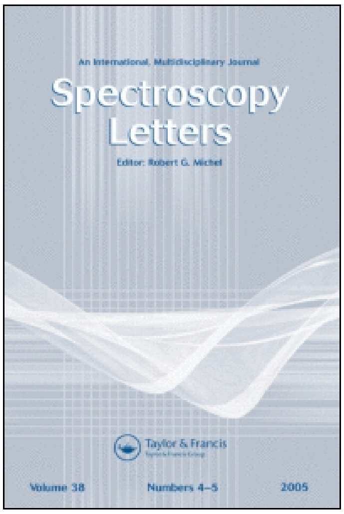

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Analysis of Charge-Transfer Complex Absorption Spectra and the Applicability of the Mulliken two-State Model

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ANALYSIS OF CHARGE-TRANSFER COMPLEX ABSORPTION SPECTRA AND THE APPLICABILITY OF THE MULLIKEN TWO-STATE MODEL

Keywords: charge transfer complex, intensity borrowing, extinction coefficients, oscillator strength, absorption spectrum modeling, 1,2,4,5-tetracyanobenzene

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ABSTRACT

Complete absorption spectra, free from interference due to an unbound acceptor and donor, of several charge-transfer complexes have been examined. These spectra serve as a significant test to the applicability of the Mulliken two-state model for this series of complexes. The appearance of multiple new absorption bands and the trend in the observed oscillator strength of the CT transitions and the localized excitation within the complex spectrum require significant expansions of Mulliken's 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 are predicted based on the gas-phase ionization potentials of the donors and the electron affinity of the acceptor in excellent agreement with the observed spectra achieved. The integrated absorption intensities of the localized bands within each CT complex spectrum have been measured and used as an indicator of the extent on intensity borrowing by the CT transition. These measurements show that for the better donors used in this study, i.e. hexamethylbenzene and pentamethylbenzene, intensity borrowing is not significant. However, for the poorer donors used, an increasing contribution of the LE within the CT absorption bands is observed. A multi-state model, which includes the localized excited state of the acceptor, as well as additional ion-pair states, is the minimum required to describe these complexes.

INTRODUCTION

Mulliken presented the currently accepted theory of CT complex formation in a series of papers in the early 1950's.[1-3] He depicted the ground and excited states of the CT complex as a linear combination of the wave functions for non-bonded interactions and the ion-pair state in what is known as the two-state model. This model has since been expanded to include multiple acceptor and donor ion-pair states in addition to localized excitations (LE).[4-12] The wave functions of interest are usually depicted as follows:

$$\Psi_G = a(\Psi_{AD}) + \Sigma_i b_i(\Psi_{A-D+})_i + \Sigma_j c_j(\Psi_{A-D+})_j \quad (1)$$

$$\Psi_{CT} = \Sigma_i a^*{}_i(\Psi_{A-D+})_i - b^*(\Psi_{AD}) - \Sigma_j c^*{}_j(\Psi_{AD*})_j \quad (2)$$

$$\Psi_{LE} = \Sigma_j a^{**}{}_j(\Psi_{AD*})_j - \Sigma_i b^{**}{}_i(\Psi_{A-D+})_i - c^{**}(\Psi_{AD}) \quad (3)$$

where Ψ_{LE}, Ψ_{CT}, Ψ_{LE} , are the wave functions for the ground, charge-transfer, and localized excited states of the complex, respectively and Ψ_{AD}, $\Psi_{A\text{-}D+}$,Ψ_{AD*} are the wave functions depicting the non-bonded interactions within the complex, the ion-pair states, and the locally excited states, respectively.

There are several experimental observations that justify the use of this more elaborate set of functions over the simple two-state model. The appearance of multiple new bands in the spectrum of the complex is relatively common.[4-11] Additional acceptor and donor ion-pair states must be included to account for this effect and their introduction into the model has become relatively well established. In the specific case of the acceptors and donors used in this study a total of four possible ion-pair states are considered.

The inclusion of locally excited states into these functions has been based on the observed trend in the magnitude of the oscillator strength of the CT absorption.[3-5,7,8,14] The oscillator strength (*f*) is related to the transition dipole ($\mu_{E\text{-}G}$) using the expression:[15]

$$f \cong 4.7 \times 10^{-7}\, \nu_{max}\, (\mu_{E\text{-}G})^2 = 4.39 \times 10^{-9} \int \varepsilon\, d\nu \qquad (4)$$

where ν_{max} is the frequency of the maximum absorbance in cm^{-1} and $\mu_{E\text{-}G}$ is the transition dipole moment. Using the two-state wave functions (i.e. ignoring local excited states and limiting the ion-pair states to one) the transition dipole for the primary CT transition may be evaluated using quantum theory,

$$\mu_{E\text{-}G} = -e \int \Psi_E \sum r\, \Psi_G\, d\tau \cong a^*b(\mu_1 - \mu_0) + (aa^* - bb^*)(\mu_{01} - \mu_1 S_{EG}) \qquad (5)$$

where μ_1 and μ_0 are the dipole moments of the non-bonded and ion-pair states, respectively, and μ_{01} is the transition dipole between them. The term S_{EG} is the overlap integral between the ground and excited state wave functions and the coefficients, a, a*, b, b* are as defined in equations 1, 2 above. For weakly bound complexes, the first term in the solution dominates and the transition dipole should increase with increasing b. According to equation 1, b reflects the ion-pair contribution in the ground state, which should also increase as the ionization potential of the donor decreases, all else being equal. Thus, for a family of related complexes the extinction coefficient for the CT transition should decrease as the donor ionization potential increases according to the two-state model. In several reported cases the oscillator strength for the first CT absorption band increases as the donor ionization potential increases,[8,14] which is in opposition to the prediction based on the two-state model. Based on this observation it was suggested that the local excited states should be included into the wave functions depicted in equations 1-3.

Unlike the addition of multiple ion-pair states, the addition of LE states has not been significantly tested and several alternative explanations may be suggested to account for this effect. These include contact charge-transfer interactions,[4-6] difficulties associated with the overlap of multiple CT bands, and unfortunately, incorrectly determined constants. The simple observation of increasing oscillator strength does not in itself justify the addition of localized states to the theoretical model.

What is proposed is a relatively simple test to ascertain if it is important to include the LE in the model wave functions. If LE states mix significantly with the CT, the LE absorption bands within the spectra of the complexes would be perturbed. Specifically, the LE oscillator strength should decrease if intensity borrowing does occur. The experiments required to test this hypothesis are conceptually simple. A series of charge-transfer absorption spectra must be recorded and analyzed. The difficulty arises in that to obtain the CT complex spectrum, free from the interference of unbound acceptor or donor, knowledge of the association constant for complex formation is needed. We have developed a method[15,16] to obtain these constants and therefore the absorption spectra for complexes between 1,2,4,5-tetracyanobenzene (TCNB) as an electron acceptor and several methylated benzene electron donors. The CT spectra were then analyzed to determine whether the addition of multiple ion-pair states and local excited states are required to accurately describe these complexes.

EXPERIMENTAL

Materials 1,2,4,5-tetracyanobenzene (TCNB) was purchased from Aldrich Chemical Company and was purified by passing it through silica gel, twice, with ethylacetate as the elution solvent followed by recrystallization from chloroform twice. Hexamethylbenzene (HMB), pentamethylbenzene (PMB) , durene (DUR: 1,2,4,5-tetramethylbenzene), and mesitylene (MES) (1,3,5- trimethylbenzene) were purchased from Aldrich Chemical Company and were purified by passing them through alumina with dichloroethane as the elution solvent followed by recrystallization from ethanol. p-Xylene (PXY) was purchased from J.T.Baker and recrystallized at low temperature from chloroform. In all cases, baseline absorbance was monitored and purification was continued until no further improvements in baseline were observed. Toluene (TOL) was purchased from J.T.Baker (HPLC grade) and was used as received. The solvent used in the spectroscopic experiments, 1,2-dichloroethane (DCLE), was purchased from Sigma as HPLC grade and was used without further purification.

Methods All absorption spectra were measured at 25 ± 1 ^{0}C with a Beckman spectrophotometer Model DU-640 and were recorded as a function of the acceptor and donor concentrations. The temperature of the cell was kept constant by circulating temperature-controlled water using a circulator purchased from VWR Scientific. The data was analyzed using Microsoft Excel 98 and Specfit 2.10 (Spectrum Software Associates, Chapel Hill, N.C.).

Solutions containing acceptor and donor were prepared immediately prior to the measurement. Typically, TCNB stock solution was placed in a quartz cell and successive volumes of donor from a ca. 0.1 M stock solution or additional solvent was added using a microliter syringe. Depending on the expected absorbance range, a 10-cm or 1-cm cell was used. Data was recorded under two sets of conditions, one where the acceptor and donor were at equal concentration and then diluted and the other where the donor was at a much higher concentration than the acceptor and the donor concentration adjusted. In all cases the concentrations were less than 2×10^{-2} M. At these concentrations 2:1 complex formation was not important as determined using Job's method.[18] The analysis of the optical density data followed a previously published procedure.[11]

RESULTS

The association constants for complex formation were determined using our recently published procedure and the values are collected in Table 1. The CT spectra for TCNB in the absence of added donor and for the complexes with donors HMB, PMB, DUR, MES, PXY, and TOL, free from unbound acceptor or donor contributions, were obtained and are shown in Figures 1-7. It would be a simple matter to fit each spectrum to a series of Gaussian functions, but, in an effort to minimize the number of freely adjustable parameters, several constraints were applied.

TABLE 1

Charge-Transfer Association Constants for 1,2,4,5-Tertracyanobenzene and Methylated Benzene Donors.

Donor	K_{CT} (M^{-1})[a]	I.P. (eV)[b]	Δ_H (cm^{-1})[c]
HMB	9.07 ±0.9	7.86 -	0
PMB	6.80 ±0.6	8.00 8.30	2420
DUR	5.86 ±0.5	8.10 8.60	4030
MES	3.40 ±0.35	8.42 -	0
PXY	2.86 ±0.3	8.63 9.14	4110
TOL	1.76 ±0.2	8.78 9.00	1770

a) Association constants taken from Arnold, B.R., Euler, A., Fields, K., Zaini, R. *submitted for publication.* b) Ionization potentials (photoionization) taken from J.E. Frey *Appl. Spectrosc.Rev.* **1987**, *23*, 247-283. c) Δ_H is the difference in energy between the highest occupied molecular orbital (HOMO) and the second highest occupied molecular orbital (SHOMO) calculated from the difference between the first and second gas-phase ionization potentials.

Mathematically convenient representations of the LE absorption band of the acceptor is required to address the possibility of LE intensity borrowing. The donors all have significantly higher excitation energies than does the acceptor and the possibility of the donor LE mixing with the CT is remote. Only the acceptor LE will require consideration. The acceptor has a complicated absorption spectrum that includes vibronic structure (Figure 1 – filled circles) and the sum of seven Gaussian functions was required to accurately model the experimental spectrum.[19] No theoretical significance is

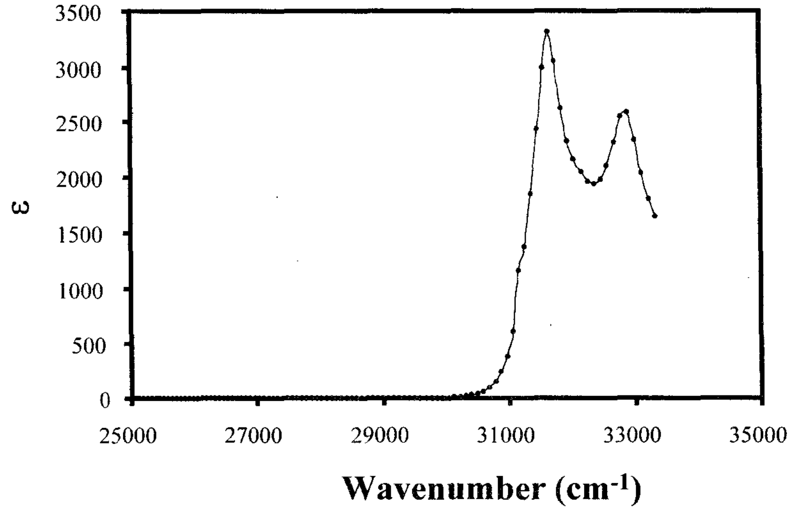

FIG 1. Absorption spectrum of TCNB in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit of a sum of seven Gaussian functions (line). (See text)

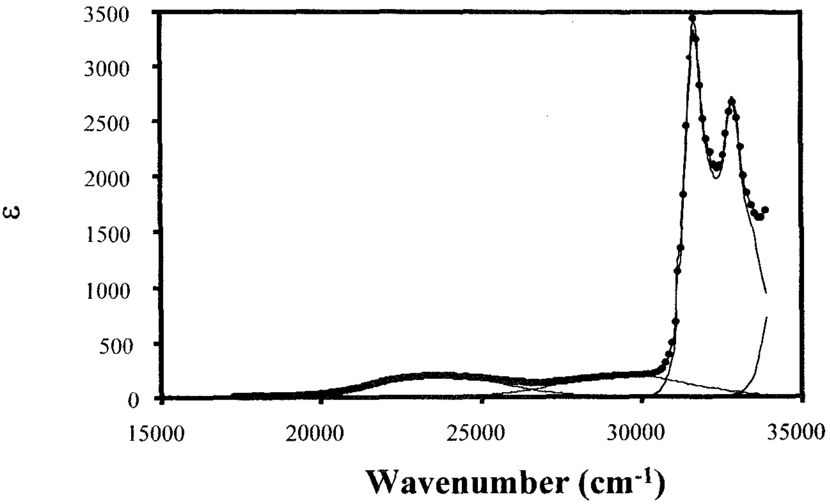

FIG 2. Absorption spectrum of the HMB/TCNB complex in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit according to equation 7 (dark line). The individual components of the CT bands and the LE are also included (gray lines). (See text)

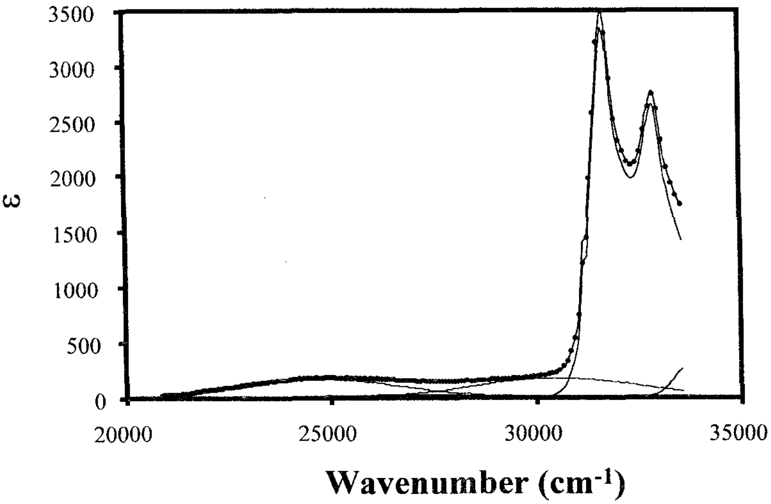

FIG 3. Absorption spectrum of the PMB/TCNB complex in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit according to equation 7 (dark line). The individual components of the CT bands and the LE are also included (gray lines). (See text)

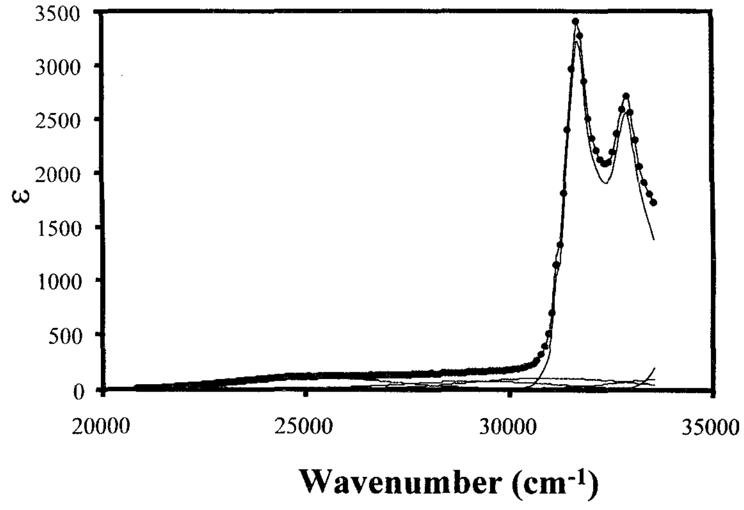

FIG 4. Absorption spectrum of the DUR/TCNB complex in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit according to equation 7 (dark line). The individual components of the CT bands and the LE are also included (gray lines). (See text)

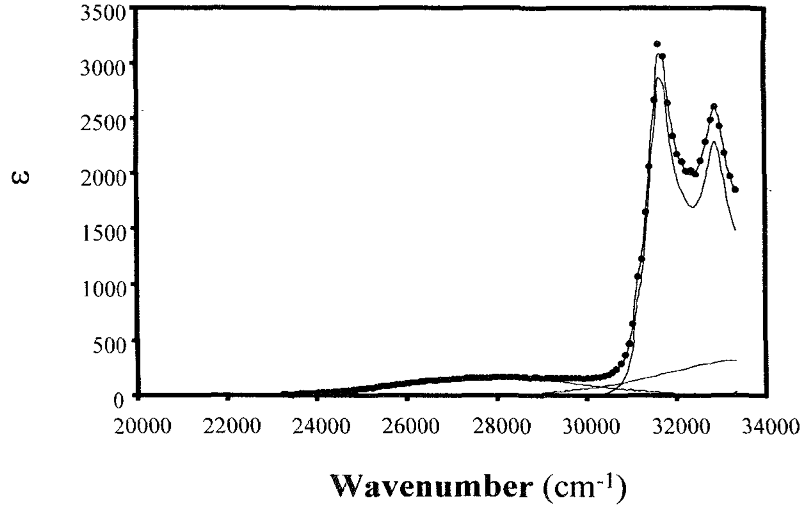

FIG 5. Absorption spectrum of the MES/TCNB complex in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit according to equation 7 (dark line). The individual components of the CT bands and the LE are also included (gray lines). (See text)

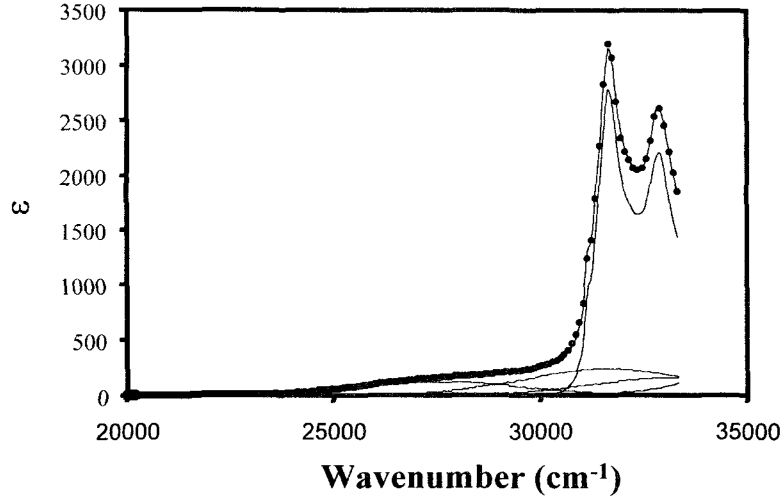

FIG 6. Absorption spectrum of the PXY/TCNB complex in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit according to equation 7 (dark line). The individual components of the CT bands and the LE are also included (gray lines). (See text)

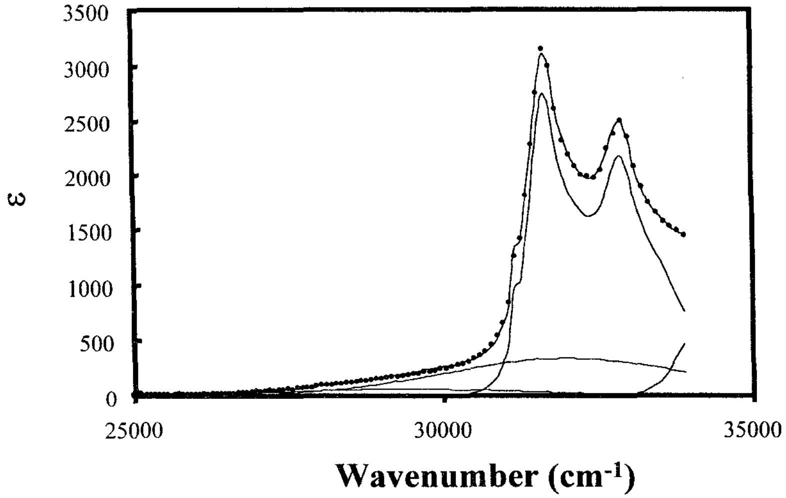

FIG 7. Absorption spectrum of the TOL/TCNB complex in 1,2-dichloroethane at 23°C (filled circles) and the simulated spectrum based on the best fit according to equation 7 (dark line). The individual components of the CT bands and the LE are also included (gray lines). (See text)

placed on the fitting parameters obtained; they simply allow the acceptor LE to be accurately and conveniently represented. The resultant fitted curve is included in Figure 1.

A slight blue shift of the acceptor LE in the spectrum for the complex is expected because the CT interaction stabilizes the ground state relative to the excited state. In addition, intensity borrowing by the CT will decrease the LE intensity. Because of this, the coefficients obtained from the fitting of the TCNB spectrum could not be used as fixed parameters directly but the addition of two adjustable parameters were required. The implementation of F_{LE} as a scaling factor allows the magnitude of the LE to be adjusted. The parameter S_{LE} uniformly shifts the position of the LE. The net effect is to change the intensity and position of the LE band without changing its shape. All of the individual components required to fit the TCNB spectrum were then taken relative to an arbitrary S_{LE}, which was originally fixed at 32000 cm^{-1}, and the LE component of the complex spectra could then be fit using only these two adjustable parameters.

A second constraint was placed on the number and positions of the observed CT absorption bands. From a molecular orbital (MO) approach, the appearance of multiple bands in CT absorption spectra is due to the interaction of several closely spaced MOs in the acceptor and donor that also participate in CT interactions. Assuming the perturbation due to complex formation is small, the energy differences between these MOs can be obtained from the spectroscopy of the individual acceptor and donors. The energy differences, $\Delta_H = E_{HOMO} - E_{SHOMO}$, for the donors were obtained from the reported gas-phase vertical ionization potentials (Table 1). The acceptor LUMO energy difference, $\Delta_L = E_{SLUMO} - E_{LUMO}$, was estimated based on the value obtained from a ZINDO/S calculation on the AM1 optimized geometry. A value of 5800 cm^{-1} was used. This value is in reasonable agreement with several previous reports of the splitting observed for other CT complexes with TCNB.[4,8,9]

The last constraint was to impose a constant bandwidth on all of the CT absorption bands. Attempts to fit these spectra without this constraint generally failed, mostly due to the large differences in oscillator strength between the strong LE and the relatively weak CT bands. In several instances, small imperfections in the fitting of the LE components led to extremely narrow absorption bands being predicted (ca. 3-5 cm^{-1} peak width at half maximum). In others, small deviations in baseline led to extremely broad absorption bands being produced (ca. 10 000 cm^{-1} or more). We viewed these as unreasonable. On average, a value of 2820 cm^{-1} was obtained from the fitting of all of the spectra. Therefore, the peak widths of all bands were constrained to 2820 cm^{-1} as an average value for the CT bandwidth.

Incorporating these constraints into the fitting equation led to equation 7 with a total of seven adjustable parameters.[20]

$$\varepsilon_\nu = h_1 e^{-(\frac{S_{CT}-\nu}{w})^2} + h_2 e^{-(\frac{S_{CT}+\Delta_H-\nu}{w})^2} + h_3 e^{-(\frac{S_{CT}+\Delta_L-\nu}{w})^2} + h_4 e^{-(\frac{S_{CT}+\Delta_L+\Delta_H-\nu}{w})^2} + F_{LE}\sum_{i=1}^{7} h_i e^{-(\frac{S_{LE}+s_i-\nu}{w_i})^2}$$

(7)

We used the solver function of Microsoft Excel 98 to obtain the non-linear least squares minimization of equation 7 to the spectroscopic data. The use of these constraints seems to be fully justified based on the excellent agreement between the model function and the experimental observations. End absorption due to donor was added in several cases to account for relatively steep increases on the high energy side of the spectra. The effect of this addition was mostly cosmetic and did not influence the other fit parameters significantly. The fitting parameters obtained for each of the CT spectra (Figures 2-7) are collected in Table 2.

DISCUSSION

There are several observations based on the results in Table 2 that require discussion. The first is to note that a shift in the LE spectrum of ca 30 cm^{-1} to higher energy is observed for all the complexes modeled. This is in complete agreement with the prediction based on CT complex formation. Its appearance says nothing about LE intensity borrowing because a shift would be expected based on simple two-state

TABLE 2

Fitting Parameters for the Charge-Transfer Absorption Spectra of the Complexes between Methylated Benzene Donors and 1,2,4,5-Tetracyanobenzene.

Donor	HMB	PMB	DUR	MES	PXY	TOL
S_{LE} (cm^{-1})[a]	32031	32024	32035	32037	32029	32026
F_{LE}[b]	1.01	1.01	0.98	0.88	0.85	0.83
S_{CT} (cm^{-1})[c]	23677	24734	25199	27881	27502	29391
h_1 (ε)[d]	202	164	109	168	123	62
h_2 (ε)	-	26	78	-	235	338
h_3 (ε)	198	174	107	329	n/a	n/a
h_4 (ε)	-	9	128	-	n/a	n/a
f_1[c]	0.00443	0.00359	0.00239	0.00369	0.00269	0.00136
f_2	-	0.00056	0.00171	-	0.00515	0.00742
f_3	0.00434	0.00381	0.00234	0.00721	n/a	n/a
f_4	-	0.00021	0.00281	-	n/a	n/a

a) S_{LE} is the shift of the LE transition within the complex spectrum. The uncomplexed LE shift was set at 32000 cm^{-1}. b) F_{LE} is the normalization constant for the intensity of the complex LE relative to the uncomplexed LE. c) S_{CT} is the frequency of the band maximum for the first CT transition. d) h_i is the height, in absorbance units, of the i-th CT transition. A dash indicates the transition is not resolved, n/a indicates that the transition occurs to higher energy than was experimentally recorded. e) f_i is the oscillator strength of the i-th transition calculated using equation 4 and $\int \varepsilon \, d\nu = \sqrt{\pi}\, h_i w$ where w is the width of the transition set to 2820 cm^{-1} (see text).

arguments. However, the magnitude of the shift is small and the expectation that the energy levels would not be significantly perturbed from the free values seems justified.

The fact that experimental data is fitted exceedingly well using the first and second ionization potentials of the donors and the calculated Δ_L for the acceptor as constraints on the number and position of the absorption bands reinforces the fact that the perturbation must be small. It is clear that the two-state model must be expanded to account for the new absorption bands. However, since the transition energies are predicable it seems the individual ion-pair states do not interact strongly among themselves. It is therefore plausible that a sequential application of the two-state model is sufficient to account for the experimental observations and several examples of this have appeared.[10,11]

The comparison of the predicted oscillator strengths for the first CT absorption bands, f_1 is also enlightening. Previous studies have proposed that intensity borrowing should manifest itself as a trend in the oscillator strengths of the CT absorption bands. A plot of the oscillator strength for the CT absorption band in each complex versus the ionization potential of the donor is shown in Figure 8. As can be seen, there does seem to be an overall decrease in intensity but certainly there is not a clear trend. This result is somewhat unfortunate because, as was described above, the oscillator strengths should increase if LE contributions are important and decrease if they do not contribute significantly.

A solution to this difficulty hinges on the realization that the first CT band is not necessarily a pure transition. For example, HMB and MES have degenerate HOMOs. The first CT absorption band is therefore the sum of contributions from both possible transitions. At this point, it is impossible to evaluate the partitioning of intensity between these two transitions and any comparison with the other donors, where degeneracy does not exist, is certainly not valid. It is therefore better to compare the sum of oscillator strengths for the first and second transitions, f_1+f_2, in all cases. Figure 8 also includes the plot of the sum of oscillator strengths. It is arguable, at best, that a trend is now observed with the total intensity decreasing as the ionization potential increases for the first few complexes, and then increasing dramatically for the last two. This suggests

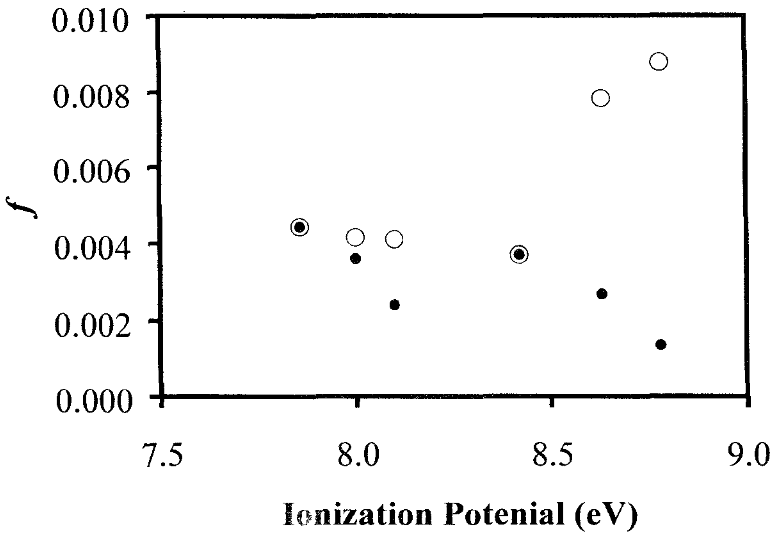

FIG 8. Plot of the oscillator strength (*f*) for the first (filled circles) and the sum of the first and second (open circles) CT absorption bands versus the gas-phase ionization potentials of the donors.

the LE may not contribute to the CT absorption intensity for the better donors studied but may, in fact, contribute significantly in the case of the weaker complexes.

As discussed above, a simple trend in the oscillator strengths is not sufficient proof of LE contributions and alternative explanations may apply. Even under the assumption that the LE does contribute, there is no direct indication of the magnitude of the contribution. As described above, a better measure might be to compare the intensity of the LE within the complex to that observed for the free acceptor. If intensity borrowing does occur the LE will decrease in intensity in a measurable way and the magnitude of the contribution can be determined.

For the HMB and PMB complexes, as can be seen in Table 2, the LE intensity within the complex compares favorably to that of the free acceptor. The LE contribution to the CT transition must be very small and therefore its addition to the wave function is not required for these complexes (i.e. $c^* \approx 0$). It is not clear whether the ca 1% increase in intensity of the LE within these CT complexes is significant. It could be due to experimental uncertainty originating with the TCNB absorption spectrum. It may be an artifact of the fitting process, which excludes contributions due to higher ion-pair states. It may be real, suggesting that the small perturbation due to the binding of the donor produces an increase in oscillator strength. Nevertheless, it is clear that the LE intensity is not measurably decreased for these complexes and therefore intensity borrowing is not important in these cases.

The situation is different for the poorer donors studied. Starting with the DUR complex the LE oscillator strength decreases until only 83% of the initial intensity remains for the TOL complex. This leaves little doubt that intensity borrowing does occur for these weaker complexes and that at least some of the observed intensity in these new absorption bands is due to LE. What is even more important is that the magnitude of the intensity borrowing may also be accessed. In fact, the magnitude of the oscillator strength decrease for the LE is significant when compared to the total oscillator strength of all the CT bands. Depending on how this intensity is partitioned among the multiple CT transitions it is possible that some of these transition actually have more LE character than CT. This being the case, the continued disputes over the classification of these transitions are now brought to a forefront. It is common usage of the label "charge-transfer transition" to indicate that the transition results in an electron transfer from the HOMO of the donor to the LUMO of the acceptor. If, as this result clearly indicates, a considerable fraction, possibly even greater than 50%, of the oscillator strength in the

"CT" transition is actually due to intensity borrowed from the localized transition, it would be incorrect to label these transitions as charge-transfer. A better label would be mixed transitions. This distinction is likely to be more than simply semantic. Clearly the photophysics and photochemistry of these weaker complexes could be considerably different than their stronger counterparts. Such differences would undoubtedly be manifest in changes in the transition moment direction, as well as in the observed magnitude. Indeed, for these weaker complexes significant LE character in the transition may be responsible for the reported relaxation process in these complexes.

CONCLUSIONS

This report describes a detailed study of the applicability of the Mulliken two-state model to the understanding of charge-transfer absorption spectra. It was shown that the addition of multiple CT states is generally required to explain the observed spectra and that the relative positions of the absorption bands could be predicted based on the gas-phase ionization potentials of the donors and the electron affinities of the acceptors.

The anomalous decrease in oscillator strength with increasing ionization potential of the donor is an insufficient test to detect intensity borrowing. It does not account for the possibility of multiple CT transitions and unequal partitioning of borrowed oscillator strength among them. The localized absorption bands within the complex spectrum should be considered and the intensity decrease measured before the magnitude of the intensity borrowing and its influence on the CT absorption can be determined. Unambiguous proof of intensity borrowing within the CT transitions of a series of complexes between 1,2,4,5-tertracyanobenzene as acceptor with methylated benezene donors is reported. In several cases, the extent of intensity borrowing is significant, such that the observed transitions should not be called CT transitions but should be referred to as mixed CT-LE transitions.

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19) Figure 1 includes the simulated spectrum of the TCNB LE that was made up as the sum of seven Gaussian functions. The following list of parameters were used in the calculation of the LE band: (listed as h_i:s_i:w_i,) 2032: 754: 1258, 502: -359: 153, 366:-865: 24, 1893: -397: 408, 589: 862: 219, 126: 132: 187, -44:-1359:574. F_{LE} and S_{LE} were set to 1.00 and 32000 cm-1 respectively for fitting the free TCNB spectrum and these terms were used as fixed parameters in the fitting of the complex absorption spectra.

20) The first four terms in equation 7 are the simulated CT absorption bands. Δ_L and Δ_H were taken from Table 1 and the widths were all fixed at w = 2820 cm^{-1}. The final summation indicates the sum of the seven Gausians required to fit the LE. The heights, widths and relative positions were fixed using the terms obtained from fitting the free spectrum[19] and F_{LE} and S_{LE} were allowed to vary.

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