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Challenges in Distinguishing Superexchange and Hopping Mechanisms of Intramolecular Charge Transfer through Fluorene Oligomers

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The temperature dependence of intramolecular charge separation in a series of donor-bridge-acceptor molecules having phenothiazine (PTZ) donors, 2,7-oligofluorene FL_n ($n = 1-4$) bridges, and perylene-3,4:9,10-bis(dicarboximide) (PDI) acceptors was studied. Photoexcitation of PDI to its lowest excited singlet state results in oxidation of PTZ via the FL_n bridge. In toluene, the temperature dependence of the charge separation rate constants for PTZ-FL_n-PDI, ($n = 1-4$) is relatively weak and is successfully described by the semiclassical Marcus equation. The activation energies for charge separation suggest that bridge charge carrier injection is not the rate limiting step. The difficulty of using temperature and length dependence to differentiate hopping and superexchange is discussed, with difficulties in the latter topic explored via an extension of a kinetic model proposed by Bixon and Jortner.

Introduction

The nature of how charge is propagated through molecular materials is at the heart of molecular electronics[1,2] as well as being of fundamental importance in the design of organic photovoltaic devices and light emitting diodes[3–5] and in understanding the photosynthetic reaction center.[6,7] Intrinsically, such charge transfer processes challenge our understanding of fundamental charge dynamics in molecular systems and numerous investigations spanning many decades have examined this question, frequently using two redox centers covalently bound to the bridge group that is under study. These bridge groups can be generally classified into three categories, σ-systems,[8,9] cofacial π-systems,[10] of which DNA is the most heavily studied,[11–13] and linear π-systems.[14–21] One linear π-system, fluorene oligomers and polymers, has emerged as one of the most effective blue emitters for OLEDs[22] and has been the object of study in a number of reports examining energy and electron transfer,[15,23,24] charge delocalization,[25,26] mobility,[27] and time-resolved measurements in thin films.[28,29]

Due to their smaller HOMO−LUMO gaps and consequently more energetically accessible orbitals, π-systems have shown the greatest potential for long distance charge transfer. This trend is consistent with the importance of energetic resonance conditions as suggested by McConnell's relation,[30]

$$V_{\mathrm{eff}} = \frac{V_{\mathrm{D1}} V_{\mathrm{NA}}}{E_1 - E_{\mathrm{D/A}}} \prod_{i=1}^{N-1} \frac{V_{i,i+1}}{E_{i+1} - E_{\mathrm{D/A}}} \qquad (1)$$

where V_{ij} are matrix elements between different sites (D, donor, A, acceptor), E_i is the energy of a particular site, and N is the number of bridge sites. McConnell's relation also suggests an exponential decay of the charge transfer rate, k_{CT}, as a function of distance between the redox centers.[9] A parameter, β, is typically used to describe that decay as shown in equation 2,

$$k_{\mathrm{CT}} = C\mathrm{e}^{-\beta r} \qquad (2)$$

where r is the redox center/redox center distance and C is a system specific constant. Determining β in equation 2 has been the object of many experimental and theoretical studies.[2,9] However, McConnell's relation is a perturbative expression and fails for small energy gaps. In this regime the bridge orbitals are expected to take on a more active role in the transfer process than simply acting as virtual states in a superexchange-type interaction. Actual occupation of bridge sites and transfer among them, giving thermally activated hopping transport, is characterized by a much weaker distance dependence and can provide efficient long distance charge transfer.[2]

The conditions for transition between superexchange and hopping transport have been of particular theoretical[11,31–34] and experimental interest.[14,15,17,35,36] Typically, one increases the number of repeat units of an oligomeric bridge to evaluate the distance dependence of k_{CT}. However, this approach has been repeatedly complicated by other system parameters that change as a function of bridge length, including bridge oxidation (or reduction) potential[14,17] and conformational distribution. The latter issue has been particularly evident in the temperature dependence of k_{CT} in linear π-systems which frequently demonstrate negative activation energies.[37,38] This complex temperature dependence suggests the existence of additional rate processes that may occlude an analysis of the transition from superexchange to hopping.

In a previous report,[15] we detailed the use of an oligomeric fluorene bridge in molecules **1**−**4**, Figure 1, as a means to avoid large changes in bridge oxidation potential as a function of

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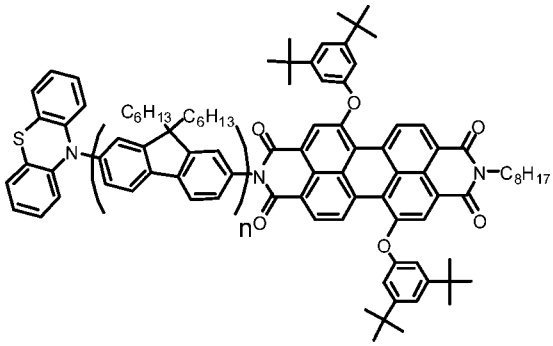

Figure 1. Structures of compounds **1**−**4** (n = 1−4).

bridge length because the oligomers exhibit relatively small variations in oxidation potential.[15,39,40] The oligomers were prepared with a phenothiazine (PTZ) electron donor and a perylene-3,4:9,10-bis(dicarboximide) (PDI) electron acceptor. In this report we show that the temperature dependence of k_{CT} is well described by the semiclassical Marcus equation. We also show that their observed behavior as a function of distance is consistent with current models of thermally activated hopping and clarify the distance dependence in the weak limit. As a consequence of their well-behaved thermal properties and the near invariance of their bridge energetics over distance, **1**−**4** are excellent candidates for exploring the transition from superexchange to incoherent hopping.

Experimental Details

The synthesis and characterization of molecules **1**−**4** have been described elsewhere.[15] Steady state absorption spectra were obtained in a 10 mm quartz cuvette using a Shimadzu 1601 UV−vis spectrophotometer. Femtosecond transient absorption measurements were made using a regeneratively amplified titanium sapphire laser system operating at a 2 kHz repetition rate, which pumps an optical parametric amplifier to provide tunable 120 fs pulses.[38] Samples were irradiated with 1.0−1.2 μJ at 532 nm focused down to a 200 μm diameter spot. The total instrument response function (IRF) for the pump−probe experiment was 180 fs. The absorbance of all samples was 0.5−0.7 at 532 nm in a 1.6-mm path length home-built quartz sample holder. The frequency-doubled, cavity-dumped titanium sapphire laser system used for the time-resolved fluorescence (TRF) measurements provides 400 nm, 25 fs pulses at approximately 1.0 nJ/pulse and has been described previously.[18] Detection was provided by a Hamamatsu C4334 Streakscope with a total instrument response time of approximately 0.4 ns in a 20 ns window. The absorbance of all samples for TRF was maintained below 0.01 at 400 nm in the same sample cell as above. Variable temperature studies were conducted using a Janis VNF-100 cryostat with a Cryo-con 32B temperature controller. Temperatures were maintained to within ± 0.05 K and allowed to equilibrate for 30 min before spectroscopic measurements.

Geometry optimizations and single-point calculations were performed in Gaussian 98 using the B3LYP functional with the 6-31G basis set. Reorganization energies of the various chromophores were calculated by taking the difference in self-consistent field (SCF) energy between the ion calculated in the neutral and ionic geometries.

Results

Transient absorption studies on **1**−**3** in toluene were conducted to determine their charge separation rate constants over a range of temperatures. Selective photoexcitation of the PDI acceptor at 532 nm with 120 fs pulses produces the locally excited state, ^{1*}PDI (broad absorption at 725 nm), which dominates the transient absorption spectra at early times, Figure 2. Intramolecular charge transfer produces the distal radical ion pair, PDI$^{-\bullet}$-FL$_n$-PTZ$^{+\bullet}$ as indicated by the sharpening of the 725 nm absorption due to the formation of PDI$^{-\bullet}$.[15,41] The kinetics of PDI$^{-\bullet}$-FL$_n$-PTZ$^{+\bullet}$ formation was observed directly by monitoring the appearance of PDI$^{-\bullet}$ at 725 nm or indirectly by monitoring the ^{1*}PDI population decay at its 620-nm stimulated emission feature, Figure 2. For **1** and **2**, following the IRF-limited formation of ^{1*}PDI, all kinetics observed at 725 nm were monoexponential, while for **3** these kinetics consistently showed a second fast, low amplitude (4−13%, 50 ps) component at all temperatures. Such multiexponential behavior may be indicative of the hopping mechanism, as has recently been suggested, although given the reduced signal-to-noise that accompanies the lower charge transfer yield of **3**, we cannot definitively assign this component. The time constant for charge transfer ($1/k_{CT}$) of **4** approaches the temporal length of the delay track in our transient absorption apparatus at temperatures below room temperature, so that charge transfer in **4** was monitored indirectly using TRF lifetime measurements of ^{1*}PDI. The temperature dependence of charge *recombination* in **1**−**4** will be the subject of a future report.

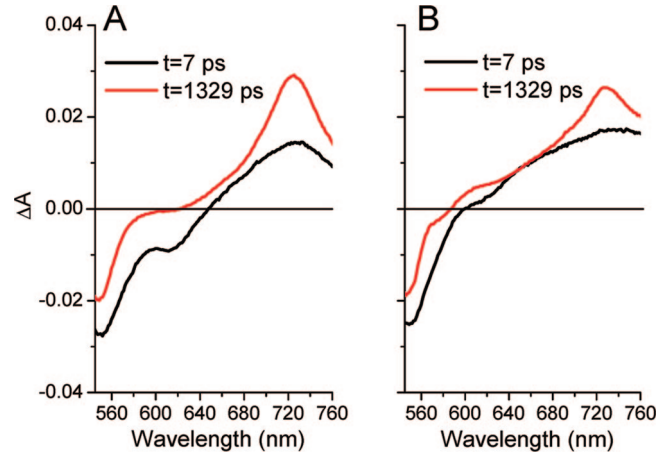

Figure 2. Transient absorption spectra of **1** in toluene with 532 nm excitation at (A) 300 K and (B) 210 K.

The rate, k_{CT}, decreases nearly monotonically with temperature over the range studied, Figure 3. To analyze the temperature dependencies of the rates we use the semiclassical Marcus equation[42] in the nonadiabatic limit,[43]

$$k_{CT} = \frac{2\pi}{\hbar} V_{eff}^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp\left(\frac{-\Delta G^{\ddagger}}{k_B T}\right) \qquad (3)$$

where $\Delta G^{\ddagger} = (\lambda + \Delta G_{RP})^2/4\lambda$, ΔG_{RP} is the free energy change of radical ion pair formation, and λ is the reorganization energy. Because these experiments are performed in toluene, a low polarity solvent, and the chromophores are large, λ is assumed to be dominated by inner-sphere reorganization. Use of equation 3 in the adiabatic limit (no T dependence in the prefactor) yields a marginally worse fit. Employing a functional form of equation 3, $k_{CT} = AT^{-1/2} \exp(-E_a/kT)$, we plot $1/T$ versus $k_{CT}T^{1/2}$ on a logarithmic plot for **1**−**3** in Figure 3. The parameters E_a and A can be easily extracted from the slope and intercept, respectively, are summarized in Table 1, and are further discussed later.

Aggregation. Our accessible temperature range for **2** and **3** is limited by two factors: charge transfer yield and inhomoge-

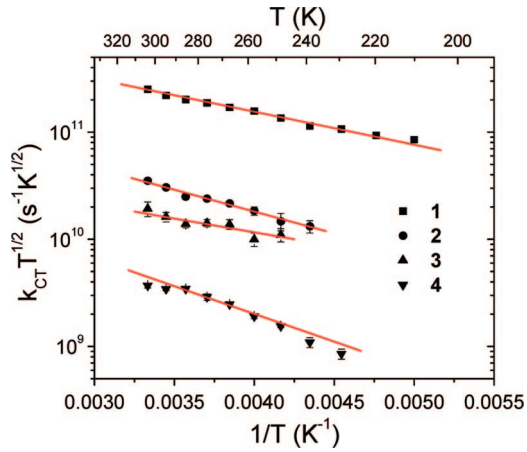

Figure 3. Semilogarithmic plot of $k_{CT}T^{1/2}$ vs $1/T$ for **1**−**4** and linear fits. Error bars are present for all data points but may be smaller than the marker.

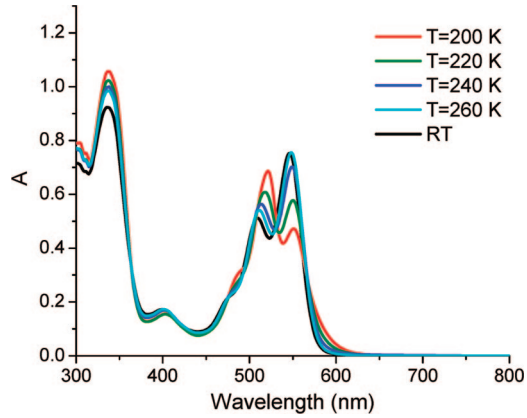

Figure 4. Steady-state UV−vis absorption of **2** in toluene over a range of temperatures showing evidence of exciton coupling.

TABLE 1: Parameters for Equation 1 Extracted from a Fit of the Kinetic Data in Figure 3

compound	E_a	A	R^2
1	492 ± 12 cm^{-1}	2.6 ± 0.2 ×10^{12} s^{-1}	0.99
2	653 ± 52 cm^{-1}	7.8 ± 2.0 × 10^{11} s^{-1}	0.98
3	411 ± 132 cm^{-1}	1.2 ± 0.9 × 10^{11} s^{-1}	0.77
4	828 ± 28 cm^{-1}	2.4 ± 0.4 × 10^{11} s^{-1}	0.95

neous broadening of the anion spectral feature. The decline in yield is consistent with the temperature independent fluorescence lifetime of unsubstituted PDI of 4.4 ns. As the temperature is lowered, k_{CT} slows and becomes comparable to the fluorescence decay rate, and the correspondingly lower yield of $PDI^{-\bullet}$ becomes more difficult to resolve from the broad overlapping ^{1*}PDI transient absorption. However, this reduction in yield alone cannot account for the broadening of the anion feature, Figure 2B. Additionally, the stimulated emission feature is also significantly diminished at lower temperatures, Figure 2B.

Steady-state absorption in the same range of temperatures and concentration, Figure 4, shows significant changes from the room temperature spectra. These changes are a result of the exciton coupling[44] that accompanies formation of cofacial, π-stacked PDI aggregates, and have been seen before in many other PDI derivatives.[5,45] The loss of the stimulated emission is also consistent with aggregation-induced exciton coupling. Excitation into the higher exciton level is symmetry allowed, but rapid internal conversion to the lower exciton level results in the excitation residing in a state that is symmetry forbidden from radiatively decaying back to the ground-state in the absence of significant vibronic coupling. The aggregation also broadens the anion transient absorption feature,[45] likely as a result of its electronic interaction with an adjacent PDI, making the anion more difficult to resolve from excited-state absorption. Interestingly, k_{CT} shows no deviation from linearity even through the onset of aggregation. This insensitivity of k_{CT} to PDI aggregation has also been observed previously,[45] and likely stems from the offsetting effects of lowering both the energy of ^{1*}PDI because of exciton coupling and the energy of $PDI^{-\bullet}$-FL_n-$PTZ^{+\bullet}$ because of the interaction of $PDI^{-\bullet}$ with an adjacent PDI. These combined effects result in little or no change in ΔG for charge separation.[45] Fluorescence spectra of **4** at the lower concentrations used for TRF do not show evidence of exciton coupling and imply that aggregation is not occurring.

Rate Analysis. Examination of Figure 3 shows k_{CT} to be well described by equation 3 over the region studied. This behavior is in stark contrast to the highly nonmonotonic behavior observed in similar systems,[37,38] in some cases over a comparable temperature range. While the spectral broadening mentioned above results in only a limited range of temperatures being accessible, more than enough temperature points are available to allow determination of the parameters of equation 3 in the vicinity of room temperature, which are summarized in Table 1, and to establish behavior at room temperature as being activated. The activation barriers, in the range of 400−800 cm^{-1}, are too low to correspond to torsional barriers between fluorenyl groups, which are on the order of 1100 cm^{-1},[27] or to the torsional barrier between a flat aromatic and an aromatic imide, which has been calculated at over 5000 cm^{-1}.[46] It is important to remember that torsional barriers must be examined as opposed to torsional frequencies since the latter can only be related to an activation barrier if the necessary displacement from equilibrium is known as well. Estimation of the activation barrier from equation 3, with ΔG_{RP} in the range of −0.11 to −0.33 eV[15] and λ = 0.6 eV,[17] yields $\Delta G^{\ddagger}$ in the range of 0.03−0.1 eV, or 250−810 cm^{-1}, in the same range as our experimental values. Values of ΔG_{RP} were calculated using Weller's method[47] of estimating radical pair energies in low polarity media from redox potentials measured in media of higher polarity, while λ was assumed to be dominated by the inner-sphere component and calculated by taking the difference in self-consistent field (SCF) energy between the ion calculated in the neutral and ionic geometries. The successful applicability of equation 3 and the matching of the activation barrier to $\Delta G^{\ddagger}$ of the Marcus equation suggest that conformational gating is not a critical factor in this temperature range and that it is valid to treat V_{eff} as being temperature independent.

Frequently, thermally induced hopping transport is labeled as being temperature-sensitive, while superexchange is discussed as temperature insensitive or independent. However, both the fundamental assumptions of Marcus theory and the form of equation 3 show this to be a misconception. With nonvanishing $\Delta G^{\ddagger}$, equation 3 predicts monotonically increasing values of k_{CT} with temperature over the range of usual liquid solvents. Vanishingly small values of $\Delta G^{\ddagger}$ can indeed result in increasing rate with decreasing temperature, as in the case of the photosynthetic reaction center.[48] Any deviations from monotonic behavior are consequently a result of the temperature dependence of the parameters in eq 3, such as λ[49] or V_{eff}.[37,38] As a result, positive activation cannot be said to be exclusively indicative of hopping, while flat or negatively activated behavior cannot be said to be exclusively indicative of superexchange. Temperature dependence could conceivably differentiate su-

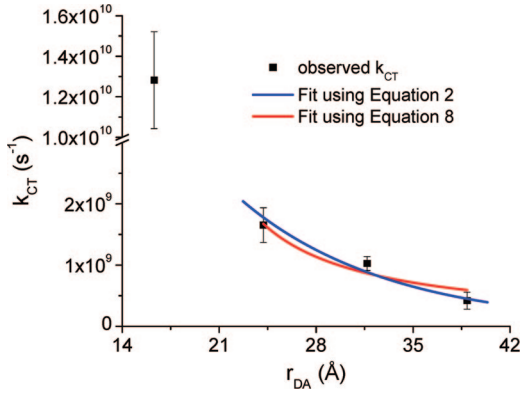

Figure 5. Dependence of charge transfer rates of **1**−**4** on distance determined from transient absorption data at room temperature. The data are presented on a linear scale and fit using eqs 2 and 8.

perexchange and hopping, if the activation energy determined from eq 3 unequivocally showed that bridge occupation was the rate limiting step.[21] The calculated values of the activation energy of bridge occupation (ΔG_{BO}) for **2**−**4** are in the range of 0.01 to 0.16 eV[15] and $\lambda = 0.35$ eV, which yields $\Delta G^{\ddagger}$ in the range of 0.09−0.19 eV, or 750−1500 cm^{-1}. These values are higher than the experimentally observed range, although the errors expected[50] from application of Weller's treatment[47] in low polarity media make it difficult to say with certainty that these two different activation energies can be differentiated. Though the small value of the experimentally observed activation energies suggest that bridge occupation is *not* the rate limiting step, hopping can still be the dominant form of transport as irreversible charge transfer may still require the dephasing that occurs upon exothermic formation of the distal radical pair.[51] This picture suggests that charge transfer will not be observed in model compounds of **1**−**4** without the PTZ donor, which was confirmed experimentally.[15]

Possessing more information about the temperature dependence of k_{CT}, we can reinterpret the length dependence of k_{CT}, presented in Figure 5.[15] As shown above, the energetic barrier to charge carrier bridge occupation has been calculated and is very close to the value of 0.2 eV reported[52,53] for bridge occupation in DNA A-tracts[54] of the form, GA_n. Bixon and Jortner[31] have analyzed thermally induced hopping transport in A-tracts produced by Giese and co-workers,[35] using a classical kinetic model,

$$D^{*}B_1...B_NA \overset{k_1/k_{-1}}{\longleftrightarrow} D^{-}B_1^{+}...B_NA \overset{k/k}{\longleftrightarrow} D^{-}B_1...B_N^{+}A \rightarrow D^{-}B_1...B_NA^{+} \quad (4)$$

where k_1 and k_{-1} refer to the rates of the charge carrier shifting on and off of the bridge from the donor, k is the rate of hopping between bridge sites, and k_t is the rate of the charge shifting onto the final trap site. This last process is assumed to be irreversible owing to fast relaxation in the dense vibronic quasicontinuum of the lower energy final trap site.[55] The classical form of eq 4 is used instead of a quantum mechanical expression because of the rapid dephasing that occurs at each individual bridge site, a consequence of the finite and nonvanishing amount of time the charge resides on each bridge site[56] and coupling to the bridge's own vibronic density of states. Bixon and Jortner's expression for the rate of accumulation of charge at the final acceptor is

$$k_{CT}(N) = \left(\frac{kk_t + kk_{-1} + (N-1)k_{-1}k_t}{kk_1k_t} + \frac{N}{k_t} + \frac{N(N-1)}{2k}\right)^{-1} \quad (5)$$

where N is the number of bridge sites.

When analyzed in the limit of $k_t \gg k_{-1}$, $k \gg k_1$ (slow population of the bridge, fast transfer to the trap site (in this case PTZ), one gets

$$k_{CT}(N) = \frac{C'}{1 + \frac{k_1}{k - k_{-1}}N} \quad (6)$$

where $C' = k_1/(1-k_{-1}/k)$. However, as shown above, the experimentally observed activation energies correlate with the formation of the distal radical pair not bridge injection, suggesting that k_t, may be rate limiting. This picture is also consistent with large scale motions required of the PTZ to form a cation.[57] In addition, the equilibrium angle between two fluorene units is considerably less than the angles between a fluorene unit and PTZ or PDI,[15] suggesting fast fluorene-fluorene charge transfer. Consequently, a more accurate limit may be $k \gg k_{-1}$, k_t, k_1, in which case the expression reduces to

$$k_{CT}(N) = \frac{C''}{1 + \frac{k_1}{k_{-1} + k_t}N} \quad (7)$$

where $C'' = k_1k_t/(k_t + k_{-1})$. Both of these forms are very similar to forms derived by Segal, Nitzan, and co-workers,[11] who also predicted a $1/(a + bN)$ form using a steady-state Liouville analysis, as well as related algebraic forms derived by Berlin and co-workers.[58] All of these expressions appear very different from the monoexponential form of eq 2. But in the limit of small β and N, eq 2 can be Taylor expanded to low order and approximated as

$$k_{CT} = Ce^{-\beta r} \approx \frac{C}{1 + \beta r} = \frac{C}{1 + \beta aN} \quad (8)$$

where a is the length of a bridge monomer in Å, which is functionally identical to eqs 6 and 7.

Depending on the relative rates in eq 4 as well as the specifics of the system, charge carrier occupation of the bridge can be directly probed spectroscopically[59,60] or implied by a delay between the appearance of one ionized redox center and the other.[61] However, in the absence of these signatures, equation 8 shows that the distance dependence alone is *insufficient* to distinguish between superexchange and thermally activated hopping because both mechanisms show such similar distance dependencies in the slowly decaying regime for small N. Fits of Figure 5 show comparable fit qualities for eqs 2 and 8 ($R^2 =$ 0.97, 0.93) as well as comparable decay parameters ($\beta = 0.09$ $Å^{-1}$, 0.06 $Å^{-1}$). However, though both fits are comparable, the very small β values that are measured in our case as well as others[14,17,21,23] and the necessarily small energy gaps that are required in these cases strongly imply that transfer is being dominated by thermally activated hopping. Similar decay parameters were also recently observed for oligomeric fluorene systems with a different donor and acceptor.[23]

Conclusion

The temperature dependence of charge separation in PTZ-FL_n-PDI leading to formation of $PDI^{-\bullet}$-FL_n-$PTZ^{+\bullet}$ is well described by the semiclassical Marcus equation in the nonadiabatic limit and shows positive activation energies. This simple

description, as well as nearly static redox potentials, makes fluorene oligomers an excellent system to explore the shift in mechanism from superexchange to hopping. Temperature dependence alone cannot distinguish between superexchange and hopping, although the experimentally determined activation energies suggest that bridge occupation is not rate-limiting. An analysis based on Bixon and Jortner's kinetic model is in agreement with the soft exponential distance dependence that is observed experimentally. Further analysis of this model suggests that distance dependence alone cannot distinguish between superexchange and hopping, although small energy gaps strongly imply the latter.

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