# Application of Time-Resolved Linear Dichroism Spectroscopy: Rapid Relaxation of Excited Charge Transfer Complexes

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Time-resolved linear dichroism spectroscopy has been used to study the charge-transfer complexes formed between methylated benzene donors and 1,2,4,5-tetracyanobenzene as acceptor. The angle between the charge-transfer absorption transition moment and the photochemically produced radical anion absorption transition moment, after relaxation, has been measured for several complexes. A simple theoretical model was used to interpret the measured values. This model correlated the extent of localized excitation mixed into the charge-transfer transitions with the results of time-resolved linear dichroism measurements. Furthermore, the comparison between the measured and predicted transition moment directions suggests that a minor geometry change occurs after excitation of these complexes. The observation of the relative transition moment vector of the initial state(s) for some of the complexes was also possible. In these cases, the initial transition moment vectors observed are not consistent with absorption due to the radical anion but are believed to originate from a different electronic state, presumable from an excited state of the CT complex. These results imply that the rapid relaxation process observed for these complexes must be electronic in nature and not purely geometric.

## Introduction

Time-resolved linear dichroism (TRLD) spectroscopy is a powerful technique that can be used to study molecular structure, solution dynamics, or molecular transformations.[1−5] A recent TRLD study of the charge transfer (CT) complex formed between hexamethylbenzene (HMB) and 1,2,4,5-tetracyanobenzene (TCNB) provided a partial description of the topochemistry of the rapid relaxation from an uncharacterized initial state (IS) to the relaxed contact radical ion pair (CRIP).[6] The first descriptions of this relaxation process appeared in a series of papers where a “delay in the formation of the charge-separated state” and a rapid relaxation of a Franck−Condon intermediate to the relaxed CRIP was observed.[7−12] The relaxation could be described as electronic or geometric in nature, or possibly a combination of these and other processes. There are significant differences between these possible descriptions. If the relaxation is electronic in nature, the relaxation and electron transfer processes occur simultaneously. If the relaxation is dominated by geometric relaxation, the electron transfer must precede relaxation. Thus, the characterization of the relaxation is of paramount importance to the understanding of the photochemical behavior of these complexes.

The results of a TRLD study on the HMB/TCNB complex indicated that the complex does experience a minor geometry change after excitation.[6] Unfortunately, direct observation of the IS was not possible due to the limited time resolution of the apparatus. Consequently, the possibility that the relaxation process is due to changes in electronic states, which may be accompanied by a small change in geometry, could not be addressed.

To date the only direct observations of the IS include the broadening of absorption spectra[7−11,13] and a blue shift in emission spectra[12] relative to those observed for the relaxed CRIP. Absorption and emission spectra of CT complexes are generally broad and featureless with significant band overlap. Observations of small differences in band shape and position are open to multiple explanations, and definitive conclusions are difficult to justify. While there is mounting evidence, which has been obtained from various experimental sources, that excitation does cause a change in the geometry of the complex,[7−27] an electronic component to the relaxation cannot be ruled out.

Mulliken presented the currently accepted theory of CT complex formation in the early 1950s.[28−30] The ground state of the CT complex was depicted as a mixture of the wave functions for nonbonded interactions and of the ion-pair state. According to this model, the excitation of the complex should result in direct transfer of an electron from the donor to the acceptor. It has been proposed that the localized excited states of the acceptor or donor may also play a significant role in these absorptions, and therefore an expansion of the simple two-state model is required. Our studies of the CT complexes formed between TCNB as acceptor and methylated benzene donors have shown conclusively that the two-state model is not uniformly applicable to these CT complexes.[31] Significant intensity borrowing from the localized excitation band (LE) of the acceptor was proven[31] in the case of several TCNB complexes and has been proposed for many other types of CT complexes as well.[32,33]

There are three goals for this report. First, we expand on our previous study of the HMB/TCNB complex and include the measurement of the relative transition moment vector (TMV) directions of several CT complexes where the LE contribution to the absorption is significant. A simple method of estimating the TMV directions based on the analysis of ground state absorption spectra is presented. Second, the agreement between the estimated TMV directions and the measured values allows

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a partial description of the topochemical change associated with the relaxation process and therefore places restrictions on the possible relaxation mechanisms. Third, the topochemical constraints on the relaxation mechanism are shown to preclude geometric relaxation as the sole cause of the dichroism change that is associated with the relaxation process. Instead, these results favor an electronic relaxation mechanism as opposed to a purely geometric relaxation.

## Experimental Section

**Methods.** The picosecond pump−probe apparatus used in these experiments has been described in detail elsewhere.[34] Solutions of TCNB and methylated benzene donors (both $10^{-2}$ M) were placed in a quartz cuvette with 1,2-dichloroethane (DCLE) as solvent. At these concentrations the samples consist mainly of 1:1 complexes, and the formation of 2:1 complexes has been shown to be negligible.[31] Ground state absorption spectra were obtained using a Beckman DU 640 UV−vis spectrometer. For time-resolved measurements, the samples were stirred using a magnetic stirrer and 200 pulse pairs were averaged for each delay setting. The resultant decay traces were fit using a simplex computer routine to find the nonlinear least squares minimum of the error between a model function and the observed data trace.

The calculation of structures and electronic properties of the complexes followed standard procedures using HyperChem[35] release 5.0 on a 420 MHz IBM-compatible personal computer equipped with a Pentium II processor.

**Materials.** TCNB was purchased from Aldrich Chemical Co. and was purified by passing it through silica gel twice with dichloromethane as the eluting solvent, followed by recrystallization from chloroform twice. Pentamethylbenzene (PMB) and durene (DUR: 1,2,4,5-tetramethylbenzene) were purchased from Aldrich Chemical Co. and were purified by passing them through alumina with DCLE as the eluting solvent, followed by recrystallization from ethanol. *p*-Xylene (PXY) was purchased from J. T. Baker and recrystallized at low temperature from chloroform. Mesitylene (MES: 1,3,5- trimethylbenzene) was purchased from J. T. Baker and was purified by passing through activated alumina and recrystallized from chloroform. In all cases, baseline absorbance was monitored and purification was continued until no further improvements in baseline were observed. DCLE and toluene (TOL) were purchased from Sigma as HPLC grade and were used without further purification.

## Results

The structures and electrochemical potentials[36] of the acceptor and donors used in this study are shown in Chart 1. The ground state absorption spectra of the methylated benzene/TCNB complexes, free from residual absorbance due to unbound acceptor and donor, are shown in Figure 1. These spectra were obtained by mixing stock solutions of acceptor and donor (ca. $2 \times 10^{-2}$ M) at 25 °C in DCLE. Contributions due to the individual, unbound acceptor and donor have been subtracted using the mass balance relationship and the previously published association constants.[37] Analysis of these spectra in terms of simple molecular orbital models has been reported.[31] This analysis showed that the relative positions of the complex absorption bands could be accurately predicted and that the fractional decrease in localized absorption intensity could also be assessed.

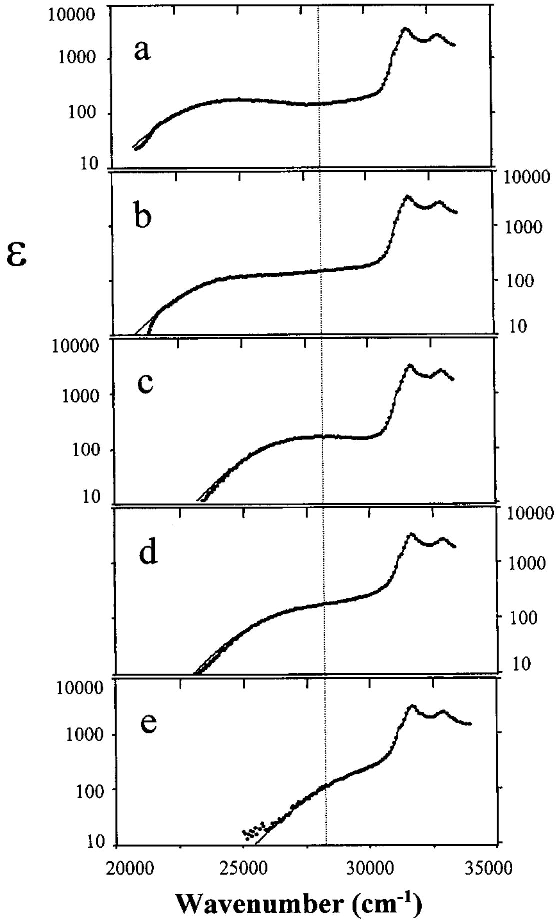
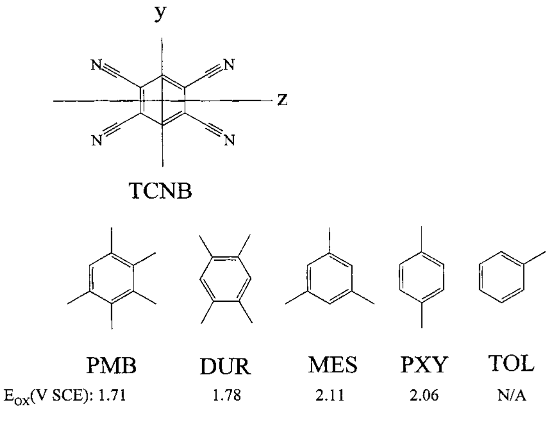


**Figure 1.** Absorption spectra of the methylated benzene/TCNB complexes obtained by mixing stock solutions of acceptor and donor (ca. $2 \times 10^{-2}$ M) at 25 °C in 1,2-dichloroethane where (a) PMB/TCNB, (b) DUR/TCNB, (c) MES/TCNB, (d) PXY/TCNB, (e) TOL/TCNB. The spectra of the unbound acceptor and donor were subtracted assuming association constant for complex formation from ref 36. The dashed line indicates the excitation wavelength for time-resolved studies of 28 200 cm$^{-1}$ (355 nm).

**CHART 1**



Picosecond pump−probe transient absorption spectra were obtained at very short time delays ($t \sim 0$ ps) and at relatively long delays ($t \sim 100$ ps or greater) for all of the complexes studied. A set of absorption spectra for the TOL/TCNB complex is shown in Figure 2. An absorption band with a maximum at 468 nm that has been attributed to TCNB radical anion was observed after irradiation of all complexes studied.[7−9,38] The time-resolved absorption spectrum obtained after ca. 100 ps does not change significantly from complex to complex, indicating that if the radical cations absorb in this region, their absorption must be weak in comparison to that due to the radical anion. For several of the weaker complexes studied, including the TOL/

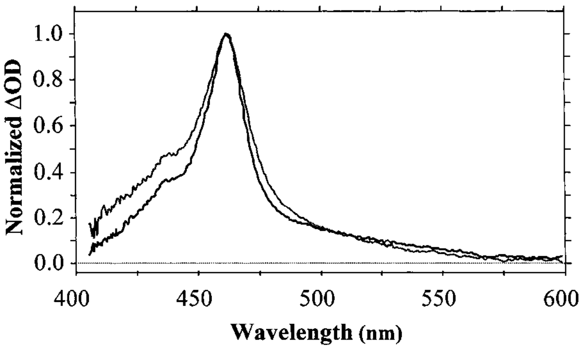


**Figure 2.** Picosecond pump−probe transient absorption spectrum obtained at $t = 0$ (gray line) and 100 ps (solid line) after 355-nm excitation of the TOL/TCNB CT complex. Spectra are normalized to the maximum absorption. The band with a maximum at 468 nm has been assigned previously to TCNB radical anion. After 100 ps of delay, the spectra no longer change shape.

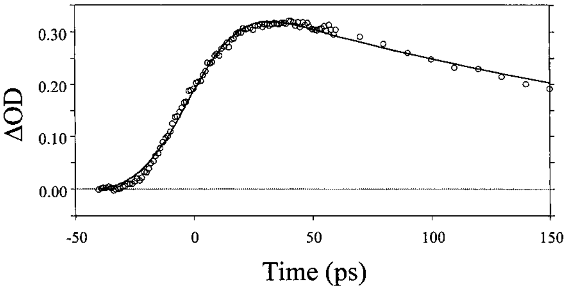


**Figure 3.** Picosecond pump−probe transient absorption decay trace obtained using 355-nm excitation of the PMB/TCNB CT complex and observed at 468 nm polarized at the magic angle (open circles). The line indicates the best fit of the observed trace using a single-exponential decay convoluted with a 35 ps instrument response.

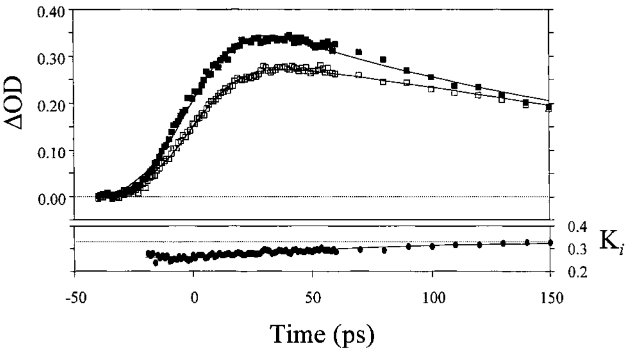


**Figure 4.** Top panel: Picosecond pump−probe transient absorption decay traces obtained using 355-nm excitation of the PMB/TCNB CT complex and observed with 468-nm light polarized parallel (open boxes) and perpendicular (filled boxes) to the excitation. The lines show the best fit of the individual dichroic traces assuming a single-exponential decay component to the dichroism decay in addition to the parameters obtained by fitting the magic angle trace (Figure 3). Bottom panel: Plot of the orientation factor as a function of time, calculated using the above dichroic traces (filled circles). The solid line indicates the fit of orientation factor based on the parameters obtained from the fit of the individual traces above. The dashed line indicates a $K$ value of 0.333.

TCNB complex shown in Figure 2, a rapid sharpening of the absorption band centered at 468 nm was observed at short time delays (less than ca. 100 ps), confirming the earlier reports of this phenomena.[7−9,13,38]

The decay trace for the PMB/TCNB CT complex recorded at 468 nm after excitation with 355-nm light is shown in Figure 3. The analysis of this trace follows the previously published report on the HMB/TCNB complex.[6] The excitation used was linearly polarized along the laboratory *Z*-axis, and the probe beam was linearly polarized at 54.7° with respect to the laboratory *Z*-axis, i.e., at the magic angle.[39] Because of the angle between the pump and probe beam polarizations, the effect of the anisotropic distribution of excited state orientations is not observed in these traces. The shape of the decay trace is exclusively due to the formation and decay of the ion pair convoluted with the instrument response function. The extinction coefficient of the radical anion at 468 nm is several orders of magnitude larger than the ground state complex at this wavelength, and the fluorescence quantum yield of these complexes is very low (ca $10^{-4}$ or less) with emission maxima at longer wavelengths. Thus, ground state bleaching and stimulated emission will not contribute to the transient decays observed. The currently accepted model of the dynamics of photochemically produced ion pairs requires the ion pair decay to be fit to a two-exponential function with an offset.[38] In an effort to reduce the number of adjustable parameters, the magic angle trace was analyzed as a single-exponential decay.[40] The rapid relaxation process for this specific complex has not been reported, although it can be estimated to be 5−6 ps in DCLE based on the results for related complexes.[41] Such a rapid relaxation cannot be resolved by our apparatus and need not be included in the kinetic scheme. The fit of the data is included in Figure 3 (solid line) and the fitting parameters are included in the Supporting Information (Table S1).

Two additional decay traces were recorded and are shown in Figure 4. In the first trace (open circles) the probe beam was linearly polarized along the laboratory-*Z* axis (i.e., parallel to the excitation), and in the second (filled circles) 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 shown in Figures 3 and 4 were collected under identical conditions. The shape of the traces shown in Figure 4 is due to a composite of the ion pair decay, and the randomizing rotations of the ion pairs in solution superimposed on the instrument response profile of the laser system. The dichroic traces were fit assuming a single-exponential anisotropy component in addition to the parameters obtained from the fit of the magic angle data. Thus, both dichroic traces were simultaneously fit using a total of three adjustable parameters, i.e., a common rate constant and two independent preexponential factors. The fitted line is included in Figure 4 (solid line) and the fitting parameters are included as Supporting Information (Table S1).

Similar traces were obtained for the DUR/TCNB CT complex (Supporting Information Figures S1 and S2). For this complex, as was the case for the HMB and PMB complexes, the relaxation is again too short to be resolved by our apparatus.[9,41] The magic angle trace was fit to a single exponential decay, and both dichroic traces were simultaneously fit using one common rotational time constant and two independent preexponential factors, in addition to the predetermined magic angle parameters. The fitting parameters are included as Supporting Information (Table S1).

The MES/TCNB complex was also studied, but the decay traces showed surprisingly little dichroism (Supporting Information Figures S3 and S4). Either the photoselection process was inefficient in this case or the angle between the relaxed state TMV and the ground state absorption moment is close to the magic angle. The latter choice seems to be the most reasonable based on the trend emerging from the analysis of this family of complexes. Because of the absence of dichroism in this sample, the rotational time constant could not be evaluated.

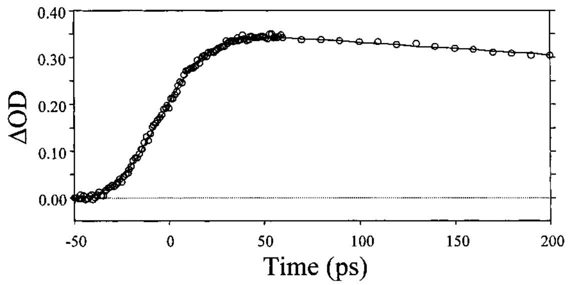


**Figure 5.** Picosecond pump−probe transient absorption decay trace obtained using 355-nm excitation of the PXY/TCNB CT complex and observed at 468 nm polarized at the magic angle (open circles). The line indicates the best fit of the observed trace using a two-exponential function (rapid growth followed by slow decay) convoluted with a 35 ps instrument response.

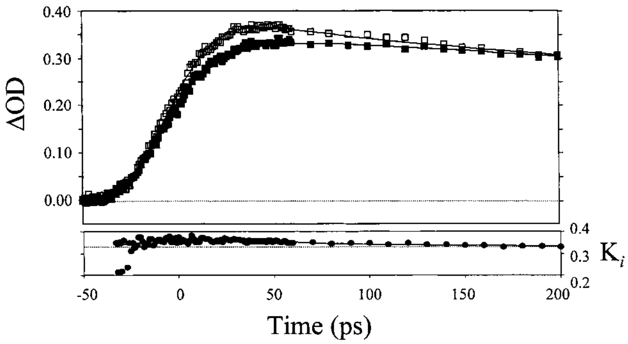


**Figure 6.** Top panel: Picosecond pump−probe transient absorption decay traces obtained using 355-nm excitation of the PXY/TCNB CT complex and observed with 468-nm light polarized parallel (open boxes) and perpendicular (filled boxes) to the excitation. The lines show the best fit of the individual dichroic traces assuming a two-exponential decay component to the dichroism in addition to the parameters obtained by fitting the magic angle trace (Figure 5). Bottom panel: A plot of the orientation factor as a function of time, calculated using the above dichroic traces (filled circles). The solid line indicates the fit of orientation factor based on the parameters obtained from the fit of the individual traces above. The dashed line indicates a *K* value of 0.333.

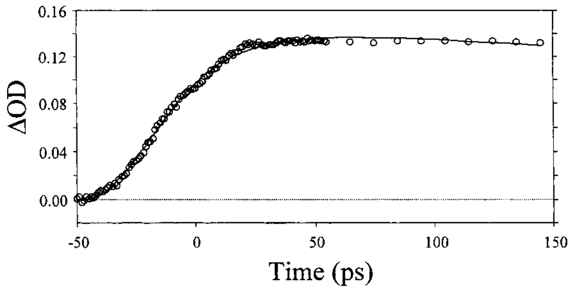


**Figure 7.** Picosecond pump−probe transient absorption decay trace obtained using 355-nm excitation of the TOL/TCNB CT complex and observed at 468 nm polarized at the magic angle (open circles). The line indicates the best fit of the observed trace using a two-exponential function (rapid growth followed by slow decay) convoluted with a 35 ps instrument response.

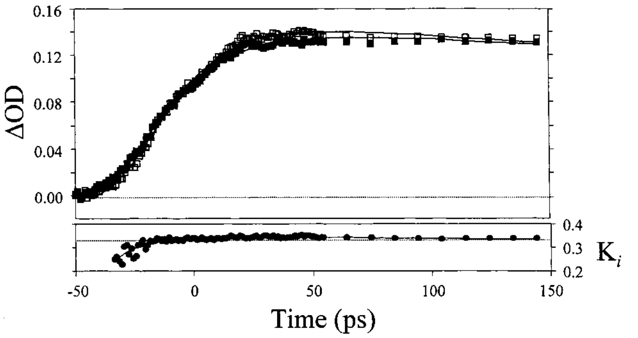


**Figure 8.** Top panel: Picosecond pump−probe transient absorption decay traces obtained using 355-nm excitation of the TOL/TCNB CT complex and observed with 468-nm light polarized parallel (open boxes) and perpendicular (filled boxes) to the excitation. The lines show the best fit of the individual dichroic traces assuming a two-exponential decay component to the dichroism in addition to the parameters obtained by fitting the magic angle trace (Figure 7). Bottom panel: Plot of the orientation factor as a function of time, calculated using the above dichroic traces (filled circles). The solid line indicates the fit of orientation factor based on the parameters obtained from the fit of the individual traces above. The dashed line indicates a *K* value of 0.333.

The magic angle trace and the set of dichroic traces for PXY/TCNB are shown in Figures 5 and 6, respectively. It was immediately apparent that these traces would be more difficult to interpret. The measured dichroism increases, as has been the trend, but the decay of the dichroism was no longer adequately fit to a simple single exponential function. The rapid relaxation for this complex is now slow enough that our laser system can observe the effect directly, although not completely resolve it with any accuracy. To fit these data the model must contain at least three dynamic contributions: the rapid relaxation, molecular rotation and the ion pair decay. The molecular rotation time constant was fixed by assuming the same time constant as obtained for the HMB, PMB, and DUR complexes. Taking the average value gives $\tau_{\mathrm{OR}} = 60$ ps. This leaves the ion decay and rapid relaxation rate constants undetermined. The magic angle data and both dichroic traces were simultaneously fit to a three exponential function. In this function the $\tau_{\mathrm{OR}}$ value was fixed; the remaining rate constants were common to all three data sets and the preexponential terms were left unrestricted. The estimate of the time constant for the rapid relaxation obtained was 11 ps, in excellent agreement with that obtained for this complex previously.[9,41] The fitted line is included in Figures 5 and 6 (solid line) and the fit parameters obtained are included as Supporting Information (Table S1).

The magic angle and dichroic traces for the toluene complex are shown in Figures 7 and 8, respectively. It is unmistakable that these traces are made up of at least three components. Proceeding as above, the molecular rotation time constant was again fixed at $\tau_{\mathrm{OR}} = 60$ ps. The ion decay rate and the rapid relaxation rate constants were obtained by fitting the magic angle decay trace and both dichroic traces simultaneously to a three-exponential function with one exponent held constant. The estimate of the time constant for the rapid relaxation obtained is 22 ps, in excellent agreement with that obtained previously for this complex.[9] The fitted line is included in Figures 7 and 8 (solid line) and the fitting parameters are included as Supporting Information (Table S1).

## Discussion

**Molecular Reorientation, $\tau_{\mathrm{OR}}$.** Thus far it has been assumed that the time course of the observed dichroic effect is related to the reorientation of the sample through rotational diffusion. It has been shown that the average molecular rotational diffusion rate constant can be determined by Debye−Stokes−Einstein diffusion theory.[42] The calculated value, which assumes stick boundary conditions and a spherical probe shape, was approximately 90 ps in 1,2-dichloroethane at room temperature.[6] The experimental value of the time constant obtained by fitting the data was $\tau_{\mathrm{OR}} = 60 \pm 15$ ps. The agreement between the calculated and observed rotation time constants supports the assumption that the eventual loss of orientation was due to random rotational motion of the complex. On the other hand, the second, shorter time constant observed in some of the TRLD experiments must not be due to random motions. Anisotropic rotation of excited molecules has been observed and could potentially account for the shorter time constant. However, the degree of anisotropy required in the present case is excessively large, particularly for a complex that is nearly spherical in shape. Additionally, the fact that this anisotropic event is also recorded in the magic angle traces precludes the possibility of simple rotational anisotropy. Instead, this second time constant must reflect an additional, directed event that influences the TMV direction. Thus, the dynamics of the rapid relaxation is described by the second time constant, and topochemical information about this process can be extracted from the magnitude of the dichroic effect. A similar observation was reported for the tetracyanoethylene/pyrene CT complex, and the interconversion between different ion pair structures was proposed.[19]

**TRLD.** The anisotropic nature of light absorption is used to produce partially oriented samples of excited states by a process known as photoselection.[1−5] If such samples are subsequently probed with a second beam of linearly polarized light of wavelength $\lambda$, before the samples have time to reorient through random motion, the measured absorbance obtained when the electric vector of the probe beam is parallel ($OD_{Z(\lambda)}$) compared to the absorbance perpendicular ($OD_{Y(\lambda)}$) to the laboratory $Z$-axis may be different. The ratio of these absorbances at wavelength ($\lambda$), at any time, is defined as the dichroic ratio, $d_\lambda = OD_{Z(\lambda)}/OD_{Y(\lambda)}$. It is particularly convenient to describe uniaxial orientation in terms of orientation factors, as opposed to other, perhaps better known, order parameters.[4,5,43] Assuming the sample is made up of linear absorbers with no overlapping transitions, the orientation factor for the $i$th transition is obtained from the dichroic ratio using the expression $K_i = d_\lambda/(d_\lambda + 2)$. The magnitude of $K_i$ reflects both the extent of alignment of the sample and the angle between the initial absorption TMV and the probe TMV within the molecular frame. The degree of alignment of the sample is reflected in the magnitude of the mutually orthogonal principal orientation factors, $K_X$, $K_Y$, $K_Z$. Assuming the bleaching of the ground state is negligible, the principal orientation factors for linear absorbers are given by photoselection theory: $K_Z = 0.60$ and $K_X = K_Y = 0.20$.[4,5] Once the principal orientation factors are established, eq 1 allows the absolute value of the angle between the excitation TMV and the probe TMV to be calculated.

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

The ODs expected for the relaxed state, in the absence of random rotational motion and rapid relaxation, can be calculated from the fit parameters by assuming $t = 0$. The orientation factor for the $z$-polarized transition of TCNB was than calculated, and eq 1 was used to determine the absolute values of the angles, $|\phi_{\mathrm{CRIP}}|$, between the CT TMV and the CRIP TCNB radical anion TMV for all of the complexes studied. The $|\phi_{\mathrm{CRIP}}|$ values obtained are collected in Table 1.[44]

It is appropriate to take stock of the general trends observed in the data to help organize the remaining discussion. The trend in the TMV angles for this series of complexes decreases with donor according to HMB ≈ PMB > DUR > MES > PXY > TOL. Clearly, $|\phi_{\mathrm{CRIP}}|$ varies with the electron donating ability of the donor. The MES complex appears to be out of order if the common practice of basing donating ability on oxidation potential is used (Chart 1). Specifically, the reported oxidation potential of MES falls between that of PXY and TOL, not between DUR and PXY. The reason for the reversal of MES and PXY is not clear, but the same reverse order was observed for the magnitude of the association constants,[37] the position of the $\lambda_{\mathrm{MAX}}$ of the CT band,[31] as well as for the gas-phase oxidation potentials.[45]

**TABLE 1: Transition Moment Vectors for the Charge Transfer Complexes between Methylated Benzene Donors and 1,2,4,5-Tetracyanobenzene**

| donor | $f_{\mathrm{LE}}$[a] | $\lvert\mathbf{M}_{\mathrm{MIX}}\rvert$[b] | $\lvert\mathbf{M}_{\mathrm{MIX}}\rvert_{\mathrm{CALC}}$[c] | $\lvert\phi_{\mathrm{CRIP}}\rvert$[d] | $\phi_{\mathrm{CALC}}$[e] |
|---|---|---|---|---|---|
| HMB[f] | 0.000 | $1.5 \times 10^{-30}$ | $1.5 \times 10^{-30}$ | 70 | 80 |
| PMB | 0.000 | $1.7 \times 10^{-30}$ | $1.5 \times 10^{-30}$ | 68 | 80 |
| DUR | 0.008 | $1.6 \times 10^{-30}$ | $1.6 \times 10^{-30}$ | 61 | 66 |
| MES | 0.018 | $1.3 \times 10^{-30}$ | $1.7 \times 10^{-30}$ | 54 | 60 |
| PXY | 0.025 | $1.8 \times 10^{-30}$ | $1.8 \times 10^{-30}$ | 46 | 56 |
| TOL | 0.060 | $1.9 \times 10^{-30}$ | $1.9 \times 10^{-30}$ | 48 | 53 |

[a] $f_{\mathrm{LE}}$ is the fraction of the LE transition moment presumed to be coupled with the CT transition. The values shown are based on the measured spectra from ref 31. [b] The average value of $|\mathbf{M}_{\mathrm{MIX}}|$ obtained by spectral integration of the first two bands in the CT spectrum in units Cm. The values shown are based on the results of ref 31. [c] The magnitude of $|\mathbf{M}_{\mathrm{MIX}}|$ obtained using eq 2 according to the vector addition scheme shown in Figure 9 in units of Cm (for more detail please see text). [d] The measured angle between the ground state mixed transition moment vector and the TCNB aromatic ring (after relaxation). [e] The predicted angle between $\mathbf{M}_{\mathrm{MIX}}$ and the TCNB molecular $z$-axis. [f] The HMB/TCNB data was taken from ref 6.

It is also interesting to note that the extent of localized excitation (LE) borrowing in the CT band and the rate of the rapid relaxation process also follow the reverse order. This apparent correlation suggests that the TMV angles, the LE intensity borrowing and the occurrence of relatively slow relaxation rates may be related. To test this hypothesis, the TRLD data were analyzed in terms of a simple theoretical model that was used to predict the directions of the CT absorption TMV and the CRIP TMV and therefore the angle between them. These predicted angles were then compared to the measured $|\phi_{\mathrm{CRIP}}|$ angles, and a description of the topochemical change due to the relaxation was obtained.

**Analysis of $\phi_{\mathrm{CRIP}}$.** At this point we have no information about how $|\phi_{\mathrm{CRIP}}|$ relates to the molecular frame. We must first describe the possible structures of the ground state complexes and then predict the relevant TMV directions based on theoretical considerations. The TRLD results can then be described in terms of the geometry of the CRIP relative to the starting CT complex and the relaxation of the excited state.

Mulliken theory gives insight into the possible structures and TMV directions for ground state complexes.[28−30,33] A significant test of the Mulliken two-state model has been published where the absorption spectra of charge transfer complexes were examined.[31] The appearance of multiple new absorption bands, the trend in the observed oscillator strength of the CT transitions, and decrease in intensity of the LE within the complex spectrum all require significant expansions of the simple two-state model. Multiple new CT absorption bands are frequently encountered and their appearance has been explained in terms of multiple ion pair states participating in CT interactions. The relative positions of these bands were accurately predicted based on the gas phase ionization potentials of the donors and the electron affinity of the acceptor. Excellent agreement between the predicted and observed spectra was achieved.[31] The integrated absorption intensities (oscillator strengths) of the localized bands within each CT complex spectrum were also measured. A decrease in localized excitation oscillator strengths implicated intensity borrowing by the CT transition. These measurements showed that an increased contribution of the LE within the CT absorption bands is observed as the donor strength decreased.

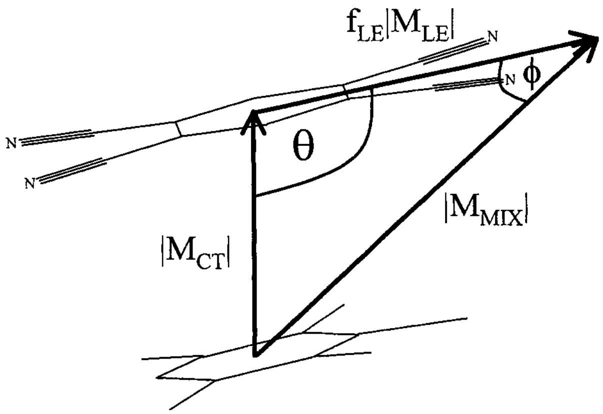


**Figure 9.** Diagram depicting the influence of the LE TMV on the CT TMV and the angle $\phi$. The addition of a component of $M_{LE}$ to $M_{CT}$ results in the observed TMV $M_{MIX}$.

The picture that emerged from the analysis of the CT spectra reveals that the CT transition is not completely explained by the two-state model but must include significant LE contributions.[44] A vector addition scheme, where the pure CT transition moment ($\mathbf{M}_{\mathrm{CT}}$) and the contribution of the LE transition moment ($f_{\mathrm{LE}_i}\mathbf{M}_{\mathrm{LE}}$), will be required to account for the LE influence on the observed transition moment ($\mathbf{M}_{\mathrm{MIX}}$).[46] Such a scheme, based solely on vector addition under the assumption of minimal perturbation of the individual transition moments, is depicted in Figure 9. Numerical evaluation of $\mathbf{M}_{\mathrm{MIX}}$ for the specific complex *i* was accomplished using eq 2:

$$|\mathbf{M}_{\mathrm{MIX}_i}|^2 = |\mathbf{M}_{\mathrm{CT}_i}|^2 + f_{\mathrm{LE}_i}(|\mathbf{M}_{\mathrm{LE}}|)^2 - 2(f_{\mathrm{LE}_i})^{0.5}|\mathbf{M}_{\mathrm{CT}_i}||\mathbf{M}_{\mathrm{LE}}|\cos(\theta_i) \quad (2)$$

where, $\mathbf{M}_{\mathrm{CT}i}$ is the pure CT transition moment anticipated for complex *i* due exclusively to CT interactions, $\mathbf{M}_{\mathrm{LE}}$ is the transition moment for the LE of TCNB, $f_{\mathrm{LE}_i}$ is the fraction of the LE intensity incorporated into the specific mixed transition, and $\cos(\theta_i)$ is the cosine of the angle between the pure CT TMV and the LE TMV for the complex *i*.

Two predictions can be made based on the application of this model. First, the $\mathbf{M}_{\mathrm{MIX}}$ values should increase for the poorer donors as intensity borrowing from the LE increases, assuming the pure CT transition moment remains relatively constant. This prediction appears to be qualitatively correct for this series of complexes[31] and reports of this phenomenon in other families of complexes have also appeared.[32,33] The model also predicts that the angle between $\mathbf{M}_{\mathrm{MIX}}$ and the TCNB long in-plane axis, $\phi_{\mathrm{CALC}}$, will decrease as the LE contribution increases. To test this prediction, insight into the nature of the relaxation process is required to directly compare the $\phi_{\mathrm{CALC}}$ angles and the measured $|\phi_{\mathrm{CRIP}}|$ values.

It is of interest to see if quantitative agreement between the predictions based on eq 2 and experimental values can be achieved. To make such a comparison, the parameters $\mathbf{M}_{\mathrm{LE}}$, $\mathbf{M}_{\mathrm{CT}_i}$, $f_{\mathrm{LE}_i}$, and $\cos(\theta_i)$ must be numerically evaluated based on independent measurements.

The magnitude of $\mathbf{M}_{\mathrm{LE}}$ is obtained by integrating absorption intensity of free TCNB in DCLE.[45] Numerical evaluation results in a value of $|\mathbf{M}_{\mathrm{LE}}\ | = 4.5 \times 10^{-30}$ Cm (or 1.34 D). The LE, which is of $\pi-\pi^*$ character, is required by symmetry to be in the plane of the TCNB aromatic ring. ZINDO/S calculations on the AM1 optimized geometry show that the transition dipole is directed along the molecular *z*-axis. The weak interactions between the acceptor and donor in the ground state are unlikely to cause significant perturbation of this relatively strong transition.

Detailed analysis of the remaining quantities requires knowledge of the ground state structure in addition to an understanding of the interaction between the various states responsible for the multiple absorption bands and a far more rigorous evaluation of the absorption spectra than is currently possible. It is not clear that current theories, at any level, would be able to predict these quantities with accuracy. To progress from this point we first admit that we may not be able to determine the quantities $f_{\mathrm{LE}_i}$ and $\cos(\theta_i)$ with accuracy, regardless of the computational force we apply. Instead we realize that the best we can do is offer estimated values on the basis of simple models and include a discussion of the uncertainty in the evaluated quantities. Indeed, the estimated values may not be as inaccurate as it might at first seem.

Analysis of the ground state absorption spectra of these complexes concluded that at least four new transitions were responsible for the observed absorption.[31] It was found that a minimum of two transitions contribute significantly to the absorption at the wavelength used to excite the samples (355 nm as indicated in Figure 1). Thus, the observed orientation, and therefore the angle, cannot be due to a single TMV but is instead due to the weighted average of several possible contributions. In effect, the experimentally determined angle must also reflect the average value of all possible outcomes. While this is unfortunate in terms of finding the individual contributions from each transition, we have already accepted that the individual contributions are beyond our present capability and that average values are the best that we expect. Thus the inability to deconvolute all of the individual contributions is no longer a concern.

The magnitude of $\mathbf{M}_{\mathrm{CT}}$ was estimated by averaging the integrated intensity of the two lowest energy bands in both the HMB and PMB complexes. It has been shown that the sum of the intensities for the first two bands is nearly constant for both of these complexes and that the observed absorptions are likely to be pure CT in nature.[31] Furthermore, both of these bands are excited at the laser wavelength for all of the complexes used in this study. Therefore, instead of trying to separate the individual contributions we will simple use the average values. Numerical evaluation results in a value of $|\mathbf{M}_{\mathrm{CT}}| = 4.8 \times 10^{-30}$ Cm (or 1.45 D).

The angle, $\theta$, can be estimated from the ground state geometry as was described in detail in our previous study of the HMB/TCNB complex.[6] Technically the position of the center of charge density of the donor is required, but it will be assumed that the center of charge density and the center of mass coincide for all of the donors used. Even for the non-centrosymmetric donors PMB and TOL, this assumption involves negligible additional uncertainty. The problem then reduces to knowing the ground state structures of the complexes of interest. Crystal structures of the HMB[48a] and MES[48b]/TCNB complexes, as well as several related complexes,[49] indicate that these complexes form offset sandwich structures, with the two $\pi$ planes approximately parallel and separated by ca. 3.5 Å. This separation corresponds to an offset along the molecular *x*-axis of 3.5 Å. Offsets in both *z*- and *y*-directions are also observed in all cases. Calculations at various levels qualitatively agree with these structures, although in several cases multiple ground state structures that differ in the magnitude of the *z*- and *y*-offsets were also predicted. Our analysis also agrees with the previously published calculated structures of the TOL/TCNB complex.[14] Instead of assuming a single structure for these complexes, it was preferable to allow the separation to vary between 3.3 and 3.9 Å, the *z*-axis offset to vary between 0.3 and 0.9 Å, and the *y*-axis offsets to vary between 0 and 0.7 Å. Rotation of the donors with respect to their out-of-plane axes can be shown to be inconsequential to the determination of $\cos(\theta_i)$.[50] Thus, the centers of mass of all donors are expected to fall within the cube defined by a diagonal between the points (3.9, 0, 0.35) and (3.5, 0.7, 0.9). All possible orientations of the donors within this cube will be considered in the determination of the TMV directions. Hence the angle $\theta_i$ varies between 84 and 76° for all geometries under consideration.[51] This range of values is also consistent with that expected based on spectroscopic analysis of single crystals of related complexes.[49] A value of $\theta_i = 80° \pm 4°$ will be assumed in the remaining discussion.

The last quantity needed is $f_{\mathrm{LE}}$. The analysis of the ground state absorption spectrum of the complex yields the magnitude of the total intensity borrowed but gives no indication of the partitioning of this intensity among the various CT transitions. Here again it seems impossible to predict the separate components to determine the influence of the LE on any one of the transitions individually. Since the transitions are relatively close in energy, it seems reasonable to assume equal partitioning of the LE intensity among all four of the new transitions.

With estimates of all of the required parameters in hand, it is now a relatively simple matter to calculate the angle between $\mathbf{M}_{\mathrm{MIX}}$ and molecular *z*-axis, $\phi_{\mathrm{CALC}}$, and the absolute magnitudes of the mixed transition moment, $|\mathbf{M}_{\mathrm{MIX}}|$. The individual parameters are collected in Table 1 along with the values predicted based on the application of eq 2.

Comparison of the predicted and measured values of $\phi$ reveals that excellent agreement in both the magnitudes and relative TMV directions was achieved based on this simple model and a clear choice in the sign of $\phi_{\mathrm{CRIP}}$. Based on this choice, the positive values of $\phi_{\mathrm{CRIP}}$, as depicted in Figure 9, will be adopted. It is noteworthy that the calculated angles are uniformly larger than the experimentally determined angles. Recall that $\phi_{\mathrm{CALC}}$ was taken to be the average angle between $\mathbf{M}_{\mathrm{MIX}}$ and the molecular *z*-axis. This angle corresponds to the angle expected between $\mathbf{M}_{\mathrm{MIX}}$ and the TCNB radical anion absorption in the absence of influences due to relaxation. On the other hand, $\phi_{\mathrm{CRIP}}$ depicts the angle after relaxation from the IS to the CRIP. It is possible that this small difference in angle may reflect a change in geometry after excitation of the complex. Such a change could cause an overall rotation of the complex and therefore change the observed angle, which we have defined as a topochemical change to the observed orientation.[52]

The present measurements do not allow the complete topochemical change to be described in detail because the complete set of Euler angles is not accessible. Furthermore, if several relaxation pathways are active, the weighted average value of all possible topochemical angles is observed. Notice that even random rotational motion with infinite reaction paths can also be described as a rotation through a single angle. Thus, detailed analysis of the topochemical change requires knowledge of the reaction mechanism(s) responsible for the observed rotation. There are a few examples where the average orientation of photochemical products has been analyzed in terms of the orientation of the starting materials and the mechanism for the photochemical reaction,[19,53−56] including our earlier report on the HMB/TCNB complex.[6]

It follows that the difference between the $\phi_{\mathrm{CALC}}$ and $\phi_{\mathrm{CRIP}}$ angles reveals a topochemical increment, given by $\phi_{\mathrm{TOPO}} = \phi_{\mathrm{CRIP}} - \phi_{\mathrm{CALC}}$, of $\sim 7°$. While other interpretations are possible, a geometrical relaxation of the IS intermediate to the relaxed CRIP is consistent with this observation.[6] Notice that the measured $\phi_{\mathrm{CRIP}}$ for the TOL complex is larger than $\phi_{\mathrm{CRIP}}$ for the PXL complex, while the model predicts the reverse order. It is possible that the assumption of equal partitioning of the LE intensity is not valid in the TOL complex. It is also possible that the topochemical increment is unusually small for the TOL complex when compared to that of the other complexes. The supposition that the ground state complex adopts an offset geometry while the CRIP adopts a more symmetrical geometry is probably valid only for centrosymmetric donors. For the TOL complex there is no a priori requirement for the ground state geometry and CRIP geometry to be different.

While minor differences between the measured and predicted angles are evident it does appear that the model is more or less correct. This amounts to admitting that the TMV directions and the ground state geometry are as described above and that perhaps a small geometry change does occur but its effect on the observed orientation amounts to a rotation of approximately 7°.

**TRLD: Determination of $\phi_{\mathrm{IS}}$.** Close examination of the details of our model reveals that predicted values of $\phi_{\mathrm{CALC}}$ can be equated with the relative angles expected for the IS, $\phi_{\mathrm{IS}}$, only if the IS TMV is identical to the TCNB radical anion TMV. Direct evaluation of $\phi_{\mathrm{IS}}$ was possible for the PXY and TOL/TCNB complexes. In these cases the early time regime in the dichroic traces reveals that the TMV direction for the IS must be significantly different than the model predicts. For both of these complexes, the orientation factor at early times deviates significantly from that observed for the relaxed CRIP values ($\phi_{\mathrm{CRIP}}$). The fitting procedure gives estimates of an initial orientation factor of ~0.2 when the relaxation parameters are included in the analysis of the initial ODs. Thus the angle between $\mathbf{M}_{\mathrm{MIX}}$ and the IS TMV must be close to 90°. Consequently, the angle between $\mathbf{M}_{\mathrm{MIX}}$ and the molecular *z*-axis (TCNB radical anion absorption moment) would be larger than the model predicts by as much as 35°. Even given the crudeness of the method used herein it would seem unreasonable that the estimated angles could be incorrect by 35°. If this angle were actually this large, a significant topochemical increment would be required to occur to obtain the observed orientation as determined by the $\phi_{\mathrm{CRIP}}$ angles. Such large changes are contrary to what is expected based on the relatively minor geometric change on going from an offset ground state structure to the more symmetric CRIP and are not supported by the results of the HMB and PMB complexes. While it is possible, even likely, that each complex may experience a slightly different topochemical change upon excitation, differences between complexes of ca. 35° in rotation seems unreasonable and an alternative explanation is required.

One possible alternative is to suggest that the IS absorption TMV is not directed along the molecular *z*-axis but is instead at an angle with respect to the *z*-axis. Since it is unlikely that TCNB radical anion transition is significantly perturbed, this is paramount to describing the IS as electronically distinct from the radical anion. Thus, the IS is not an ion pair at all but must instead be described as an electronic excited state of the charge transfer complex. It is reasonable to speculate that absorption of a photon by the IS state would result in the formation of an upper excited state localized on either the acceptor or donor. For this to be achieved, vector addition of the IS TMV to $\mathbf{M}_{\mathrm{MIX}}$ must result in an excited dipole that is parallel to the $y-z$ plane. One could then speculate that an angle close to 90° with respect to $\mathbf{M}_{\mathrm{MIX}}$ should be observed, in agreement with the experiment.

## Conclusions

TRLD spectroscopy was used to study excited CT complexes. These studies showed that TRLD spectroscopy is sensitive to the influence of localized intensity borrowing within the CT absorption moment. A simple model was used to interpret the measured values. This model allowed a direct comparison between the measured and predicted angles that suggests a relatively minor geometry change occurs after excitation of these complexes. In those complexes where the initial states could be observed directly, the observed transition moment vectors were not consistent with absorption due to the radical anion but are believed to originate from a different electronic state of the excited CT complex. This result implies that the rapid relaxation process observed for these complexes must be electronic in nature and not purely geometric.

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**Supporting Information Available:** A table of the parameters obtained using the least-squares analysis of the transient absorption traces for all of the complexes studied (Table S1) and figures showing the magic angle and dichroic decay traces for the DUR and MES /TCNB complexes (Figures S1-S4) are available. This information is available free of charge via the Internet at http://pubs.acs.org.

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(39) Two different axis systems were used in the description of the TRLD data. The first axis system describes the orientation of the sample within the laboratory frame of reference. For this purpose, mutually orthogonal axes were depicted using uppercase letters ($X$, $Y$, $Z$). The directions of these axes within the laboratory frame were defined by the polarization direction of the photons used to excite the sample as being along the $Z$-axis. A second set of axes was needed to describe the molecular configurations of the donor and acceptor within each complex. Lowercase letters, ($x$, $y$, $z$) were used for this purpose. The origin was defined as the center of mass of TCNB, and the axes were defined as shown in Chart 1. The positions of donors within the ground state complexes were then given relative to the TCNB center of mass.
(40) The description of the CRIP, SSRIP, and free radical ion dynamics requires five rate constants to be determined if the currently accepted model is used (see ref 38). In the present study, the fact that the ion pair decay components were fit adequately to a single exponential is not meant to suggest they accurately portray the ion pair dynamics. The traces used in this study were recorded with optimal resolution for the determination of the anisotropy decay. As such they cannot reflect the ion pair dynamics with accuracy.
(41) The relaxation time constants for several TCNB methylated benzene complexes have been recorded in acetonitrile solvent. The toluene/TCNB complex was studied in several solvents including acetonitrile and 1,2-dichloroethane. Based on the minor solvent dependence observed in the toluene complex, the complex relaxation time constants in 1,2-DCLE can be estimated to be similar to, if perhaps a little larger than, those obtained in acetonitrile (see ref 9).
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(44) A clarification is required at this point. It is customary, although not always correct, to call any absorption band that appears after mixing an acceptor and donor a CT transition. For many of the complexes of interest in the present study, the transition in question may not be purely CT in nature and in some cases may not even be dominated by a CT contribution. We continue to use the term CT transition for the sake of simplicity and continuity with the established literature. It should be understood that we are simply identifying the new transition and not making a statement about its character. In due course we will be making a distinction between the pure CT TMV and the mixed CT−LE TMV that is measured herein.
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(50) The rotation of the donors simply changes the degree of overlap between the HOMO and HOMO-1 combinations with the acceptor orbitals. As this does not change the TMV direction within the molecular frame it is not important in the context of the current discussion.

(51) The angle of interest is that between the vector connecting the donor center of mass to the origin and the $z$-axis. This angle is given by $|\theta| = \tan^{-1}(z/(x^2 + y^2 + z^2))$ where $(x, y, z)$ are the coordinates of the donor center of mass.

(52) Recall that an isotropic solution irradiated with light that is linearly polarized along the laboratory $Z$-axis produces a uniaxially oriented sample of excited states by photoselection. Immediately following excitation, the $Z$-axis in the laboratory frame, the unique orientation axis within the molecular frame, and the average direction of the TMV responsible for absorbing the photon, in this case $M_{MIX}$, all coincide. For any geometric relaxation process that converts the FC into the CRIP, the average position of the molecular frame with respect to the orientation axis (and the laboratory $Z$-axis) may change. The new position of the molecular frame is related to the previous position by a sequence of successive rotations as defined by Euler angles. For uniaxially oriented samples, such as those of interest to the present discussion, all physical rotations that cause a significant change in the orientation of the sample, on average, can be defined in terms of a rotation through a single angle. We define this angle as a topochemical angle, and the apparent rotation is described as causing a topochemical increment to the observed orientation.

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