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Influence of Localized Excited States on the Transition Moment Directions of Charge Transfer Complex Absorptions

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The influence of localized excited (LE) states on the spectroscopy of charge transfer (CT) complexes has been examined for a series of complexes formed between methyl-substituted benzene donors and 1,2,4,5-tetracyanobenzene as acceptor in 1,2-dichloroethane and octanenitrile solvents. A molecular orbital model was used to describe the appearance of multiple CT absorption bands that occur in the spectra of these complexes. The influence of LE states in these CT absorptions was explored using time-resolved linear dichroism spectroscopy where the direction of the CT transition moment vector (TMV) was used to probe the magnitude of intensity borrowing. The TMV directions for each of the observed CT transitions within the absorption spectra were determined for several complexes. In some cases, the observed CT transitions were interpreted as being pure CT transitions; in others the observed transitions are influenced significantly by a LE transition. The correlation between the TMV directions and the transition energy suggests that the magnitude of intensity borrowing is influenced not only by the energy difference between the CT and LE transitions but also by the specific character of the transitions under consideration.

Introduction

Mulliken presented the currently accepted theory describing the formation and spectroscopy of charge transfer (CT) complexes in a series of papers in the early 1950s.[1−5] The ground and excited states of CT complexes were depicted as linear combinations of nonbonded and ion-pair wave functions in what has become known as the two-state model. It has been established that the appearance of multiple absorption bands within CT spectra requires multiple ion-pair states to be considered.[6−8] The observation of anomalous increases of CT oscillator strengths with increasing donor oxidation potential in related complexes has been described.[6−10] This observation is in direct conflict with the trend predicted by the two-state model. Contributions from localized excited (LE) states have been considered to justify these findings.

The measurement of transition moment vector (TMV) directions of CT transitions can be a sensitive probe of contributions from LE states.[11−13] The vector addition scheme shown in Figure 1 has been used to describe how LE intensity contributes to the absorption and influences the observed TMV ($\mathbf{M}_{\mathrm{CT}i}$).[12,13] The pure CT TMV ($\mathbf{M}_{\mathrm{CT}}$) is defined as the component of the observed TMV that is due to the transfer of an electron from the donor to the acceptor. The contribution of the LE to the observed TMV is given by $(f_{\mathrm{LE}i})^{0.5}\mathbf{M}_{\mathrm{LE}}$, where $f_{\mathrm{LE}i}$ is the fraction of LE oscillator strength mixed into the observed CT transition and $\mathbf{M}_{\mathrm{LE}}$ is the LE TMV. Recall that the transition moment is related to the square root of the oscillator strength.[7] It has been customary to identify all new absorption bands that appear after mixing a donor and acceptor as CT transitions. This classification is correct only when LE states do not contribute to the observed transition and the two-state model is valid. In keeping with the established literature, we also refer to these new absorptions as CT transitions without reference to the character of the transition. The distinction between pure CT TMV and observed CT TMV, which may also include a contribution due to the LE, should be clear after considering the vector addition scheme in Figure 1.

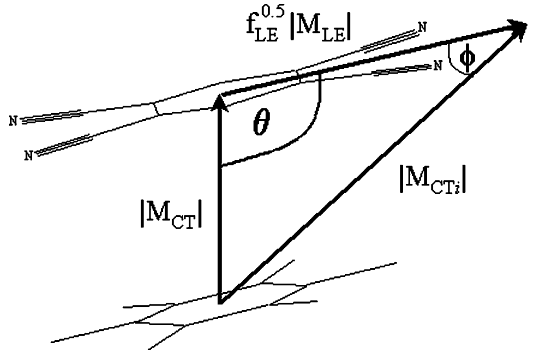

Figure 1. Vector addition scheme depicting the contribution of the LE TMV ($f_{\mathrm{LE}i}^{0.5}|\mathbf{M}_{\mathrm{LE}}|$) to the pure CT TMV ($|\mathbf{M}_{\mathrm{CT}}|$) to give the observed TMV ($|\mathbf{M}_{\mathrm{CT}i}|$).

Two predictions can be made based on the vector addition scheme depicted in Figure 1. First, $\mathbf{M}_{\mathrm{CT}i}$ will increase in magnitude as the intensity borrowing from the LE increases for θ equal to or greater than 90° as will be the case in all of the complexes of interest to this report. Thus, the observed CT extinction coefficient will increase as the magnitude of intensity borrowing increases. This prediction has been the basis of the arguments used previously to describe the anomalous increase of CT oscillator strengths.[6−10] The well-known relationship between the oscillator strength and the radiative rate constant suggests that the lifetime of the excited state should decrease as intensity borrowing increases, as has been reported for related complexes.[14] Second, the model also predicts LE intensity borrowing will influence the direction of $\mathbf{M}_{\mathrm{CT}i}$ within the molecular frame. Spectroscopic measurements on single crystals

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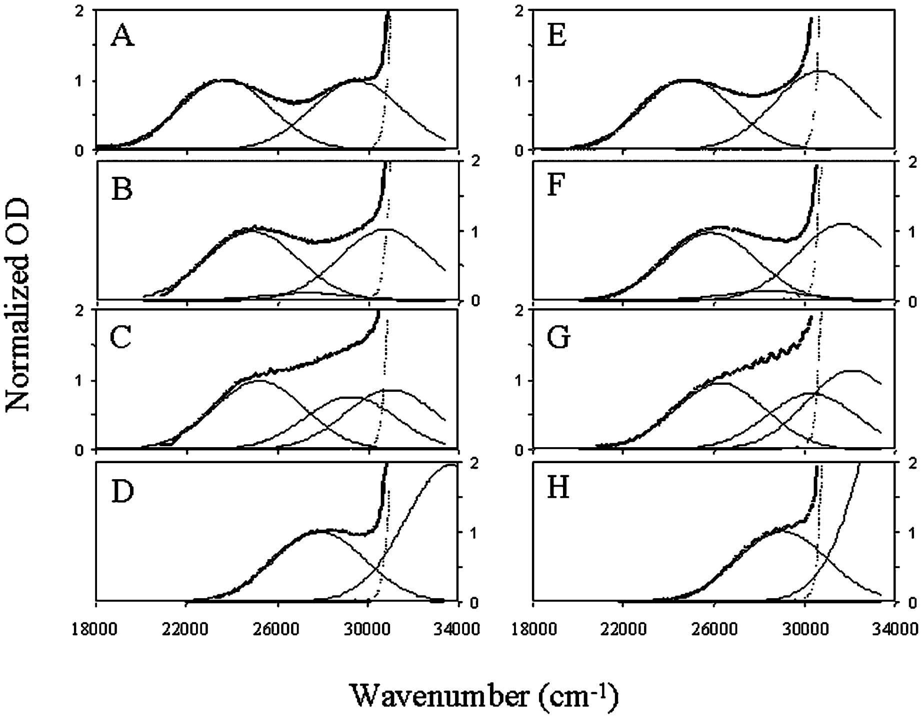

Figure 2. Normalized absorption spectra (thick lines) of (A) HMB/TCNB in DCLE; (B) PMB/TCNB in DCLE; (C) DUR/TCNB in DCLE; (D) MES/TCNB in DCLE; (E) HMB/TCNB in OCN; (F) PMB/TCNB in OCN; (G) DUR/TCNB in OCN; (H) MES/TCNB in OCN. The Gaussian curves (thin lines) represent the individual CT transitions as required using eq 1 and the fit parameters collected in Table 1 with the height of the CT1 band normalized to 1. The dotted line is the onset of the TCNB LE absorption.

of CT complexes[15] and the results of time-resolved linear dichroism (TRLD) measurements have shown that CT TMV directions are extremely sensitive to contributions from LE states.[12,13]

In a preliminary report, we described the influence of LE intensity borrowing on the TMV directions of CT complexes formed between the acceptor 1,2,4,5-tetracyanobenzene (TCNB) and methyl-substituted benzene donors.[12] It was assumed that the LE intensity borrowed was partitioned equally among the multiple CT transitions observed in the absorption spectra of these complexes. In the current report, we reexamine several complexes in two different solvents and use multiple excitation wavelengths to allow the contributions from individual CT transitions to be differentiated. The results of these experiments are used to explore the partitioning of LE intensity among the various CT transitions and to describe how the degree of intensity borrowing is influenced by the energy difference between the CT and LE transitions.

Experimental Section

Methods. The picosecond pump–probe apparatus used in the time-resolved linear dichroism experiments has been described in detail elsewhere.[16] Excitation pulses were obtained by isolating the third harmonic of a Continuum PY61C Nd:YAG laser. Focusing the 355-nm laser pulse into a 10-cm quartz cell and isolating the stimulated Raman emission at 404 nm (H_2O) or 446 nm (cyclohexane) allowed these additional excitation wavelengths to be utilized. White light continuum pulses were generated by focusing 12 mJ of residual 1064-nm laser pulse into a 10-cm cell containing a 1:1 mixture of H_2O/D_2O.

Solutions of TCNB and donor in the appropriate solvent, each approximately 10^{-2} M, were placed in quartz cuvettes. Ground-state absorption spectra were recorded using a Beckman DU 640 UV–vis spectrometer. During time-resolved data collection the samples were stirred using a magnetic stirrer and 200 pulse pairs were averaged to obtain a ΔOD measurement at each delay setting. The resultant traces were fit using a simplex computer program to find the nonlinear least squares minimum of the error between a model function and the observed data.

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. Hexamethylbenzene (HMB), pentamethylbenzene (PMB), and durene (DUR) were purchased from Aldrich and were purified by passed them through alumina using 1,2-dichloroethane (DCLE) as the eluting solvent, followed by recrystallization from ethanol. Mesitylene (MES) was purchased from J. T. Baker, purified by fractional distillation, and passed through alumina prior to use. DCLE was purchased as HPLC grade from Aldrich and used as received. Octanenitrile (OCN) was purchased from Aldrich, purified by fractional distillation, and passed through alumina prior to use.

Results

The ground state absorption spectra of HMB, PMB, DUR, and MES (10^{-2} M) in the presence of TCNB (10^{-2} M) in DCLE and OCN solvents are shown in Figure 2. The observed optical densities were normalized to the height of the lowest energy CT absorption band in each spectrum. Excitation of the DUR/TCNB complex in DCLE with 446-nm light resulted in the observation of a new species that absorbed maximally at 468 nm. This species has been identified previously as the TCNB radical anion produced within the laser pulse. The production and decay of the TCNB radical anion in DCLE is recorded in the trace shown in Figure 3. This trace was obtained with the excitation beam linearly polarized along the laboratory *Z*-axis and the probe beam polarized at 54.7° (magic angle) with respect to the laboratory *Z*-axis. This configuration ensures that the observed trace is due exclusively to the formation and decay

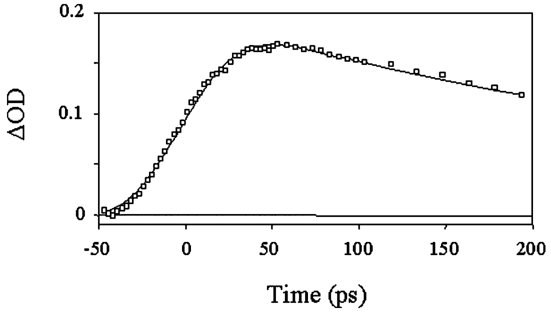

Figure 3. Picosecond pump−probe transient absorption decay trace of the DUR/TCNB complex in DCLE excited at 446 nm and observed with 468-nm light polarized at the magic angle. The solid line indicates the best fit of the observed trace using a single-exponential decay convoluted with a 40 ps instrument response.

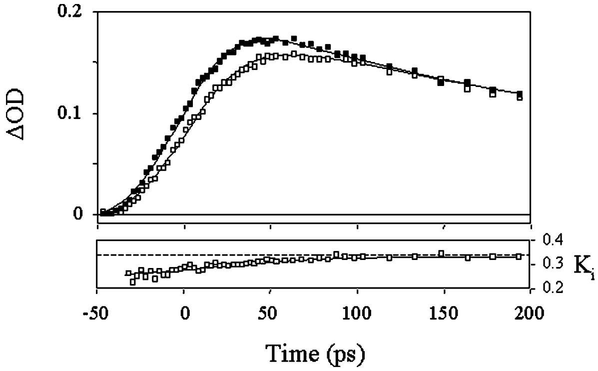

Figure 4. Top panel: Picosecond pump−probe transient absorption decay trace of the DUR/TCNB complex in DCLE excited at 446 nm and observed using 468-nm light polarized parallel (open boxes) and perpendicular (closed boxes) to the excitation. The solid lines indicate the best fit of the dichroic traces assuming a single-exponential anisotropy decay in addition to the parameters obtained from the magic angle trace (Figure 3). Bottom panel: Plot of the orientation factor as a function of time calculated from the dichroic traces. The solid line indicates the fit of the orientation factor based on the parameters obtained from the dichroic traces. The dashed line represents the isotropic K_i value of 0.333.

of the ion-pair and does not include dichroic information. The magic angle trace was analyzed as a single-exponential decay. A rapid relaxation process with an 8 ps lifetime in acetonitrile has been reported for this complex.[17] This process is significantly faster than the instrument response of our apparatus to be resolved accurately and was therefore not included in the kinetic scheme. Least-squares analysis of the magic angle trace yielded the following parameters: $A_{MA} = 0.203$ (OD) and $k_{MA} = 2.6 \times 10^9\ s^{-1}$ with an instrument response of 40 ps assuming a Gaussian profile.

Two additional decay traces were recorded as shown in Figure 4. In the first trace (empty boxes) the probe beam was linearly polarized along the laboratory *Z*-axis, i.e., parallel to the excitation, and in the second (filled boxes) the probe beam was polarized within the laboratory XY-plane, i.e., perpendicular to the excitation. Except for the polarization of the probe beam, all three traces were collected under identical conditions. The shapes of the two traces shown in Figure 4 are due to ion-pair formation and decay as well as the randomizing rotations of the ion-pairs in solution. The set of dichroic traces were fit assuming a single-exponential anisotropy decay, along with two anisotropy preexponential factors, one for each trace. The parameters obtained from the fitting of the magic angle trace were used as fixed values in the analysis of the dichroic data. For the traces shown in Figure 4, the anisotropy decay rate constant was $k_{OR} = 3.24 \times 10^{10}\ s^{-1}$ and the preexponential factors were $A_{\|} = -0.0574$ (OD) for the parallel trace and $A_{\perp} = 0.0209$ (OD) for the perpendicular trace.

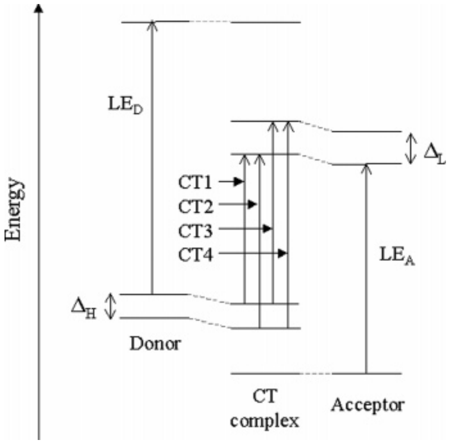

Figure 5. Energy level diagram depicting the electronic transitions associated with a CT complex. The LE transitions that occur in the acceptor and donor are still allowed and should be observed in the absorption spectrum of the complex, although they may be perturbed slightly.

Similar sets of traces were collected for the DUR/TCNB complex using 355- and 404-nm excitation in DCLE and OCN. These traces were analyzed as described above and the results are given as Supporting Information (Table 1S). Also included as Supporting Information are results for the HMB, PMB, and MES complexes with TCNB using multiple excitation wavelengths in both solvents.

Discussion

CT Absorption Spectra. Normalized absorption spectra of the CT complexes formed between TCNB and methyl-substituted benzene donors in DCLE and OCN solvent are shown in Figure 2. These absorption spectra were analyzed based on the energy level diagram shown in Figure 5.[18] The highest occupied molecular orbital (HOMO) and second-highest occupied molecular orbital (SHOMO) of the donor interact with the lowest unoccupied molecular orbital (LUMO) and the second-lowest unoccupied molecular orbital (SLUMO) of the acceptor. Consequently, as many as four CT transitions may be observed in the absorption spectra of these complexes. These transitions are depicted in Figure 5 and designated as CT1 for the lowest energy transition (HOMO − LUMO) through CT4 for the highest energy transition (SHOMO − SLUMO).

It has been shown that complex formation does not perturb the acceptor and donor significantly such that the relative energies of the molecular orbitals within the complex can be estimated using properties of the individual acceptor and donor.[6,7,18] The molecular orbital diagrams of the HMB/TCNB complex are shown in Figure 6. Each orbital is readily identified as predominately belonging to either the HMB (SHOMO and HOMO) or TCNB (LUMO and SLUMO) moieties. Similar molecular orbital diagrams were obtained for PMB and DUR complexes with TCNB. In each case the calculated electron density on the adjacent ring is small, although not zero, as required for relatively weak transitions with low oscillator strength.

The energy difference between the LUMO and SLUMO of TCNB, Δ_L, was estimated using a ZINDO/S calculation on the AM1-optimized ground-state geometry. This calculation

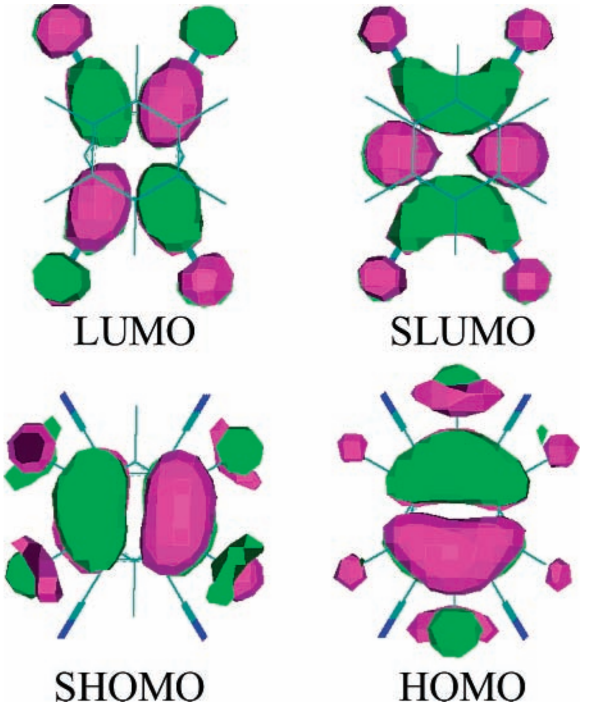

Figure 6. Calculated molecular orbitals for the HMB/TCNB complex looking along the axis connecting the centers of mass of the acceptor and donor. The HMB is on the top and TCNB is on the bottom.

TABLE 1: Characterization of the Absorption Spectra of 1,2,4,5-Tetracyanobenzene Complexes with Methyl-Substituted Benzene Donors

donor	E_{ox} (eV)[a]	ΔH (cm^{-1})[b]	solvent	E_{CT1} (cm^{-1})[c]	h_2[d]	h_3[e]
HMB	1.59	0	DCLE	23680	[f]	0.98
			OCN	24860	[f]	1.11
PMB	1.71	2420	DCLE	24730	0.16	1.06
			OCN	25880	0.13	1.12
DUR	1.78	4030	DCLE	25190	0.74	0.98
			OCN	26290	0.84	1.19
MES	2.11	0	DCLE	27880	[f]	1.96
			OCN	29030	[f]	3.99

[a] Donor oxidation potential vs SCE from ref 19. [b] Energy difference between the HOMO and SHOMO of the donor calculated from the difference between the first and second gas-phase ionization potentials from ref 20. [c] Energy at the maximum of the lowest energy CT1 transition. [d] Height of CT2 transition intensity relative to CT1. [e] Height CT3 transition intensity relative to CT1. [f] CT1 and CT2 are degenerate so that $h_1 + h_2 = 1$.

gives $\Delta_{\mathrm{L}} = 5800$ cm^{-1}, which is consistent with the energy difference between the S_0-S_1 and S_0-S_2 transitions observed in the TCNB ground-state absorption spectrum. The energy differences between the HOMO and SHOMO, Δ_{H}, were estimated using the reported gas-phase vertical ionization potentials[20] for each donor. The Δ_{H} values are collected in Table 1.

Examination of the values collected in Table 1 reveals that the Δ_{H} values for all of the donors examined are smaller than Δ_{L} of TCNB. The second-lowest energy absorption band (CT2) in the CT spectra will always correspond to the SHOMO−LUMO transition and will occur at an energy given by $E_{\mathrm{CT2}} = E_{\mathrm{CT1}} + \Delta_{\mathrm{H}}$. For HMB and MES, the HOMO and SHOMO are degenerate ($\Delta_{\mathrm{H}} = 0$) such that, in the absence of significant perturbation, these two transitions will appear as a single absorption band. Thus, for HMB and MES complexes CT1 and CT2 will be degenerate. In all cases, CT3 will describe the HOMO−SLUMO transition. The energy at which CT3 should occur is given by $E_{\mathrm{CT3}} = E_{\mathrm{CT1}} + \Delta_{\mathrm{L}}$, where $\Delta_{\mathrm{L}} = 5800$ cm^{-1}. Finally, CT4 will correspond to the SHOMO−SLUMO transition and should occur at an energy given by $E_{\mathrm{CT4}} = E_{\mathrm{CT1}} + \Delta_{\mathrm{H}} + \Delta_{\mathrm{L}}$. For the HMB and MES complexes, CT3 and CT4 will again appear as a single, degenerate, absorption band.

Attempts to fit the CT absorption spectra by allowing the bandwidths to change occasionally resulted in the prediction of exceedingly broad (>10 000 cm^{-1}) or unusually narrow bands (3−5 cm^{-1}). These results were viewed as unreasonable and were attributed to artifacts of the fitting procedure.[18] Examination of the majority of the predicted absorption bands revealed a relatively narrow range of widths for those bands that appeared to be fitted correctly. Based on this observation, an average bandwidth of $w = 2820$ cm^{-1} was adopted. While there is no theoretical basis to believe that these bandwidths should all be the same, the fact that this restriction allowed all of the spectra to be modeled with accuracy, as shown in Figure 2, was viewed as sufficient justification for our purpose.

With restrictions on the number, relative energies, and widths of the CT transitions in place, the relative OD at any frequency, $\mathrm{OD}_{\mathrm{REL}}(\nu)$, was calculated using only four adjustable parameters (Equation 1).

$$\mathrm{OD}_{\mathrm{REL}}(\nu) = e^{-((E_{\mathrm{CT1}}-\nu)/w)^2} + h_2 e^{-((E_{\mathrm{CT1}}+\Delta_{\mathrm{H}}-\nu)/w)^2} + h_3 e^{-((E_{\mathrm{CT1}}+\Delta_{\mathrm{L}}-\nu)/w)^2} + h_4 e^{-((E_{\mathrm{CT1}}+\Delta_{\mathrm{H}}+\Delta_{\mathrm{L}}-\nu)/w)^2} \quad (1)$$

Here, E_{CT1} is the position of the first CT absorption band maximum in wavenumbers and h_2, h_3, and h_4 are the heights of the CT2, CT3, and CT4 transitions at their maxima, respectively, all relative to the height of CT1. Recall that the height of CT1 has been assigned a value of 1. For the PMB and DUR complexes the CT4 transition lies completely under the TCNB LE absorptions. For these two complexes h_4 was omitted from the analysis. The fits to the CT absorption spectra according to eq 1 are included in Figure 2 and the resulting parameters are collected in Table 1.

Comparisons between the CT1 transition energies reported in Table 1 reveal two important trends. First, in either solvent, E_{CT1} increases as the oxidation potential of the donor increases. This observation is consistent with predictions based on the Mulliken two-state model. Second, for any given donor, E_{CT1} is approximately 1150 cm^{-1} higher in OCN than in DCLE. Such a large shift in the absorption spectrum with changing solvent is not expected based on simple continuum solvation models.[13] Specific solute−solvent interactions have been suggested, although the exact nature of these interactions are not understood.[6,13,22−24] Note that in Figure 2 the onset of the TCNB LE transition does not change appreciably with changing solvent or donor. The observed changes in the CT transition energies with solvent and/or donor correspond to changes in the energy difference between the CT and LE transitions, with the energy difference decreasing as the CT transition energy increases.

Comparisons among the relative band heights collected in Table 1 show clearly that the height of CT3 relative to CT1 (h_3) increases with increasing transition energy. In addition, h_3 is larger in OCN than in DCLE for each complex. These observations serve as additional examples of the anomalous increase of CT oscillator strengths with increasing donor oxidation potential, and are inconsistent with expectations based on the two-state model. Contributions from the LE must be significant in some of these complexes. Furthermore, the LE contributions appear to increase in significance as the energy difference between the CT and LE transitions decreases. These findings demonstrate that the borrowed LE intensity does not partition equally among the various CT transitions of a given

TABLE 2: Transition Moment Vector Directions of 1,2,4,5-Tetracyanobenzene Complexes with Methyl-Substituted Benzene Donors

donor	solvent	λ_{ex} (nm)^a	OD_{CT1}^{b}	OD_{CT2}	OD_{CT3}	$\|\phi\|$°^{c}
HMB	DCLE	446	1.0	^{d}	0	71
		404	0.9	^{d}	0.1	70
		355	0.1	^{d}	0.9	70
HMB	OCN	446	1.0	^{d}	0	70
		404	1.0	^{d}	0	69
		355	0.3	^{d}	0.7	63
PMB	DCLE	446	1.0	0	0	71
		404	0.9	0.1	0	70
		355	0.3	0.1	0.6	68
PMB	OCN	404	1.0	0	0	65
		355	0.6	0.2	0.2	61
DUR	DCLE	446	1.0	0	0	70
		404	0.9	0.1	0	70
		355	0.3	0.5	0.2	61
DUR	OCN	404	1.0	0	0	64
		355	0.3	0.5	0.2	59
MES	DCLE	404	1.0	^{d}	0	60
		355	0.9	^{d}	0.1	54
MES	OCN	355	1.0	^{d}	0	54

^{a} Excitation wavelength (nm). ^{b} Fractional contribution of the specified CT transition to the observed OD at the excitation wavelength. ^{c} Estimated error ± 2°. ^{d} For this donor CT1 and CT2 are degenerate such that OD_{CT2} is included in OD_{CT1}.

complex. Unfortunately, the magnitudes of the LE contributions cannot be determined directly from these measurements. Thus, TRLD spectroscopy was used to further explore the nature of the CT transitions.

TRLD Spectroscopy. Descriptions of TRLD spectroscopy and the methods of analysis of dichroic data have been published previously.[11−13,25,26] The analysis of dichroic traces allows the orientation factors for specific CT transitions to be calculated according to $K_i = OD_{\|}/(OD_{\|} + 2OD_{\perp})$. The orientation factors are related to the absolute angle, $|\phi_i|$, between the CT TMV excited and the TCNB radical anion TMV and the principal orientation factors K_Z, K_Y, and K_X as shown in Equation 2.

$$|\phi_i| = \tan^{-1}\sqrt{\frac{K_Z - K_i}{K_i - K_Y}} \qquad (2)$$

The principal orientation factors for the present case are $K_Z = 0.6$ and $K_Y = K_X = 0.2$, as required by photoselection theory.[25,26] Using these principal orientation factors, the relative angles between the transition moment vectors, $|\phi_i|$, were calculated for each complex. These values were collected in Table 2.

To determine how these angles relate to the molecular frame, knowledge of the individual TMV directions is required. The pure CT TMV will always be directed between the centers of charge density from the donor to the acceptor in accord with the two-state model.[6,7,11] The center of charge density and center of mass coincide for TCNB and all of the donors used except PMB, although equating the centers of mass and charge density for PMB introduces negligible additional uncertainty. The absorption spectrum of the TCNB radical anion has been studied experimentally[27] and using ZINDO/S calculations on the AM1 optimized geometry.[12] It has been determined that the TCNB radical anion TMV coincides with the long in-plane molecular axis of TCNB. The lowest energy LE of TCNB has also been examined and has been shown to have a TMV direction that also corresponds to the long in-plane axis of TCNB.[12,13] Thus, the angle ϕ, as depicted in Figure 1, will be equal to the angle between the observed CT TMV and the TCNB radical anion TMV only if excitation does not lead to a significant change in the orientation of the complex.

In a previous report,[11,12] a small topochemical change in the orientation of the complex was suggested based on the difference between the angles predicted using calculated structures and X-ray analyses of similar complexes and those obtained experimentally. For the present discussion it is reasonable to proceed under the assumption that excitation does not lead to a directed rotation of the complex and then describe the possible ramifications of this assumption later.

To evaluate the magnitude of the LE contribution to the observed CT transition, an estimate of θ is required. Consider the limiting case in which the LE does not contribute to the observed CT transition. In this case, $f_{LE} = 0$ and the angle θ is simply the complement of the angle measured using TRLD spectroscopy, again assuming relaxation of the excited state does not result in a rotation of the complex. A measured angle of $|\phi| = 70 \pm 2°$ has been reported for the HMB/TCNB complex in DCLE where intensity borrowing is known to be negligible.[11] Crystal structures and calculations yield similar ground-state geometries for all of the complexes used in this study, indicating that all of these complexes should have similar values of θ.[11] Excitation into the lowest energy CT band of the HMB/TCNB complex in OCN also gave $|\phi| = 70 \pm 2°$, suggesting that θ was not influenced on changing the solvent from DCLE to OCN.[13] The angle θ was therefore fixed at $\theta = 180° - 70° = 110°$ for all of the complexes studied in both solvents.

Values of ϕ were obtained experimentally using three excitation wavelengths, specifically 446, 404, and 355 nm. The band analysis of the absorption spectra in Figure 2 allows the contribution of each individual CT transition to the observed absorbance at any given excitation wavelength to be determined (Table 2). When a single CT band was excited, the measured angle $|\phi|$ describes the angle between that CT TMV and the TMV of the TCNB radical anion probed. All of the complexes included in this study can be excited exclusively into the CT1 transition using the appropriate excitation wavelength. Therefore, the CT1 TMV directions can be determined precisely from the analysis of the dichroic data.

For the DUR/TCNB complex in DCLE, 446-nm light excites only the CT1 transition. The analysis of the dichroic traces for this complex (Figure 4) leads to an orientation factor of $K_i = 0.248$ and a corresponding angle of $|\phi| = 70 \pm 2°$. This angle is identical to that observed for the HMB/TCNB complex in DCLE where LE mixing was shown to be insignificant. It follows that the CT1 transition of the DUR/TCNB complex in DCLE is also a pure CT transition with negligible contribution from LE. Similarly, negligible intensity borrowing is observed for the CT1 transitions of the HMB/TCNB complex in OCN and the PMB/TCNB complex in DCLE where the measured angles are also $|\phi| = 70 \pm 2°$. In contrast, excitation of the CT1 transition of the PMB/TCNB complex in OCN results in a value of $|\phi| = 65 \pm 2°$, suggesting that intensity borrowing does occur for this specific complex in this solvent. For the DUR/TCNB complex in OCN, and the MES/TCNB complex in DCLE and in OCN, the values of $|\phi|$ determined from the dichroic traces are 64°, 60°, and 54°, respectively. When these values of $|\phi|$ were plotted versus the transition energies, as shown in Figure 7 (empty boxes), a distinct trend was identified. The plot shows clearly that the measured angle $|\phi|$ decreases as the CT−LE transition energy difference decreases. This trend is consistent with the magnitude of LE intensity borrowing increasing, as indicated by the change in angle ϕ, as the CT−LE transition energy difference decreases.

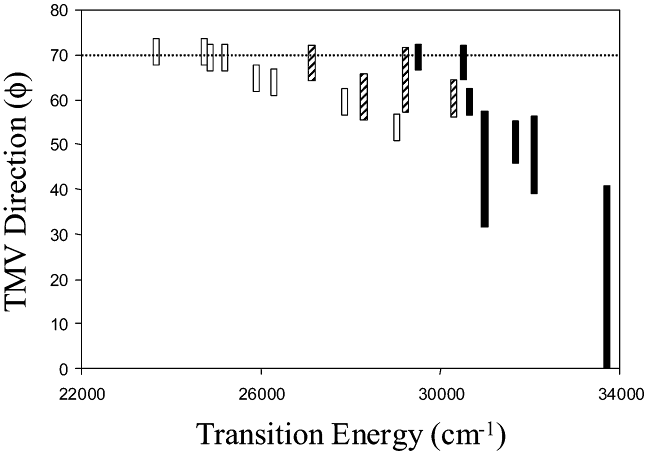

Figure 7. Plot of the TMV direction versus the transition energy for each group of CT transitions with CT1 transitions indicated by the empty boxes, the CT2 transitions by the hashed boxes, and CT3 transitions by the filled boxes. The length of each box is an indication of the uncertainty in the measured angle.

TABLE 3: Energies and Transition Moment Vector Directions for CT Transitions of 1,2,4,5-Tetracyanobenzene Complexes with Methyl-Substituted Benzene Donors

donor	solvent	$E_{CT1}{}^a$	$\phi_{CT1}{}^b$	$E_{CT2}{}^a$	$\phi_{CT2}{}^b$	$E_{CT3}{}^a$	$\phi_{CT3}{}^b$
HMB	DCLE	23680	71			29480	70
HMB	OCN	24860	70			30660	60
PMB	DCLE	24730	71	27150	70−66	30530	70−66
PMB	OCN	25880	65	28300	65−56	31680	56−48
DUR	DCLE	25190	70	29220	70−58	30990	58−32
DUR	OCN	26290	64	30320	64−57	32090	57−41
MES	DCLE	27880	60			33680	40−0
MES	OCN	29030	54			34830	n/a

[a] Energy of the absorption maximum of the specified CT transition given in cm^{-1}. [b] Transition moment vector angle for the specified CT transition. Estimated error ± 2°.

Precise determinations of the TMV directions for CT3 were possible for the HMB/TCNB complex in the two different solvents. The measured value of $\phi = 70 \pm 2°$ for this complex in DCLE was compared to $\phi = 60 \pm 2°$ for the same complex in OCN.[13] The decrease in angle in OCN compared to DCLE was accompanied by an increase in CT transition energy, a decrease in the CT−LE transition energy difference, and a larger contribution due to LE within the observed CT3 TMV.

The DUR/TCNB complex in DCLE has overlapping transitions at 404 and 355 nm. For overlapping transitions the measured value of $|\phi|$ will be a weighted average of the all of the TMV directions that contribute to the absorption. At 404 nm, 90% of the total absorbance of the complex is due to CT1 with CT2 being responsible for the remaining 10% based on the band shape analysis. At this excitation wavelength a measured angle $|\phi| = 70 \pm 2°$ was again observed. The CT1 TMV angle was assigned an angle of $\phi = 70°$ and therefore does not include a measurable LE contribution. The CT2 TMV angle may also be $\phi \sim 70°$, but it could be as low as $\phi_{CT2} \sim 50°$ without causing the observed angle to fall below the experimental error of 2°. When the same complex is excited at 355 nm, the measured angle falls to $|\phi| = 61 \pm 2°$.[12] At this wavelength, CT1 contributes 30% of the total absorbance, CT2 contributes 50%, and CT3 contributes the remaining 20%. It is now clear that CT2 or CT3, or possibly both, must contain a significant LE contribution. The uncertainties associated with the determinations of the spectral contributions and the measured angles do not allow precise values for the individual TMV directions to be obtained. However, an acceptable range of values for ϕ_{CT2} and ϕ_{CT3} can be established based on the following criteria. CT3 will always be closer in energy to the LE transition than CT2 for a given complex in a given solvent. CT3 should therefore include a larger LE contribution than CT2 because the probability of intensity borrowing increases as the energy difference between the transitions decreases. Similarly, because CT2 will always be closer in energy to the LE than is CT1, it too should always include a higher LE contribution than CT1. A lower limit for ϕ_{CT2} (and the upper limit for ϕ_{CT3}) is established when $\phi_{CT2} = \phi_{CT3}$ and an upper limit for ϕ_{CT2} (and the lower limit for ϕ_{CT3}) is established when $\phi_{CT1} = \phi_{CT2}$. Applying these conditions for the DUR/TCNB complex in DCLE gives acceptable values of the TMV directions when $\phi_{CT2} = 70° - 58°$ and when $\phi_{CT3} = 58° - 32°$. Similar considerations are used to establish acceptable ranges for the transitions of the DUR/TCNB complex in OCN and the PMB/TCNB complex in DCLE and OCN. These additional angles are listed in Table 3 and were also included in the plot in Figure 7.

The dependence of the intensity borrowing on the CT−LE transition energies within each group of transitions can now be compared. The plot in Figure 7 suggests that the onset of intensity borrowing occurs at different CT transition energies for each group of transitions. The angle ϕ starts to fall below 70° for the CT1 transitions (empty boxes) when the transition energies approach 26 000 cm^{-1}, whereas ϕ does not decrease until nearly 30 000 cm^{-1} for the CT3 transitions (filled boxes). As an example, the CT3 transition energy of the HMB/TCNB complex in DCLE is comparable to the CT1 transition energy of the MES/TCNB complex in OCN but the TMV angles are significantly different: $\phi_{CT3} = 70°$ for HMB/TCNB in DCLE versus $\phi_{CT1} = 54°$ for MES/TCNB in OCN. The emerging pattern suggests that the CT−LE energy gap dependence of intensity borrowing is different for the CT1 and CT3 transitions. The magnitude of intensity borrowing is not only dependent on the energy of the CT transition but also the character of that transition.

It is now possible to address the assumption of a directed, topochemical rotation of the complexes following excitation. In a previous report, θ was estimated based on available crystallographic data and on the results of calculated ground-state structures using several levels of theory.[11−13] A value of $\theta = 100 \pm 4°$ was adopted, which differs from the measured value by about 10°. It was proposed that a rapid structural change led to a topochemical rotation which was responsible for the ~10° discrepancy in all of the complexes examined, including the four of interest in this study. If a directed rotation in which all of the excited complexes follow a single reaction coordinate were to occur, all of the complexes would experience similar rotational movement and the experimentally observed TMV directions would reflect a contribution due to this rotation. Changing solvent from DCLE to OCN does not influence the ground state geometry and therefore it seems unlikely that the rotational motions would change significantly upon changing solvent. Therefore, all of the complexes, in both solvents, should experience the same rotational movement and the TMV directions determined in this report would all be underestimated by about 10°. The conclusions drawn from the data presented would still be valid.

Other causes of the difference in the predicted and observed values of θ cannot be ruled out. The absolute value of the angle ϕ will depend on the mechanism responsible for the observed discrepancy in specific, although currently unknown, ways. What is important in the context of the present report is that any mechanism used to describe the differences in the predicted and observed θ will not change the relationships between the reported values of ϕ. Thus, the conclusions drawn in this report would remain unchanged.

Conclusions

The influence of locally excited states on the absorption spectra of several CT complexes was investigated. Using a simple molecular orbital approach, the relative intensities of the individual CT bands within each absorption spectrum were determined. For TCNB complexes in DCLE and OCN, it was shown that the intensity of the CT transition increases as the oxidation potential of the donor increases. Furthermore, the absorption band ratios also increase as the CT transition energies are blue-shifted ~1150 cm^{-1} on going from DCLE to OCN. These observations serve as additional examples of the anomalous increase of CT oscillator strengths with increasing donor oxidation potential and support the use of a multistate model in which the contribution of LE states must be considered.

Further support for the necessity to include LE states when considering CT absorption spectra was obtained using time-resolved linear dichroism spectroscopy. The direction of the CT transition moment vector was used as a probe of the magnitude of LE intensity borrowing. The use of multiple excitation wavelengths allowed the individual CT transitions within each absorption spectrum to be analyzed and the partitioning of borrowed LE intensity into these transitions to be determined. It was shown that the magnitude of LE intensity borrowing is not only dependent on the energy difference between the CT and LE transitions, but is also dependent on the character of the CT transition.

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Supporting Information Available: Supporting Information includes sets of dichroic and magic angle traces of the decays at all three excitation wavelengths and in both solvents (Figures 1S−19S) in addition to the tabulated fit parameters obtained from the analysis of these traces (Table 1S). This information is available free of charge via the Internet at http://pubs.acs.org.

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