state emission can be determined after the evaluation of the time-resolved emission traces. For the MES/TCNB complex, about 10% of the total observed steady-state emission intensity must be due to emission from the IS and does not originate from the
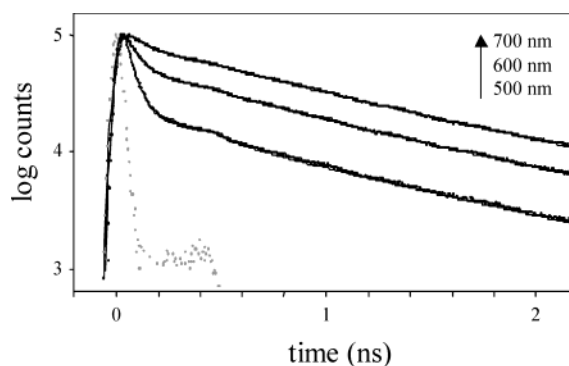
relaxed CRIP. The normalized reduced emission spectrum of the MES/TCNB IS was reconstructed from the time-resolved traces and is also included in Figure 3 (open circles). The experimentally determined IS spectrum agrees remarkably well with the emission predicted from the fit of the CT absorption spectrum.

It is possible that the CT absorption and IS emission of the MES/TCNB complex correspond to transitions between the same two electronic states. If this hypothesis is correct, analysis of the absorption would reveal information about the IS, including estimates of the radiative and nonradiative decay constants. Furthermore, the analysis of the steady-state emission spectrum could be used to describe the ET processes of the CRIP, but only after subtraction of the significant IS component. Comparisons between the reorganization parameters for the IS intermediate and those for the direct formation of a CRIP are premature. Further studies are required before definite trends in these values can be established and firm comparisons can be made. It will also be of interest to understand how solvent, temperature, and the structures of the acceptors and donors influence the relaxation of the IS. Additional studies along these lines are in progress.

Conclusions

Two contrasting cases in CRIP formation have been demonstrated. For the HMB, PMB, and DUR/TCNB CT complexes in DCLE, the Mulliken two-state model was valid and the emission and absorption spectra were described using a single set of ET parameters. Relaxation from the IS to the CRIP must proceed within a single electronic state and is most likely related to minor changes in geometry and solvent polarization. For the MES/TCNB complex, the two-state model was not valid and the analysis of the absorption and emission spectra requires two different sets of ET parameters. In the MES/TCNB case, the analysis of the absorption spectrum should reveal details about the IS produced after excitation of the CT complex, while analysis of the emission spectrum, corrected for the contribution of the IS emission, should describe the ET processes of the CRIP.

JA049387M