Photochemistry

Chimia 51 (1997) 82
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Grammaticakis-Neumann Prize Winner 1996: Prof. *Matthew B. Zimmt*

The Swiss Society of Photochemistry and Photophysics has awarded the *Grammaticakis-Neumann* Prize to Prof. *Matthew B. Zimmt*, Brown University, Providence, USA. The *Grammaticakis-Neumann* Prize is awarded to young scientists for excellent research in the field of photochemistry.

Matthew Zimmt received his Ph.D. from Columbia University, New York, in 1985, under the direction of Prof. *N. Turro*, and did postdoctoral studies with Prof. *M.D. Fayer* at Stanford University. In 1987, he was assigned Assistant Professor at Brown University in Providence, Rhode Island, where he is now Associate Professor since 1993.

The prize was attributed to *Matthew Zimmt* in recognition of his excellent contribution to the elucidation of photochemical and photophysical processes by the use and development of original methods for spectroscopic analysis of complex molecular model compounds.

The following article contains the basic contents of the *Grammaticakis-Neumann* Lecture held by *Matthew Zimmt* on the occasion of the Prize Award Ceremony on October 1, 1996.

Chimia 51 (1997) 82–89
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Intramolecular Electron-Transfer Studies as a Function of Bridge Topology: The Importance of Solvent-Mediated Donor-Acceptor Electronic Coupling

Matthew B. Zimmt*

Abstract. The donor-acceptor electronic coupling matrix elements, $|V|$, for photoinduced, intramolecular electron-transfer (ET) reactions in one linear and three C-shaped molecules have been determined from the temperature dependence of ET rate constants. The coupling matrix element in the linear molecule was found to be solvent-independent. By contrast, the coupling matrix elements in two of the three C-shaped molecules exhibit significant solvent dependence. Donor-acceptor coupling matrix elements were calculated for the linear and C-shaped molecules in the absence and presence of solvent molecules using the generalized *Mulliken-Hush* theory. Together, the experimental and theoretical results indicate that solvent molecules, and not the covalent bridge, mediate the electronic coupling in the C-shaped molecules. Preliminary studies of ET rate constants as a function of solvent bulk are also described.

1. Introduction

Electron transfer (ET) reactions play important roles in chemistry, biology, and technology. Over the last twenty years, the chemical community has developed an increasingly sophisticated understanding of the factors that control the kinetics of these fundamental reactions. Throughout this development, *Marcus* theory [1] and its semiclassical analogs [2] provided a framework for organization of observations and for *a priori* design of molecular performance. These theories furnish descriptions of the activation free energy for ET (more generally termed a *Franck-Condon*-weighted density of states, FCWDS) in terms of intrinsic reaction barriers, the solvent (λ_S) and vibrational (λ_V) reorganization energies, and the thermodynamic driving force for reaction ($-\Delta G^o$). In systems involving D(onor) and A(cceptor) sites separated beyond *van der Waals* contact, the ET rate constant is often expressed as $k_{ET} = (2\pi/\hbar)\,|V|^2$ FCWDS, where $|V|$ is the magnitude of the electronic coupling matrix element between D and A. Many of the most interesting studies per-

---

**Correspondence*: Prof. Dr. M.B. Zimmt
Department of Chemistry
Brown University
Providence, Rhode Island 02912, USA

Photochemistry

Chimia 51 (1997) 82
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Grammaticakis-Neumann Prize Winner 1996: Prof. *Matthew B. Zimmt*

The Swiss Society of Photochemistry and Photophysics has awarded the *Grammaticakis-Neumann* Prize to Prof. *Matthew B. Zimmt*, Brown University, Providence, USA. The *Grammaticakis-Neumann* Prize is awarded to young scientists for excellent research in the field of photochemistry.

Matthew Zimmt received his Ph.D. from Columbia University, New York, in 1985, under the direction of Prof. *N. Turro*, and did postdoctoral studies with Prof. *M.D. Fayer* at Stanford University. In 1987, he was assigned Assistant Professor at Brown University in Providence, Rhode Island, where he is now Associate Professor since 1993.

The prize was attributed to *Matthew Zimmt* in recognition of his excellent contribution to the elucidation of photochemical and photophysical processes by the use and development of original methods for spectroscopic analysis of complex molecular model compounds.

The following article contains the basic contents of the *Grammaticakis-Neumann* Lecture held by *Matthew Zimmt* on the occasion of the Prize Award Ceremony on October 1, 1996.

Chimia 51 (1997) 82–89
© Neue Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Intramolecular Electron-Transfer Studies as a Function of Bridge Topology: The Importance of Solvent-Mediated Donor-Acceptor Electronic Coupling

Matthew B. Zimmt*

Abstract. The donor-acceptor electronic coupling matrix elements, |V|, for photoinduced, intramolecular electron-transfer (ET) reactions in one linear and three C-shaped molecules have been determined from the temperature dependence of ET rate constants. The coupling matrix element in the linear molecule was found to be solvent-independent. By contrast, the coupling matrix elements in two of the three C-shaped molecules exhibit significant solvent dependence. Donor-acceptor coupling matrix elements were calculated for the linear and C-shaped molecules in the absence and presence of solvent molecules using the generalized *Mulliken-Hush* theory. Together, the experimental and theoretical results indicate that solvent molecules, and not the covalent bridge, mediate the electronic coupling in the C-shaped molecules. Preliminary studies of ET rate constants as a function of solvent bulk are also described.

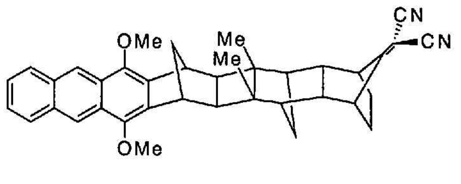
1. Introduction

Electron transfer (ET) reactions play important roles in chemistry, biology, and technology. Over the last twenty years, the chemical community has developed an increasingly sophisticated understanding of the factors that control the kinetics of these fundamental reactions. Throughout this development, *Marcus* theory [1] and its semiclassical analogs [2] provided a framework for organization of observations and for *a priori* design of molecular performance. These theories furnish descriptions of the activation free energy for ET (more generally termed a *Franck-Condon*-weighted density of states, FCWDS) in terms of intrinsic reaction barriers, the solvent (λ_S) and vibrational (λ_V) reorganization energies, and the thermodynamic driving force for reaction ($-\Delta G^o$). In systems involving D(onor) and A(cceptor) sites separated beyond *van der Waals* contact, the ET rate constant is often expressed as $k_{ET} = (2\pi/\hbar)|V|^2$ FCWDS, where |V| is the magnitude of the electronic coupling matrix element between D and A. Many of the most interesting studies per-

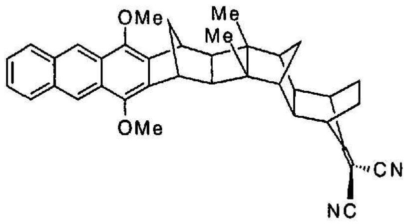
---

**Correspondence*: Prof. Dr. M.B. Zimmt
Department of Chemistry
Brown University
Providence, Rhode Island 02912, USA

CHIMIA 51 (1997) Nr. 3 (März)



CN-1



CN-2

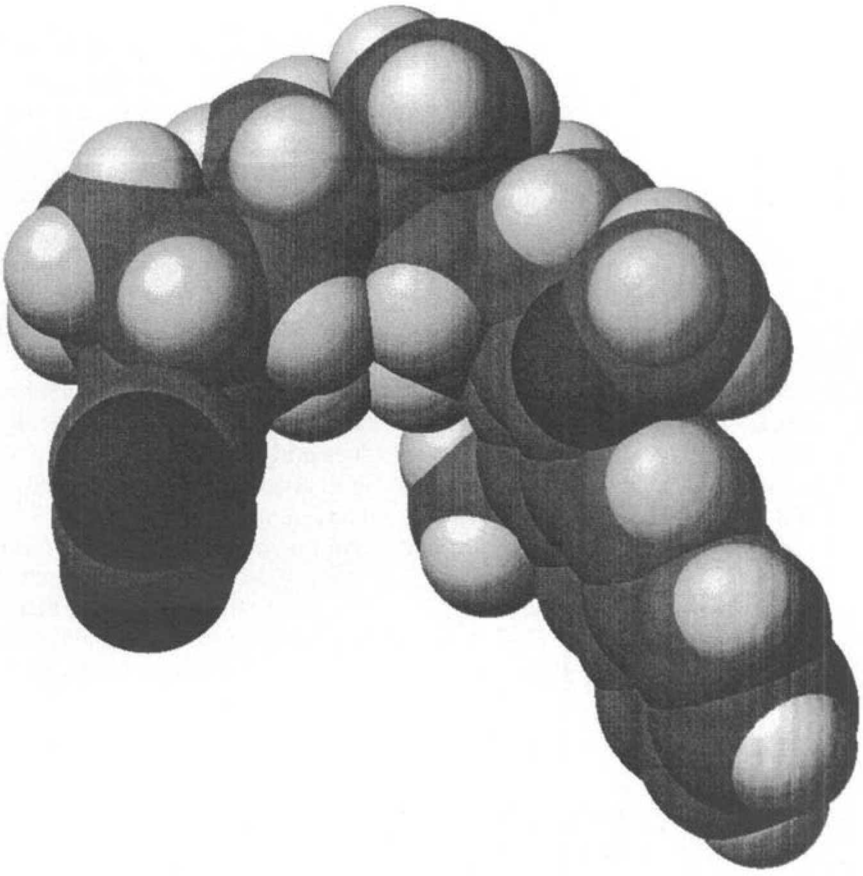


Fig. 1. *CPK model showing the cavity between the dicyanoethylene acceptor* (left) *and the dimethoxyanthracene donor* (right) *into which solvent may enter*

formed during the last twenty years have corroborated predictions from *Marcus* theory as to the effects of driving force [3], solvent polarity [3a], polarizability [4], and temperature [5] on the FCWDS and on the rate constants of ET reactions. These studies make it possible to calculate or experimentally derive adequate estimates of the FCWDS for many ET systems. In turn, this has opened the door to structural investigations of $|V|$, the donor-acceptor electronic coupling matrix element.

The electronic interaction between the D and A sites may be envisioned to arise *via* numerous 'pathways' [6]. The simplest of these, and that which is chemically most intuitive, arises from the direct overlap of the D and A wavefunctions. Net overlap between the redox sites generates a nonzero resonance integral and large D/A electronic coupling [7]. The rapid decay in wavefunction amplitude with increasing distance from the nucleus limits significant contributions of this type to D/A pairs lying within 1 or 2 Å of *van der Waals* contact. Electronic interactions between D and A at larger separations are readily understood in terms of superexchange pathways [8][9]. In the superexchange picture, the availability of an electron or a hole for transfer to a redox partner is communicated by mixing of the medium's conduction and valence-band wavefunctions with those of the D and A. D/A interactions mediated by way of the environment's electronic bands results in kinetically useful coupling and a significant increase in the length scale over which electron transfer can occur, compared to direct overlap. The extended distance range of superexchange-mediated electronic coupling has been demonstrated in the elegant studies of *Closs* and *Miller* [10], *Paddon-Row* and *Verhoeven* [11], *Stein* and *Lewis* [12], and others. In these systems, the electronic coupling is attributed to mediation by the bonding and antibonding orbitals of the bridge that covalently links D and A. This role of the bridge is strongly supported by a host of theoretical formalisms and studies of 'through bond coupling' [6][13–18].

Despite the increased range of coupling arising from superexchange pathways, the rapid attenuation of $|V|$ with bridge length (*ca.* 40% reduction with each bond) [10][11] indicates that the largest coupling contributions arise from the shortest, most direct pathway between D/A. Most studies of long-distance, intramolecular ET conclude that the wavefunctions of the bridge comprise the 'most direct path'. Contributions of the surrounding environment to mediation of $|V|$ in intramolecular ET systems have, generally, been ignored. However, it is not clear that this assumption is valid. *Miller* first demonstrated the existence of the *Marcus*-inverted region in investigations of ET between D and A randomly distributed in frozen glasses [19]. These studies demonstrated that, given sufficient time, single-step ET reactions can occur across D/A separations of 30 Å [20]. The decrease of $|V|$ with increasing separation in glasses is only slightly steeper than that observed in covalently linked D-bridge-A molecules. Studies of ET in proteins, which may be simplistically viewed as reproducibly organized glasses, also demonstrate ET across a 'solvent' environment [21]. Clearly, non-covalent interaction with the surrounding medium can mediate $|V|$. Investigations of ET in solvent-separated ion pairs, from the labs of *Gould* and *Farid* [22], *Matag* [23], *Vauthey* [24], and others have further demonstrated that $|V|$ is mediated by fluid solvent lying between or around D and A. Thus, additional studies of the solvent's role in mediating $|V|$ in intramolecular ET systems appears warranted.

Starting in 1992, we initiated a program to investigate the potential role of solvent mediation of $|V|$ for ET reactions in structurally rigid D-(B)ridge-A molecules. The principal advantages of using rigid DBA molecules in these investigations are *1*) the structural information one can obtain regarding D/A separation and orientation, 2) reduced sensitivity of ion-pair structure to solvent characteristics (compared to changes in ion-pair geometry which may arise in bimolecular studies in fluid media), and 3) the ability to modulate electronic properties of the solvent (compared to what may be achieved in proteins and glasses). The challenges of this approach are the considerable synthetic demand and the complexity of separating bond and solvent-mediated contributions to $|V|$.

The D/A electronic coupling matrix element for the photoinduced, charge-separation reactions of DBA molecules **CN-1** and **CN-2** prompted our interest in solvent-mediated coupling. In acetonitrile (MeCN), $|V|$ was evaluated as 160 cm^{-1} and 140 cm^{-1}, respectively [25]. The near equality of the coupling matrix elements for these two molecules was surprising given that the bridge in **CN-2** contains an *s-cis* linkage. Experimental [26] and theoretical [27] studies have demonstrated that deviations from all-*trans* bridge topology, through inclusion of *gauche* or *s-cis* linkages, reduces D/A coupling magnitudes significantly, *e.g.*, by factors of three or more. In contrast to the results in MeCN, $|V|$ for **CN-1** in tetrahydrofuran (THF) was found to be 40% larger than $|V|$ for **CN-2** in THF. The comparable $|V|$ across linear and bent bridges in MeCN, the apparent solvent dependence of $|V|$ for **CN-2** and the topology of the **CN-2** bridge, which creates a cavity directly between D and A into which solvent can enter (*Fig. 1*), prompted speculation that $|V|$ for **CN-2** might be mediated by both the bridge and molecules of the solvent. As noted above, solvent mediation of $|V|$ has been demonstrated in glasses, proteins, and for ion pairs in fluid solvent. In addition, one study implicated solvent mediation of $|V|$ for intramolecular ET reactions [26b].

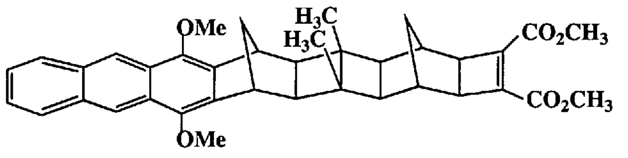
2. Molecules and Methods

In order to learn more about solvent mediation of $|V|$ and to evaluate its role in intramolecular ET reactions, we sought to characterize ET rate constants in DBA molecules with the following characteristics:

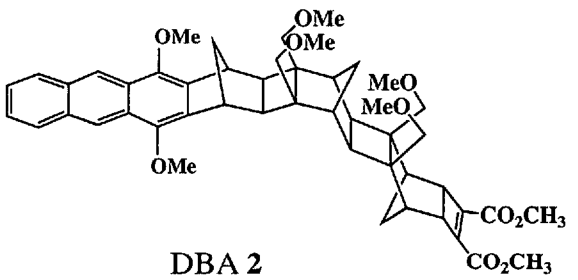
1) a rigid bridge which holds the D and the A at a fixed separation and whose topology is such that only solvent molecules occupy the space lying directly between the redox partners,
2) incorporation of bridge-structural features that eliminate or drastically reduce bridge-mediated coupling so that solvent molecules comprise the dominant coupling pathway,
3) simple synthetic routes that offer flexibility in designing DBA structures.

In a prior study, we found that electronic symmetry strongly modulates D/A coupling matrix elements for intramolecular, photoinduced charge-separation reactions [25][28]. $|V|$ across the all-*trans* bridge of DBA **1** is *ca.* 10 times smaller than $|V|$ across the all-*trans* bridge in **CN-1**. Both molecules have an all-*trans* bridge comprised of seven bonds and an approximate mirror-plane symmetry element bisecting D, B, and A. The electronic configuration of the (donor) anthracene S_1 state is well described by promotion of an electron from the antisymmetric HOMO to the symmetric LUMO [29]. In **CN-1**, the acceptor LUMO is symmetric with respect to the mirror-plane symmetry element. Thus, photoinduced transfer of an electron from the D LUMO to the A LUMO is symmetry-allowed. By contrast, the acceptor LUMO in **1** is antisymmetric with respect to the mirror plane. Photoinduced transfer of an electron between the D and A LUMOs is accompanied by a change in state symmetry and is, therefore, formally electronically forbidden ($|V| = 0$). The matrix element is nonzero, presumably due to vibronic effects. Central to our interests, the magnitude of through bond contributions to $|V|$ can be minimized by using DBA molecules with symmetry-forbidden topology and by incorporating one or more *s-cis* linkages within long bridges.

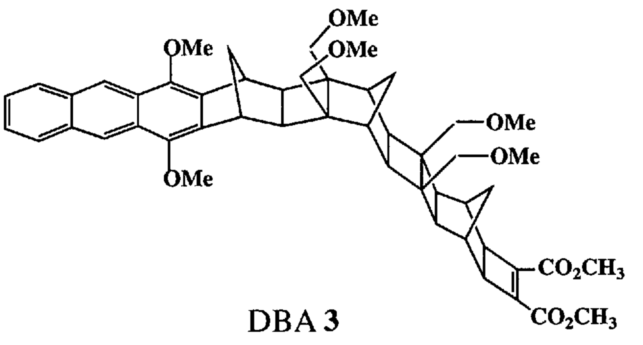
DBA molecules **1**–**4** [30] were used to investigate the potential role solvent-mediated coupling. The bridges are based on the elegant and effective norbornane/cyclo-



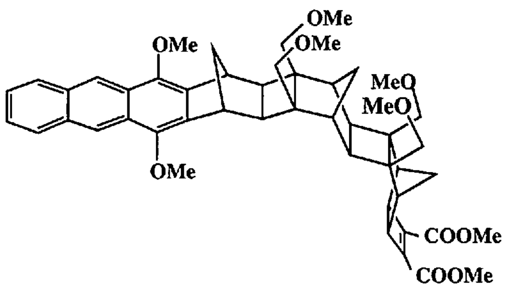
DBA 1



DBA 2



DBA 3



DBA 4

butane structures designed and studied by *Paddon-Row* and coworkers [11]. The rigidity of these polycyclic bridges provides well-defined D/A separations and orientations. The bridges in DBA molecules **2**, **3**, and **4** have 9, 10, and 9 bonds, respectively. In these three molecules, the D/A separation (10.2, 10.6, and 7.1 Å, respectively) spans a cavity which solvent may enter [31]. DBA **1**, with seven bonds in the bridge and a D/A separation of 11.5 Å, serves as a control for the method used to extract |V| from the kinetic data (*vide infra*). The bridge in **1** occupies the space directly between D and A. Solvent-inclusive pathways are longer and consequently should contribute less to the overall coupling than the direct, bridge-mediated pathway. If the analysis method is appropriate, the extracted |V| for **1** should be relatively independent of the solvent.

The ET rate constants in **1**–**4** were determined from time-resolved fluorescence measurements as $k_{ET} = 1/\tau_{DBA} - 1/\tau_{DB}$. τ_{DBA} is the fluorescence lifetime of the anthracene excited state determined for the DBA molecule in the solvent and at the temperature of interest. τ_{DB} is the fluorescence lifetime of the anthracene, determined for the same solvent and temperature, in a DB molecule with the identical bridge, but lacking the dimethyl maleate acceptor group. The anthracene excited-state decay rate constants in the DB molecules are nearly temperature-independent (activation energies < 0.5 kJ/mol) in all the solvents investigated. The fluorescence decay kinetics of the DBA molecules exhibit larger activation energies (6–18 kJ/mol). Lifetimes greater than 500 ps were determined using both time-resolved fluorescence spectrometers at Brown [25] and at the University of Pittsburgh [31]. Lifetimes shorter than 500 ps were determined in Pittsburgh.

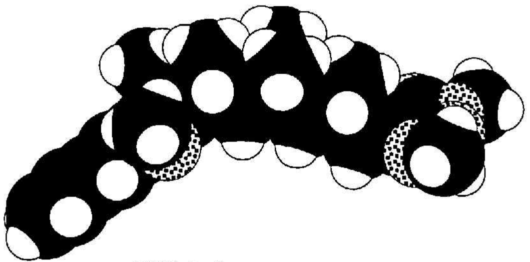
Table 1. *Solvent Dependence of* |V| (cm^{-1}) *in DBA* **1–4** [31]

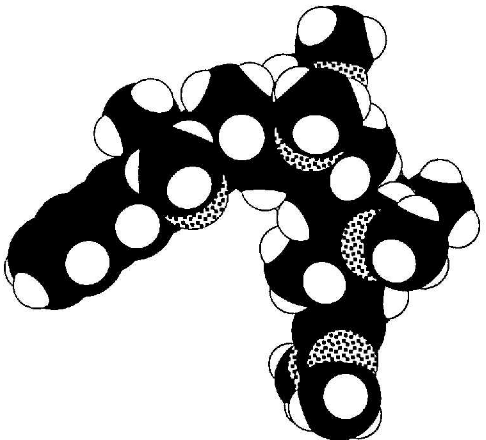
Solvent	DBA **1**	DBA **2**	DBA **3**	DBA **4**
PhCN	15 ± 3	8 ± 2	9 ± 3	69 ± 12
MeCN	19 ± 4	–[a]	3.5 ± 2	23 ± 5
DMA	19 ± 4	–[b]	–[b]	16 ± 5
THF	20 ± 7	–[b]	–[b]	–[b]

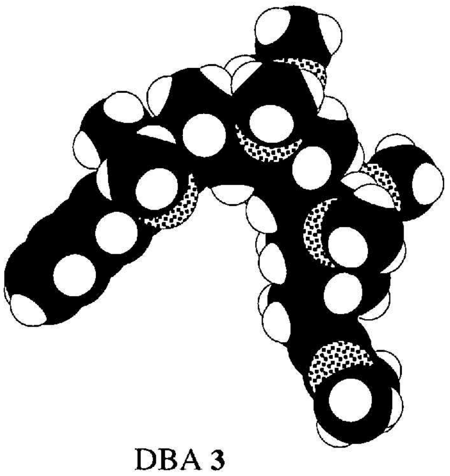
[a] ET rate constants too slow to analyze. [b] ET rate constants not determined in this solvent.

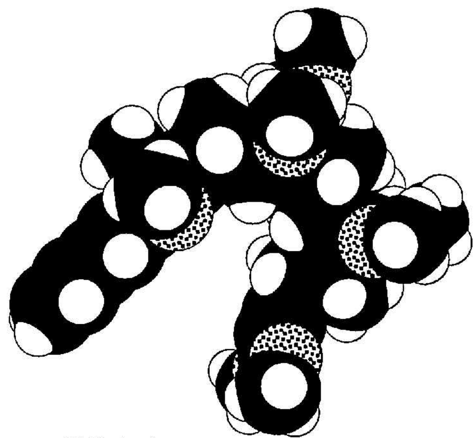
Numerous groups have successfully used the single quantized mode, semiclassical expression [2] to interpret ET rate constant data in a wide variety of chemical systems. Each term within the summation in the *Eqn.* represents a contribution to the rate constant, starting from the zero-point vibrational level of the reactant and ending in one of the vibrational levels of the product.

$$\boxed{k_{ET} = \frac{2\pi|V|^2}{\hbar\sqrt{4\pi kT\lambda_s}} \sum_{n=0}^{\infty} e^{-S}\left(\frac{S^n}{n!}\right)\exp\left(\frac{-(\Delta G^\circ + \lambda_s + n\hbar\omega)^2}{4\lambda_s kT}\right) \qquad S = \frac{\lambda_v}{\hbar\omega}}$$


DBA 1


DBA 2


DBA 3


DBA 4

The semiclassical ET rate constant is controlled by five parameters; $|V|$, the D/A electronic coupling matrix element; $-\Delta G^o$, the reaction driving force; λ_S, the low-frequency (primarily solvent) reorganization energy; λ_V, the high-frequency reorganization energy arising from structural changes of the donor and the acceptor upon ET; $\hbar\omega$, the average energy spacing of the quantized mode undergoing reorganization upon ET. The latter four parameters determine the FCWDS and must be specified in order to derive $|V|$ from a measured rate constant. Previously, estimates of λ_V (0.39 eV) and $\hbar\omega$ (1410 cm^{-1}) were obtained from an analysis of the CT emission spectra produced by a three-bond bridge analog of **1**–**4** and from AM1 calculations [25]. In the present investigation, $|V|$ and the FCWDS are separated through analysis of the ET rate constant temperature dependence. The temperature dependence of ΔG^o and λ_S must be taken into account. The driving force and low-frequency reorganization energy at each temperature, *T*, were modeled as $\Delta G^o(T) = \Delta G^o(295\ K) + \Delta\Delta G^o(T)$ and $\lambda_S(T) = \lambda_S(295\ K) + \Delta\lambda_S(T)$, where $\Delta\Delta G^o(T)$ and $\Delta\lambda_S(T)$ were calculated using continuum models [32]. An estimate of $\Delta G^o(295\ K)$ was calculated using conventional continuum models [5f][32]. In addition, $\Delta G^o(295\ K)$ values within ± 0.3 eV of the continuum result were also used (*vide infra* and *Fig. 3*) to explore the sensitivity of the extracted $|V|$ to the assumed value of the driving force [33]. The remaining two parameters, $|V|$ and λ_S(295 K) were extracted from the temperature-dependent, ET rate constant data by nonlinear, least squares regression analysis.

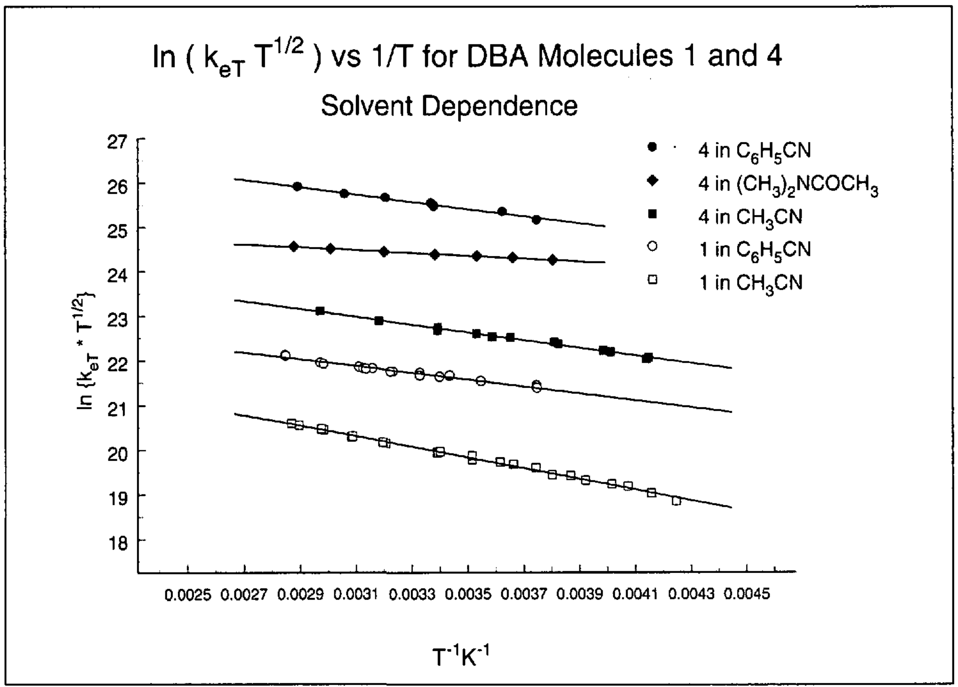


Fig. 2. *Modified* Arrhenius *plots of ln* $k_{ET}T^{1/2}$ vs. *1/T for DBA molecules* 1 *and* 4

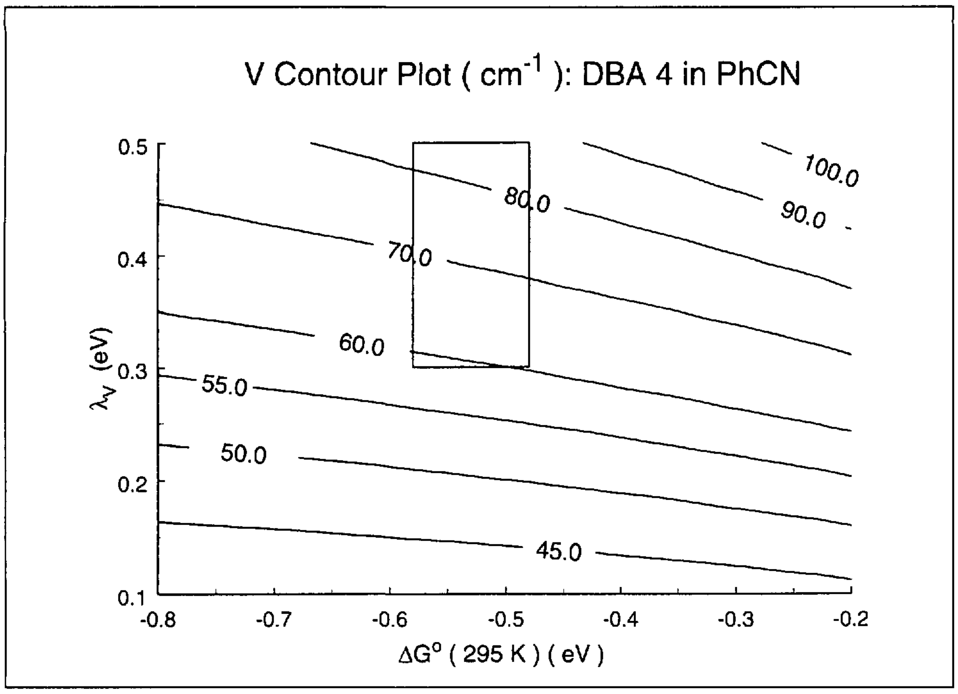


Fig. 3. *Contour plots of* $|V|$ *for DBA 4 in PhCN* vs. *the assumed values of* λ_V *and* $\Delta G^o(295\ K)$, *obtained from nonlinear regression analysis of the temperature-dependent* k_{ET} *data.* The constant contour lines are in units of cm^{-1}. The box outlines a region defined by prior estimates of λ_V (0.3–0.5 eV) and ΔG^o(295 K) ± 0.05 eV calculated using continuum models.

Presuming that this method of analysis provides reasonable estimates of $|V|$, how can through solvent and through bond contributions be separated? DBA **1** with the shortest (7 bond) and most effective (all-*trans*) bridge is expected to have the largest contribution of through bond coupling to $|V|$. Furthermore, solvent-mediated contributions to $|V|$ should be negligible in this compound (*vide supra*). The extent to which the extracted values of $|V|$ for **1** vary with solvent is one measure of the success or failure of the assumptions used to extract $|V|$ from the ET data. $|V|$ for **2**–**4** should be < 15 % [34] of $|V|$ for **1** if through bond pathways are the dominant source of coupling. If solvent is the major source of D/A coupling, $|V|$ in the bent DBA molecules should be larger than the 15% prediction. More significantly, $|V|$ should exhibit much larger solvent dependence in the bent DBA molecules compared to **1**. To accentuate the solvent dependence, the variable-temperature ET studies were performed in MeCN, dimethylacetamide (DMA), benzonitrile, and THF (DBA **1** only). These ET reactions involve transfer of an electron between D and A LUMOs. In these solvents, with π-type molecular orbitals, the superexchange state comprising transfer of an electron from the D LUMO to the solvent LUMO (electron-mediated superexchange) is lower in energy than the superexchange state representing transfer of an electron from the solvent to the acceptor (hole-mediated superexchange) [20]. Decreasing the energy of the mediating, superexchange state is predicted to increase the magnitude of the resultant coupling [8][9][20]. The vertical electron affinity of PhCN is *ca.* 3.0 eV more positive than that of MeCN [35]. Thus, solvent-mediated superexchange contributions to $|V|$ are predicted to be larger in PhCN than in MeCN for **2**–**4** [36].

3. Experimental Results

Arrhenius plots of the ET rate constants from **1** and **4** along with the calculated regression results are displayed in *Fig. 2*. The ET rate constants for **4** are 10–50 times larger than those for **1**, for the same solvent. The slopes of the plots are similar, indicating comparable FCWDS temperature dependence. *Table 1* lists the regression estimates for $|V|$ from each of the DBA molecules in the investigated solvents. The uncertainty quoted for each entry was determined through variation of ΔG^o(295 K) and λ_V across a range of values (boxed region, *Fig. 3*) [33b]. The values of $|V|$ obtained for DBA **1** are nearly solvent-independent. This confirms that the methods used to calculate the temperature dependence of the FCWDS are effective for a wide range of solvent dielectric constants.

The ET rate constants for **2** in MeCN were too small to measure, precluding any comment on solvent dependence for this DBA. However, the $|V|$ determined in PhCN is half as large as $|V|$ for DBA **1** in PhCN. This $|V|$ for **2** is considerably larger than the 15% prediction based solely on through bond coupling. $|V|$ for DBA **2** and **3** in PhCN are comparable, despite the additional bond in the bridge of **3**. As the cavity size and D/A through space separation in these two molecules (10.2 and 10.6 Å, respectively) are similar, these results suggest a dominant role of solvent-mediated coupling. $|V|$ for **3** decreases *ca.* threefold upon changing the solvent from PhCN to MeCN. This trend is consistent with the simple arguments regarding superexchange state energy noted above. The absolute difference of $|V|$ in these two solvents is small, leading to nearly overlapping uncertainty limits. The results from DBA **4** do not suffer a similar problem. $|V|$ in PhCN is three times larger than in MeCN and four times larger than in DMA. The difference in these values are much larger than the uncertainty limits. In PhCN, $|V|$ for **4** is four times larger than $|V|$ for **1**, despite the additional two bonds and two *s-cis* links in the bridge of **4**. $|V|$ for **1** and **4** are comparable in MeCN and DMA. These results demonstrate that solvent provides the dominant pathway for mediation of D/A coupling in DBA **4** and, at the very least, makes significant contributions to D/A coupling in DBA **2** and **3**.

Table 2. *Calculated Values*[a]) *of* $|V|$ (cm^{-1}) *in the Presence and Absence of a Solvent Molecule* [39]

Condition	DBA 1	DBA 2	DBA 3	DBA 4
Vacuum	4	< 0.2	< 0.2	< 0.2
MeCN in cavity	6	–[b])	–[b])	7
PhCN in cavity	22	–[b])	–[b])	46
PhCN out of cavity	11	–[b])	–[b])	< 1

[a]) Root mean square of value calculated at various solvent configurations. [b]) Calculation not performed.

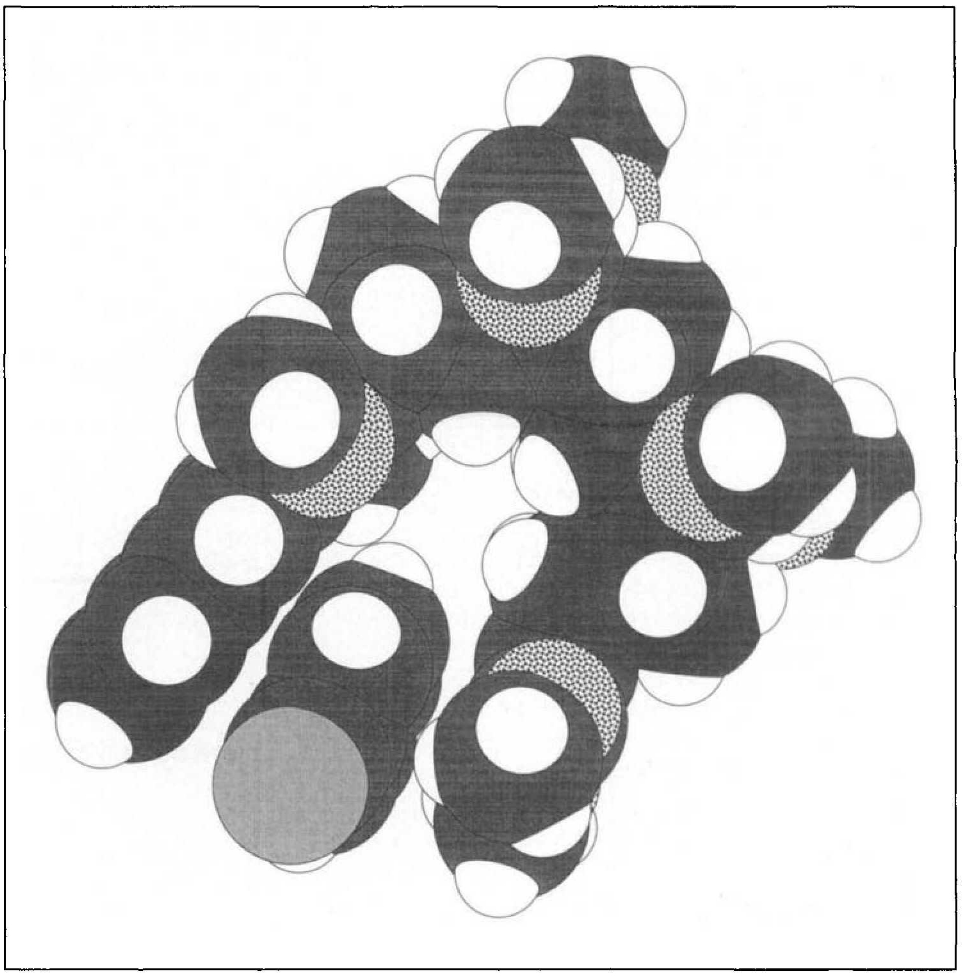


Fig. 4. *CPK model of* **4** *showing a molecule of PhCN in the cavity between D and A*

4. Theoretical Results

The procedure employed to extract $|V|$ from the kinetic data requires the use of a number of models and assumptions. Although the solvent independence of $|V|$ determined for **1** provides a measure of confidence in the procedure, it is desirable to obtain independent estimates of $|V|$. *Newton* and *Cave* [37] developed a generalization of the *Mulliken-Hush* model [38] which may be used to calculate D/A coupling magnitudes in the presence or absence of solvent. Their method was used to calculate $|V|$ for the photoinduced, charge-separation reaction of **1**–**4** in a vacuum and for **1** and **4** with a single solvent molecule lying adjacent to the DBA [39]. The latter calculations were performed with the solvent positioned either within (*Fig. 4*) or outside of the cavity of **4** (concave side of **1**). The results are presented in *Table 2*. The calculations confirm that bond-mediated coupling is negligible across the long, bent bridges in molecules **2**–**4**. Introduction of a solvent molecule increases the calculated coupling. The composition, placement, and orientation of the solvent molecule has a large impact on the calculated $|V|$ [39]. For **4**, the magnitude and solvent dependence of the single-solvent calculations agree remarkably well with the experimental results. In contrast, the calculations for **1** exhibit a larger solvent dependence of $|V|$ than was experimentally observed. Placement of the PhCN molecule next to anthracene, on the convex face of **1**, yields a $|V|$ of 11 cm^{-1}. In this position, the solvent is too far from the acceptor to effect solvent mediation of $|V|$. It is possible that bond-mediated coupling in this system is enhanced by symmetry breaking induced by interaction with PhCN [39]. This point is currently under investigation. Overall, the calculated results support the conclusion that $|V|$ is predominantly mediated by solvent in **4**.

5. In the Cavity or not in the Cavity, that is the Question

The theoretical and experimental studies demonstrate the importance of solvent mediation of coupling in DBA **4**. An apparent prerequisite for solvent-mediated coupling is the presence of a solvent molecule within the DBA cavity (*Fig. 4*). The occupation of the cavity by solvent has not been confirmed by NMR or X-ray crystallographic investigations. To ascertain the importance of solvent entry into the cavity, the fluorescence dynamics from **4** have been measured in a family of alkylated benzenes: benzene, cumene, 1,3- and 1,4-di(isopropyl)benzene, 1,3,5-tri(isopropyl)-benzene, and mesitylene. The lowest-energy conformation of the isopropyl groups projects one methyl group above and below the benzene ring. This conformation prevents entry of the aromatic nucleus into the cavity of **4**, at least from the edge containing the alkyl substituent. If the aromatic nucleus of the solvent must enter the cavity to mediate coupling, the presence of bulky alkyl groups should reduce the solvent's ability to mediate D/A coupling.

The fluorescence decays from **4** are bi-exponential in the alkylated benzenes, whereas, the fluorescence decays in MeCN, DMA, and PhCN are single exponential. The more complex decay in the weakly polar aromatics is consistent with a higher-energy charge-transfer state, which undergoes back ET to regenerate the excited anthracene [40]. All four rate constants in the kinetic scheme (*Fig. 5*) may be determined from the three parameters obtained by fitting the fluorescence decays and from the lifetime of the excited donor in the absence of an acceptor [41]. The charge separation (k_{CS}) and back ET (k_{BACK}) rate constants in each solvent are characterized by the same values of $|V|$, λ_V and λ_S [42], with ΔG^o values that are equal in magnitude but opposite in sign. ΔG^o in each solvent may be calculated from the ratio k_{CS}/k_{BACK}. A log plot of k_{CS} and k_{BACK} *vs.* the corresponding ΔG^o produces a reasonable fit to the semiclassical *Marcus* Equation [2] ($\lambda_V = 0.39$ eV, $\lambda_S = 0.21$ eV, and $\hbar\omega = 1410$ cm^{-1}) for the four solvents that are not trisubstituted (*Fig. 6*). The rate constants in mesitylene and 1,3,5-tri(isopropyl)benzene (TIP) are 1.3 and 4 times smaller, respectively, than the values calculated using the semiclassical equation and the above parameters. Mesitylene's cross section is only slightly larger than benzene's. The observed rate reduction in this solvent corresponds to a 15% decrease in $|V|$, although it is not obvious that the small difference between the observed and calculated rate constants is not associated with the FCWDS. The three isopropyl groups in TIP prevent placement of the aromatic core within the cavity of **4**. Provided the FCWDS calculation is correct, the steric inhibition to entry reduces $|V|$ for TIP by a factor of 2 compared to benzene or the monosubstituted aromatics. This is comparable to the ratio of $|V|$ found for **4** in MeCN and PhCN. Although the extent of the FCWDS contribution to the fourfold difference in calculated and measured rates in TIP must be established, this data provides at least some

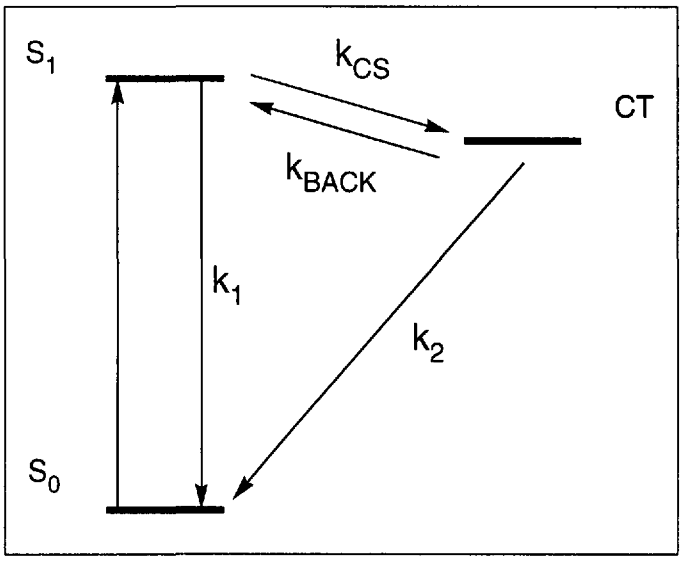


Fig. 5. *Kinetic scheme used to analyze the bi-exponential fluorescence decay from 4 in alkylated benzene solvents* (CT = charge-transfer state)

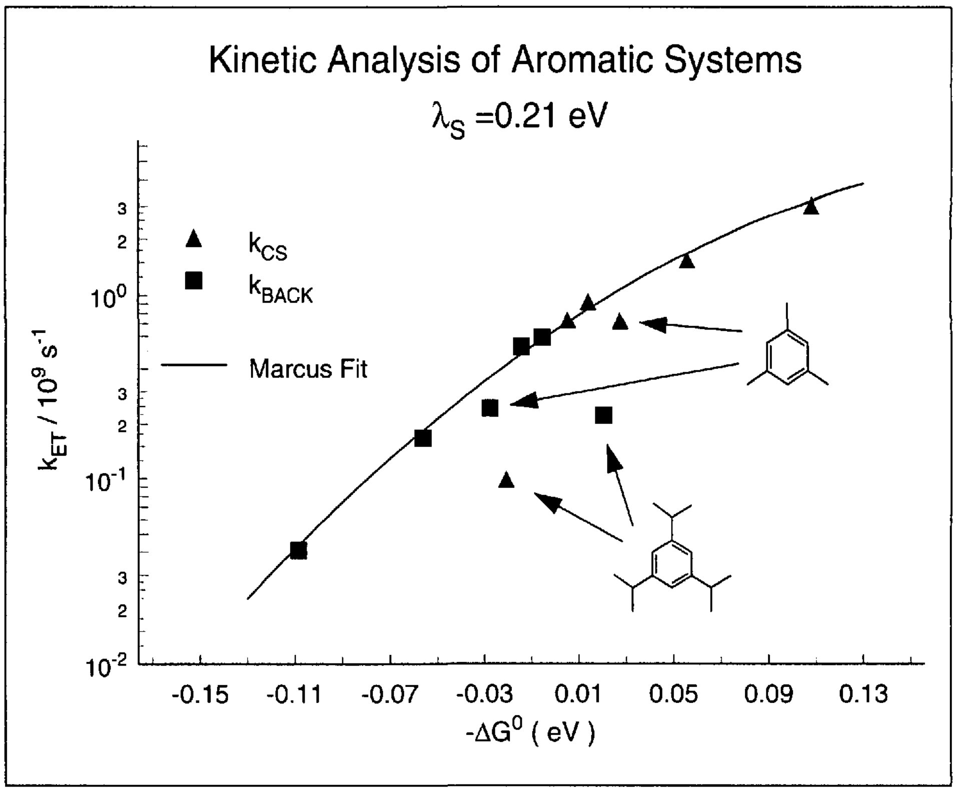


Fig. 6. *Plot of* k_{CS} *and* k_{BACK} vs. *the experimentally determined reaction-driving force*. The solid line represents k_{ET} calculated using the single quantized mode, semiclassical equation, the parameters in the text, and $|V| = 10$ cm^{-1}.

evidence that the ET rate constants are sensitive to steric bulk in the solvent.

6. Conclusion

Although still at an early stage, these investigations provide considerable evidence that *fluid* solvent is effective at mediating donor/acceptor electronic coupling. In accord with the prediction of superexchange theory [8], the magnitude of solvent-mediated $|V|$ for transfer from an excited donor to an acceptor is larger in solvents with low-energy anion states. Solvent-mediated coupling probably contributes to $|V|$ in all intramolecular ET reactions. However, for the most commonly investigated class of DBA molecules, in which the bridge lies directly between D and A and for which there is no symmetry constraint on D/A mixing, through bond contributions likely overwhelm solvent-mediated contributions to $|V|$ (compare $|V|$ in **CN-1** and **1**). For the less commonly studied, C-shaped DBA topology, solvent-mediated coupling may well turn out to be of general importance [43]. We are currently expanding our investigations to evaluate the significance of solvent-mediated coupling for ET in C-shaped DBA molecules possessing symmetry-allowed topology (and rather long bridges) and for ET reactions in which D/A coupling is likely to arise through hole-mediated superexchange (transfer of a hole from an electronically excited acceptor to a donor). Through these studies we hope to identify the types of reactions and molecules in which solvent-mediated coupling is important and to determine the principal factors controlling solvent-mediated coupling magnitudes.

I would like to express my gratitude to the *Swiss Society for Photochemistry and Photophysics* for providing the opportunity to present this summary of our investigations. It is a great pleasure to thank our wonderful collaborators, Prof. *David H. Waldeck*, Dr. *Zhe Lin*, and *Ian Read* at the University of Pittsburgh, Prof. *Robert J. Cave* at Harvey Mudd College, and Dr. *Marshall D. Newton* at Brookhaven National Laboratory. This work would not have been possible without the excellent synthetic and technical skills of Dr. *Krishna Kumar* (C-clamp studies) and Dr. *Yang Zeng* (symmetry effect studies). Financial support from the *United States National Science Foundation* and the *Camille and Henry Dreyfus Foundation* is gratefully acknowledged. Finally, I would like to thank Profs. *G. McMillan* and *C. Sukenik* (Case Western Reserve University), *N. J. Turro* and *C.E. Doubleday* (Columbia University), and *M.D. Fayer* (Stanford University) for their enthusiasm for science, guidance, and encouragement.

Received: February 4, 1997

---

[1] R.A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966.

[2] J. Jortner, *J. Chem. Phys.* **1976**, *64*, 4860.

[3] a) J.R. Miller, L.T. Calcaterra, G.L. Closs, *J. Am. Chem. Soc.* **1984**, *106*, 3047; b) I.R. Gould, D. Ege, S.L. Mattes, S. Farid, *ibid.* **1987**, *109*, 3794.

[4] a) J.T. Hupp, T.J. Meyer, *J. Phys. Chem.* **1987**, *91*, 1001; b) R.L. Blackbourn, J.T. Hupp, *ibid.* **1990**, *94*, 1788.

[5] a) R.A. Marcus, N. Sutin, *Inorg. Chem.* **1975**, *14*, 213; b) P. Finckh, H. Heitele, M. Volk, M.E. Michel-Beyerle, *J. Phys. Chem.* **1988**, *92*, 6584; c) N. Liang, J.R. Miller, G.L. Closs, *J. Am. Chem. Soc.* **1989**, *111*, 8740; d) N. Liang, J.R. Miller, G.L. Closs, *ibid.* **1990**, *112*, 5353; e) J.T. Hupp, G.A. Neyhart, T.J. Meyer, E.M. Kober, *J. Phys. Chem.* **1992**, *96*, 10820; f) J. Kroon, H. Oevering, J.W. Verhoeven, J. Warman, A.M. Oliver, M.N. Paddon-Row, *ibid.* **1993**, *97*, 5065.

[6] a) D.N. Beratan, J.N. Onuchic, *Photosynth. Res.* **1989**, *22*, 173; b) J. Jortner, *Biochim. Biophys. Acta* **1980**, *594*, 193; c) S. Larsson, *J. Am. Chem. Soc.* **1981**, *103*, 4034.

[7] I.R. Gould, R.H. Young, R.E. Moody, S. Farid, *J. Phys. Chem.* **1991**, *95*, 2068.

[8] H.M. McConnell, *J. Chem. Phys.* **1961**, *35*, 508.

[9] J. Halpern, L.E. Orgel, *Discuss. Faraday. Soc.* **1960**, *29*, 32.

[10] G.L. Closs, J.R. Miller, *Science* **1988**, *240*, 440.

[11] H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven, N.S. Hush, *J. Am. Chem. Soc.* **1987**, *109*, 3258.

[12] C.A. Stein, N.A. Lewis, G. Seitz, *J. Am. Chem. Soc.* **1982**, *104*, 2596.

[13] C.A. Naleway, L.A. Curtiss, J.R. Miller, *J. Phys. Chem.* **1991**, *95*, 8434.

[14] C. Liang, M.D. Newton, *J. Phys. Chem.* **1993**, *97*, 3199.

[15] R.J. Cave, M.D. Newton, *Chem. Phys. Lett.* **1996**, *249*, 15 .

[16] M. Braga, S. Larsson, *J. Phys. Chem.* **1993**, *97*, 8929.

[17] M.J. Shephard, M.N. Paddon-Row, K.D. Jordan, *J. Am. Chem. Soc.* **1994**, *116*, 5328.

[18] M.A. Ratner, *J. Phys. Chem.* **1990**, *94*, 4877.

[19] J.R. Miller, J.V. Beitz, R.K. Huddleston, *J. Am. Chem. Soc.* **1984**, *106*, 5057.

[20] J.R. Miller, J.V. Beitz, *J. Chem. Phys.* **1981**, *74*, 6746.

[21] a) M. Meier, R. van Eldik, I.-J. Chang, G.A. Mines, D.S. Wuttke, J.R. Winkler, H.B. Gray, *J. Am. Chem. Soc.* **1994**, *116*, 1577; b) N. Liang, C.H. Kang, P.S. Ho, E. Margoliash, B.M. Hoffman, *ibid.* **1986**, *108*, 4665.

[22] I.R. Gould, S. Farid, *J. Phys. Chem.* **1992**, *96*, 7635.

[23] N. Mataga, T. Asahi, Y. Kanda, T. Okada, T. Kakitani, *Chem. Phys.* **1988**, *127*, 249.

[24] E. Vauthey, P. Suppan, E. Haselbach, *Helv. Chim. Acta* **1988**, *71*, 93.

[25] Y. Zeng, M.B. Zimmt, *J. Phys. Chem.* **1992**, *96*, 8395.

[26] a) P. Pasman, F. Rob, J.W. Verhoeven, *J. Am. Chem. Soc.* **1982**, *104*, 5127; b) A.M. Oliver, D.C. Craig, M.N. Paddon-Row, J. Kroon, J.W. Verhoeven, *Chem. Phys. Lett.* **1988**, *150*, 366.

[27] a) R. Hoffmann, *Acc. Chem. Res.* **1971**, *4*, 1; b) R. Gleiter, *Angew. Chem. Int. Ed.* **1974**, *13*, 696; c) M.N. Paddon-Row, *Acc. Chem. Res.* **1982**, *15*, 245.

[28] Y. Zeng, M.B. Zimmt, *J. Am. Chem. Soc.* **1991**, *113*, 5107.

[29] T. Brotin, J.-P. Desevergne, F. Fages, R. Utermöhlen, R. Bonneau, H. Bouas-Laurent, *Photochem. Photobiol., A.* **1992**, *55*, 349.

[30] K. Kumar, R.J. Tepper, Y. Zeng, M.B. Zimmt, *J. Org. Chem.* **1995**, *60*, 4051.

[31] K. Kumar, Z. Lin, D.H. Waldeck, M.B. Zimmt, *J. Am. Chem. Soc.* **1996**, *118*, 243.

[32] The effective radii of the D and the A were set to 4.5 Å. The D/A separation listed in the text was used as the center-to-center separation. Conventional continuum expressions [5f] were used to calculate the change in the driving force and reorganization energy with temperature.

[33] a) Changing ΔG°(295 K) by ± 0.3 eV induces less than a 10% change in $|V|$; b) A detailed discussion of $|V|$'s dependence on the kinetic and thermodynamic models used to evaluate the data may be found in: K. Kumar, Z. Lin, I. Kurnikov, D, Beratan, D. Waldeck, M.B. Zimmt, *J. Phys. Chem.*, submitted.

[34] This number is based on a 40% reduction in $|V|$ per additional bond in the spacer and a factor of 3 reduction for an *s-cis* linkage.

[35] P.D. Burrow, A.E. Howard, A.R. Johnston, K.D. Jordan, *J. Phys. Chem.* **1992**, *96*, 7570.

[36] AM1 calculations predict that the energy required to place an electron in the LUMO of PhCN is 1.0 eV less than that required to place an electron in the LUMO of MeCN or DMA [31]. Therefore, the amide solvent is predicted to be less effective at mediating $|V|$ than PhCN.

[37] R.J. Cave, M.D. Newton, *Chem. Phys. Lett.* **1996**, *249*, 15.

[38] a) R.S. Mulliken, *J. Am. Chem. Soc.* **1952**, *64*, 811; b) N.S. Hush, *Electrochim. Acta*, **1968**, *13*, 1005.

[39] R.J. Cave, M.D. Newton, K. Kumar, M.B. Zimmt, *J. Phys. Chem.* **1995**, *99*, 17501.

[40] M.N. Paddon-Row, A.M. Oliver, J.M. Warman, K.J. Smit, M.P. de Hass, H. Oevering, J.W. Verhoeven, *J. Phys. Chem.* **1988**, *92*, 6958.

[41] Y. Gu, K. Kumar, Z. Lin, I. Read, M.B. Zimmt, D.H. Waldeck, *J. Photochem. Photobiol., A.* **1997**, in press.

[42] Use of identical λ_V and λ_S for the CS and back ET reactions presume harmonic character along the solvent and vibrational reaction coordinates. The solvent reorganization energy need not be constant for all the solvents.

[43] a) M.R. Roest, J.M. Lawson, M.N. Paddon-Row, J.W. Verhoeven, *Chem. Phys. Lett.* **1994**, *230*, 536; b) J.M. Lawson, M.N. Paddon-Row, J.M. Warman, W. Schuddeboom, A.H. Clayton, K.P. Ghiggino, *J. Phys. Chem.* **1993**, *97*, 13099.