

Charge Transfer in Donor-Bridge-Acceptor Systems: Static Disorder, Dynamic Fluctuations, and Complex Kinetics

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The influence of static and dynamic torsional disorder on the kinetics of charge transfer (CT) in donor-bridge-acceptor (D-B-A) systems has been investigated theoretically using a simple tight-binding model. In such systems, variations of the torsion angle often give rise either to static changes in the magnitude of electronic coupling along the bridge length or to dynamic fluctuations of this quantity on the certain characteristic time scale τ_{rot} . These lead to the functional breakdown of the Condon approximation. Modeling of CT beyond the Condon approximation reveals two types of non-Condon (NC) effects. If τ_{rot} is much less than the characteristic time, τ_{CT} , of CT in the absence of disorder, the NC effects was shown to be static. Due to self-averaging of electronic coupling in this fast fluctuation limit, the breakdown of the Condon approximation manifests itself as a static correction to the time-independent rate coefficient calculated for the ordered bridge with the same time-averaged electronic coupling for all pairs of adjacent subunits. As a consequence, the CT process exponentially evolves with time and therefore can be characterized by a time-independent rate coefficient w_a for the charge arrival on the acceptor (also termed the rate constant). For larger τ_{rot} , however, the NC effects become purely kinetic. In this case, the process of CT in the tunneling regime exhibits time scale invariance, the corresponding decay curves become dispersive, and the rate coefficient w_a turns out to be time dependent. In the limit of very slow dynamic fluctuations, where $\tau_{\text{rot}} \gg \tau_{\text{CT}}$, the NC effects in kinetics of CT are found (as anticipated) to be very similar to the effects revealed for bridges with the static torsional disorder. Both analytical and numerical results obtained within this limit allow the conclusion that for very slow fluctuations and/or for static disorder, the nonexponential time evolution of the CT process is due to the configuration averaging of electronic coupling. Several consequences of our theoretical findings for the interpretation of experimentally observed transients are briefly discussed. In particular, we argue that the minimal value of the falloff parameter describing the distance dependence of the time-independent rate coefficient in tunneling regime can not be less than 0.2–0.3 Å⁻¹ and that the smaller experimental value of this parameter reported in the literature for several D-B-A systems must be attributed to the multistep hopping mechanism of charge motion rather than to the mechanism of single-step tunneling.

I. Introduction

Charge transfer (CT) has long been recognized as the key process in many fields of chemistry, physics, and biology (see, e.g., reviews,^{1–7} monographs,^{8–10} and references therein). Current interest in characterization of this process on the nanoscale (1–100 nm) has been driven by further progress in such areas of practical interest as artificial solar-energy conversion,¹¹ nonlinear optics,¹² molecular electronics,^{13,14} and oxidative damage of DNA.¹⁵

A convenient model system often used to probe the mechanism of CT in molecular objects with nanoscale dimensions comprises a donor (D) and an acceptor (A) of electrons or holes connected by molecular bridge (B); for details see, e.g., refs 11, and 16–23. The number and variety of such donor-bridge-acceptor (D-B-A) systems have grown explosively in recent years. Currently they involve bridges ranging from chains of covalently linked structural subunits (such as the fluorene-based

bridge shown in Figure 1a) to stacks of disklike aromatic molecules or Watson-Crick base pairs. A representative example of bridges formed by stacked molecular subunits is provided by capped DNA hairpins (see Figure 1b), in which the stack of adenine/thymine pairs serves as an intervening linker between donor and acceptor sites of the system.

Extensive experimental and theoretical studies of intramolecular CT through bridges with a variety of chemical structures have shown that electrons or holes can be transferred from D to A through various mechanisms, in particular via single-step tunneling.^{3,9} This mechanism is operative if the “bridging states” are very high in energy compared with D and A, so that thermal population of the bridge is unlikely.²⁴ In most cases, the latter condition is fulfilled for relatively short bridges with 3–4 building blocks.^{25–29}

On the basis of conventional kinetic arguments, it is generally believed that intramolecular CT in the tunneling regime evolves exponentially with time and therefore can be characterized by simple first-order decay kinetics with a time-independent rate constant k_{CT} also called a rate coefficient.³⁰ Investigations using single-molecule spectroscopy have shown clearly that in many cases ensemble averaging is one way to provide simple first-

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order decay with a single rate coefficient;^{31–34} the same behavior is observed in radioactive decay. Early works in collision theory and gas-phase kinetics modeling also show that a single rate coefficient can be seen when a single eigenvalue totally dominates the relaxation spectrum.³⁵ In general, then, there are many, quite different situations in which a single rate coefficient describes the observed kinetics reasonably well, although the relation of this kinetic parameter with macroscopic and microscopic variables is always an important issue in theoretical and experimental studies of different systems, processes and reaction mechanisms.

Theoretical investigations of the above-mentioned problem for intramolecular CT often rely on the extension of the Condon approximation (originally used for optical spectroscopy³⁶) to the description of the CT process. The most common formulation of this approximation for CT states that electronic coupling, V , between D and A does not vary with nuclear coordinates Q . As a result, the squared transition matrix element can be factored into an electronic part and a nuclear part (Franck–Condon factor).^{1–3,37,38a,39} More recent theoretical analysis,^{39–51} however, demonstrates the intuitively reasonable result that electronic coupling is independent of Q only for rigid spacers, but does depend on nuclear coordinates if bridges are flexible and their structural subunits can undergo different types of motion. If the dependence of V on Q is parametric (for examples, see e.g. ref 9), the Condon-like factoring of the matrix element is still possible, although, according to the above-mentioned formulation, the Condon approximation is not valid. In this case the expression for the nonadiabatic thermal rate coefficient for CT can be written in the familiar form as the product of the effective electronic coupling squared $|V_{\text{eff}}|^2$ and the density of states ρ_{FC} weighted by the Franck–Condon factor and thermally averaged, that is

$$k_{\text{CT}} = \frac{2\pi}{\hbar} |V_{\text{eff}}|^2 \rho_{\text{FC}} \quad (1)$$

Note that the value of V_{eff} in eq 1 is different from the magnitude of electronic coupling estimated within the framework of the Condon approximation, since V_{eff} should be calculated at a certain coordinate $Q = Q^*$ that makes the main contribution in the overlap of nuclear wave functions. This and other non-Condon effects was established for systems with increasing complexity, varying from relatively small⁴³ and medium-sized molecular objects⁵⁰ up to polymers^{51–53} and biological macromolecules.^{54,55}

The above theoretical works, together with experimental investigations of non-Condon effects associated with bridge dynamics,^{56–59} have triggered numerous efforts to calculate k_{CT} beyond the Condon approximation.^{41,49,60–71} In most of these calculations it is implicitly assumed that for a given D-B-A system k_{CT} remains constant even if the Condon approximation does not hold. Consequently, static corrections to well-established formulas of electron transfer theory are supposed to be sufficient to quantify the influence of fluctuating electron coupling on k_{CT} as long as the non-Condon effects are relatively small.⁷⁰

Another approach to the problem of non-Condon effects in CT is used in the present work. Within the framework of this approach the kinetic characteristics of a CT process can be deduced directly from the decay curves calculated numerically without invoking *a priori* assumptions mentioned above. This makes the approach particularly useful for theoretical analysis of the tunneling regime of CT in D-B-A triads with dynamic fluctuations of the electronic coupling along the bridge induced by the torsional motion of bridge subunits.

To avoid the assumption about the existence of a time-independent rate coefficient, we performed numerical studies

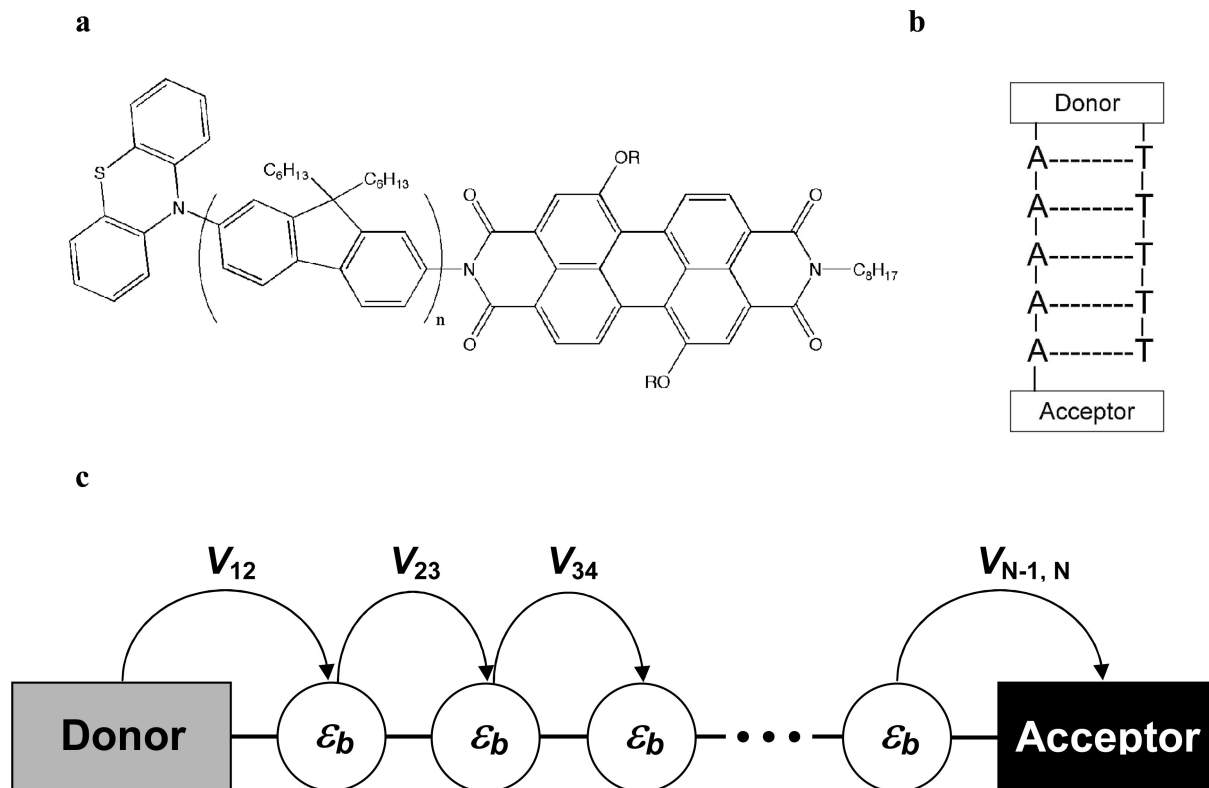


Figure 1. Examples of D-B-A systems with bridges formed by covalently linked (a) or by π -stacked (b) structural subunits and 1D chain used for theoretical modeling of these systems (c).

of the CT kinetics in D-B-A systems with disorder in the magnitude of electronic coupling that arises due to dynamic and static fluctuations of the torsion angle between adjacent structural subunits of the bridge. Since mass of these subunits is typically large, the torsion motion can be treated classically, while CT process in relatively short bridges can be treated quantum mechanically. This enables one to use the hybrid numerical quantum-classical methodologies to study the effect of static and/or dynamic fluctuations of the torsion angle on kinetics of CT. The application of these methodologies to the solutions of various problems has been considered in a number of publications.⁷² In the present work, we use the most simple to the mixed quantum-classical description of the charge propagation in D-B-A systems based on the tight-binding approximation. In addition to a number of well-known restrictions (see, e.g., ref 73), this approximation at least in its standard form does not allow the description of the intraunit vibrational relaxation and therefore our analysis can not be extended to the incoherent CT proceeding via multistep sequential hopping. The results obtained for coherent CT mechanism show the breakdown of the Condon approximation caused by dynamic and static fluctuations of the torsion angle between adjacent structural subunits has important consequences for intramolecular CT proceeding in the tunneling regime. In particular, two different types of the non-Condon effects can be distinguished based on the analysis of our computer simulation data. The non-Condon effects are shown to be purely kinetic if the characteristic time, τ_{rot} , of dynamic fluctuations associated with changes in the torsion angle (and hence in electronic coupling) is comparable with or less than the characteristic time, τ_{CT} , of CT in the absence of disorder ($\tau_{\text{rot}} \lesssim \tau_{\text{CT}}$). In this case the rate process under investigation exhibits time scale invariance^{74,75} due to the breakdown of the Condon approximation. When applied to intramolecular CT in D-B-A systems, the term “time scale invariance” signifies that electrons or holes are transferred from D to A on many different and coexisting time scales rather than on a single temporal scale defined by the reciprocal of the time-independent rate coefficient. For that reason, the calculated decay transients become nonexponential and the time evolution of the CT process should be described in terms of the time-dependent rate coefficient. Following terminology widely accepted in the literature,⁷⁵ such kinetic behavior herein is referred to as dispersive.

These features were not found in our simulations of CT through ordered flat bridges with the same equilibrium value of the torsion angle for all pairs of neighboring subunits. Furthermore, any indications of dispersive kinetics completely disappear as torsionally induced fluctuations of electronic coupling $V(t)$ become much faster than a charge motion along the analogous rigid bridge without disorder ($\tau_{\text{rot}} \ll \tau_{\text{CT}}$). Due to the self-averaging of $V(t)$ in this fast fluctuation limit, non-Condon effects become static now and manifest themselves as static corrections. The time-independent rate coefficient is now calculated for a bridge with the same time-averaged electronic coupling for all pairs of adjacent subunits. Consequently, the process of CT can be quantified in terms of a constant rate coefficient determined by the root-mean-square electronic coupling, $\sqrt{\langle V^2(t) \rangle}$. The latter finding is consistent with the Büttiker–Landauer theory of tunneling transition through a time-dependent barrier.⁷⁶ As follows from their analysis, at high modulation frequencies, the particle will see a barrier with the time-averaged height that determines the value of the time-independent transmission coefficient for tunneling.

We also investigated the other limit, in which dynamic fluctuations of the torsion angle are much slower than charge motion, i.e., $\tau_{\text{rot}} \gg \tau_{\text{CT}}$. In this case the dispersive behavior of the process is retained, but the shape of the kinetic curve almost coincides with that calculated for bridges with static torsional disorder. The analytical and numerical results obtained within this limit show that for very slow fluctuations and/or for static disorder, the nonexponential time evolution of the CT process is due to the configuration averaging of electronic coupling.

The results of our numerical studies as a whole demonstrate that kinetic non-Condon effects in the time evolution of the CT process can be discussed in terms of a time-dependent rate coefficient. The temporal behavior of this kinetic parameter indicates that intramolecular CT in D-B-A systems can be considered as the first example of time scale invariance in a chemical reaction governed by quantum mechanical tunneling. To our knowledge, time scale invariance was previously reported only for classical rate processes^{74,75} with one exception being the relaxation of the wave function induced by a slowly varying perturbation inside the potential barrier.⁷⁷ In addition, our results show that even a single first-order process can exhibit nonexponential decay with time. Therefore observations of nonexponential transients in time-resolved experiments designed to study different rate processes, in particular intramolecular CT,^{22,78–81} should not be necessarily considered as a signature of a complex reaction mechanism that involves several elementary steps with different constant rate coefficients.

II. Qualitative Consideration of Torsional Non-Condon Effects

A convenient starting point for qualitative analysis of the non-Condon effects caused by dynamic fluctuations of torsion angle between bridge molecular subunits n D-B-A systems is the Fermi’s golden rule expression for the nonadiabatic CT rate coefficient k_{CT} . Using the Fourier representation of the δ -function

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(i\omega t) dt \quad (2a)$$

the Fermi golden rule can be written as the Fourier transform for the product of the time-dependent Franck–Condon factor, $C_{\text{FC}}(t)$, and the electronic coupling correlation function $C_{\text{V}}(t)$

$$k_{\text{CT}} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \exp(i\omega_{\text{DA}} t) C_{\text{V}}(t) C_{\text{FC}}(t) \quad (2)$$

where ω_{DA} is the Bohr frequency corresponding to the CT energy gap.^{67a–c}

It should be mentioned that the derivation of eq 2 rests on the time-dependent perturbation theory. This theory is valid when the perturbation causes system evolution within the time period much larger than the duration of the perturbation itself.^{38b} This implies that for the applicability of eq 2 to the problem under consideration, the time scale of CT along a rigid and perfectly ordered bridge, τ_{CT} , should be much longer than the characteristic time of torsional motion τ_{rot} . The latter quantity is a measure of how rapidly dynamic fluctuations of torsion angle randomize the value of electronic coupling in the given D-B-A system, while τ_{CT} can be defined as the reciprocal of the rate coefficient, k_{CT}^* , for CT in the absence of fluctuations.

The correlation function $C_{\text{V}}(t)$ in eq 2 describes the influence of dynamic fluctuations of torsion angle between neighboring bridge units on the magnitude of electronic coupling. According to the results of molecular dynamics simulations and quantum

chemical calculations,^{67d} the time dependence of this correlation function can be approximated by

$$C_V(t) = \sigma_V \exp\left(-\frac{t}{\tau_{\text{rot}}}\right) + \langle V(t) \rangle^2 \quad (3)$$

with the finite time-averaged value $\langle V(t) \rangle = V_0$ and the mean-square deviation of electronic coupling σ_V .

Let us introduce now the time scale τ_{FC} for the decay of the Franck–Condon factor $C_{\text{FC}}(t)$. Usually τ_{FC} is defined (see, e.g., ref 67c) by the time it takes to lose overlap between an initial nuclear wave packet propagated with the electron in the donor state and the same wave packet propagated with the electron in the acceptor state. If $\tau_{\text{rot}} \gg \tau_{\text{FC}}$, the integral in eq 2 can be simplified since in this case the relevant time scales can be separated. As a result, one gets

$$k_{\text{CT}} \alpha \int_{-\infty}^{+\infty} dt \exp(i\omega_{\text{DA}}t) C_V(t) C_{\text{FC}}(t) \approx C_V(0) \int_{-\infty}^{+\infty} dt \exp(i\omega_{\text{DA}}t) C_{\text{FC}}(t) \equiv C_V(0) \rho_{\text{FC}} \quad (4)$$

Furthermore, two limits become evident from eqs 4 and 3. If fluctuations of electronic coupling are so small that $\sigma_V \gg \langle V(t) \rangle^2 = V_0^2$, the expression for CT rate coefficient collapses to the familiar equilibrium form of the Marcus–Hush–Jortner equation^{1–3}

$$k_{\text{CT}} = \frac{2\pi}{\hbar} |V_0|^2 \rho_{\text{FC}} \quad (5)$$

In the opposite case of large fluctuations where $\sigma_V \ll \langle V(t) \rangle^2$, the initial value of the electronic coupling correlation function $C_V(0)$ is equal to $\langle V(0)^2 \rangle = \langle V^2 \rangle$ since σ_V in eq 3 is given by $\langle V(0)^2 \rangle - \langle V(t) \rangle^2 = \langle V^2 \rangle - V_0^2$. Hence

$$k_{\text{CT}} = \frac{2\pi}{\hbar} \langle V^2 \rangle \rho_{\text{FC}} \quad (6)$$

in accordance with the results derived earlier (see, e.g., ref 69).

Comparison of eqs 5 and 6 show that for $\tau_{\text{rot}} \gg \tau_{\text{FC}}$ large fluctuations cause the breakdown of the Condon approximation. The resultant effect is static and manifests itself as a replacement of the absolute square of the electronic coupling calculated within the Condon approximation by its time average. This can be expected since in spite of the breakdown of this approximation due to the dependence of electronic coupling on torsion angle (and hence on nuclear coordinates), the time scales associated with the decays of the Franck–Condon factor and the electronic coupling correlations function can be separated. As a result, in this case the non-Condon effect remains static and can be described in terms of time-independent corrections to eq 6. Several perturbative schemes have been proposed (see, e.g. 67c, 70 and references therein) to extend this separability to the case where $\tau_{\text{CT}} \gg \tau_{\text{rot}} \gtrsim \tau_{\text{FC}}$.

Thus, a time-dependent perturbation theory and a separation of time scales for electronic and nuclear motions enable us to justify the validity of the assumption about the existence of the time-independent rate coefficient for intramolecular CT beyond the Condon approximation in the limit of fast torsion motion $\tau_{\text{rot}} \ll \tau_{\text{CT}} = 1/k_{\text{CT}}^*$. However the situation becomes different if $\tau_{\text{rot}} \lesssim \tau_{\text{CT}} = 1/k_{\text{CT}}^*$. Now a time-dependent perturbation theory fails (see above) and a separation of time scales is not possible (as can be shown by applying the method of adiabatic elimination of the continuum to the solution of the time-dependent Schrödinger equation⁸²). Under these conditions the time evolution of the CT process can be described by a theory of irreversible random transitions.⁸³ According to this theory, dynamic fluctuations of the torsion angle θ can be described as

a stochastic process coupled to the charge transition between donor to acceptor sites due to the dependence of the transition rate coefficient $k(\theta)$ on the angular coordinate. This stochastic process is characterized by the probability density $P(\theta, t; \theta_0)$ to find the two adjacent molecular subunits in the conformation with the torsion angle between θ and $\theta + d\theta$ at time t , if at $t = 0$ the angular coordinate θ is equal to θ_0 . Following the analysis performed in ref 83, one can show that in the limit $\tau_{\text{rot}} \lesssim \tau_{\text{CT}} = 1/k_{\text{CT}}^*$ the time behavior of the CT process is nonexponential and that the probability $S(t)$ to find a charge at the donor site varies with t as

$$S(t) = \int_{\theta_0} \rho(\theta_0) \int_{\theta} P(\theta, t; \theta_0) \exp\left(-\int_0^t k(\tau) d\tau\right) d\theta d\theta_0 \quad (7)$$

Here the first integral corresponds to configuration averaging over the distribution of initial torsion angles $\rho(\theta_0)$, while $k(\tau)$ stands for the time-dependent transition rate coefficient given by

$$k(\tau) = \int_{\theta} P(\theta, \tau, \theta_0) k(\theta) d\theta \quad (8)$$

As can be seen from eqs 7 and 8, in contrast to the fast fluctuation limit the non-Condon effect becomes kinetic as fluctuations slow down, manifesting itself as the nonexponential time behavior of the CT process if $\tau_{\text{rot}} \lesssim \tau_{\text{CT}} = 1/k_{\text{CT}}^*$. Equations 7 and 8 also suggest that kinetics of CT remains nonexponential when $\tau_{\text{rot}} \gg \tau_{\text{CT}}$ and torsion motion is “frozen”. Now the function $P(\theta, t; \theta_0)$ slowly evolves with time and can be replaced by the initial distribution $P(\theta, t = 0; \theta_0) = \delta(\theta - \theta_0)$. As a result, eqs 7 and 8 yields

$$S(t) = \int_{\theta_0} \rho(\theta_0) \exp(-k(\theta_0)t) d\theta_0 \quad (9)$$

The obtained expression reveals that for $\tau_{\text{rot}} \gg \tau_{\text{CT}}$, the CT process is indeed nonexponential in time, although the equation describing the decay curve for “frozen” fluctuations turns out to be distinct from the equation derived in the case $\tau_{\text{rot}} \lesssim \tau_{\text{CT}} = 1/k_{\text{CT}}^*$ (cf. eq 7).

To get the explicit form of the time-resolved decay, we investigated the effect of static and dynamic torsional disorder on the kinetics of CT using theoretical methodology described in the next section.

III. Theoretical Methodology

III.1 A Model for Disorder. In the proposed simple model, we consider the ensemble of many isolated D-B-A systems and approximate each member of this ensemble by a one-dimensional (1D) chain of chemically connected sites corresponding to the relatively rigid molecular subunits. For the D-B-A systems shown in Figure 1a,b as representative examples, the sites correspond to the donor, the acceptor and to the building blocks of the bridge. The system in Figure 1a contains fluorene groups as the building blocks of the bridge, while for the DNA hairpin conjugates schematically depicted in Figure 1b such blocks are comprised of adenine (A):thymine (T) base pairs. For the sake of simplicity, the energy of the charge localized on a single molecular subunit of the bridge, i.e., the so-called site energy, is assumed to be the same for all sites except the donor and the acceptor.

The intramolecular motion of charge carriers along the 1D chain modeling the D-B-A system (see Figure 1c) is made possible by the electronic coupling between neighboring sites i and $i + 1$ ($i = 1, 2, \dots, N - 1$) characterized by the value of the charge transfer integral $V_{i,i+1}$. The value of the latter parameter depends both on the internal geometry of structural subunits of

the system and on the coordinate ξ associated with the intersite degrees of freedom. In what follows we assume that ξ corresponds to the torsion angle θ between two neighboring bridge subunits. Then, using the “adiabatic elimination” procedure^{84,85} analogous to the Born–Oppenheimer-like approximation in quantum mechanics, the probability, $P(\theta, t)$, that the angle between two adjacent sites is equal to a certain value θ at time t can be deduced from the solution of the rotational diffusion equation

$$\frac{\partial P(\theta, t)}{\partial t} = D_{\text{rot}} \left[\frac{\partial^2 P(\theta, t)}{\partial \theta^2} + \frac{1}{k_B T} \frac{\partial}{\partial \theta} \left(P(\theta, t) \frac{\partial U_{\text{rot}}(\theta)}{\partial \theta} \right) \right] \quad (10)$$

where D_{rot} is the rotational diffusion coefficient, k_B is the Boltzmann constant, T is the temperature, and $U_{\text{rot}}(\theta)$ is the torsion potential.

Since $V_{i,i+1}$ depends on the torsion angle, while the torsion angle, in turn, is distributed according to eq 10, the charge transfer integral for a particular chain modeling the D-B-A system should be considered within the framework of our model as a random parameter. This suggests that even for bridges involving only equienergetic structural subunits, the migration of charge from D to A proceeds along a pathway with the disorder associated with variations of the $V_{i,i+1}$ value and, hence, with changes of the electronic coupling between neighboring sites along the chain. Note that this torsional disorder should be dynamic if the charge motion is slower than the diffusion process along the θ -coordinate. Otherwise, it becomes effectively static. Indeed, if the torsion dynamics is “frozen” on the time scale of charge migration, the left-hand side of eq 10 equals zero, and the solution of the diffusion equation coincides with the Boltzmann distribution

$$P(\theta) = \frac{\exp\left(-\frac{U_{\text{tor}}(\theta)}{k_B T}\right)}{\int_0^{2\pi} \exp\left(-\frac{U_{\text{tor}}(\theta)}{k_B T}\right) d\theta} \quad (11)$$

III.2 Tight-Binding Model for Charge Transfer. Following the tight-binding approximation (see, e.g., 29 and 51 and references therein), the wave function of the charge, Ψ , is written as a linear combination of orbitals ϕ_i localized on each site, namely

$$\Psi(t) = \sum_{i=1}^N c_i(t) \phi_i \quad (12)$$

where $c_i(t)$ is the expansion coefficient satisfying the initial condition $c_i(t=0) = \delta_{1,i}$ and $\delta_{1,i}$ is the Kronecker symbol. These coefficients can be obtained by solving the set of the first-order differential equations resulting from the substitution of eq 12 into the Schrödinger equation

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H \Psi(t) \quad (13)$$

The diagonal matrix elements of the tight-binding Hamiltonian H in eq 13 correspond to the site energies ε_{ii} and for the model discussed in Section III.1 can be specified as follows

$$\varepsilon_{ii} = \begin{cases} \varepsilon_{11} & \text{for } i = 1 \\ \varepsilon_b & \text{for } 1 < i \leq N - 1 \\ \varepsilon_{NN} - \frac{i\hbar}{\tau} & \text{for } i = N \end{cases} \quad (14)$$

Here a complex part is incorporated into the diagonal matrix element associated with the acceptor site $i = N$ to take into

account that a charge reaching this site will undergo trapping with the characteristic time τ .

The off-diagonal matrix elements of the Hamiltonian for the tight-binding scheme taking into account only the nearest neighbor interactions are equal to the charge transfer integrals $V_{i,i+1} = V_{i+1,i}$ while all other off-diagonal matrix elements are zero. Thus, the H matrix in eq 13 can be written as

$$H = \begin{pmatrix} \varepsilon_{11} & V_{12} & 0 & \cdots & 0 \\ V_{21} & \varepsilon_b & & & \\ 0 & & \ddots & & \\ \vdots & & & \ddots & \\ 0 & & & & \varepsilon_{NN} - \frac{i\hbar}{\tau} \end{pmatrix} \quad (15)$$

Note that in the case of disorder solely caused by variations of the torsion angle between neighboring structural subunits of the D-B-A system, the off-diagonal elements in eq 15 depend on θ , and therefore are random.

The probability $P(t)$ that a charge will survive in the system up to time t (the so-called survival probability) can be expressed in terms of occupation probabilities $|c_i(t)|^2$ as

$$P(t) = \sum_i^N |c_i(t)|^2 \quad (16)$$

This enables one to calculate the rate coefficient w_a for the charge arrival on the acceptor. The latter quantity is often used in experiments for characterization of CT kinetics^{78,79,86} and is defined as

$$w_a = -\frac{d \ln P(t)}{dt} \quad (17)$$

Experimentally the w_a values for holes (or electrons) generated in D-B-A systems are deduced from the rise of the A^+ (or A^-) spectral band obtained from transient absorption measurements.⁸⁶ A computational procedure which allows us to find $P(t)$ and w_a theoretically is described in the next section.

III.3 Computational Method. To study intramolecular CT numerically, the wave function of the charge was propagated in time with a step of one atomic unit (2.42×10^{-17} s) using eqs 13 and 15 until a preset value of the total time t had been reached. For systems without disorder, all off-diagonal matrix elements in eq 15 were taken to be equal and the expansion coefficients $c_i(t)$ were obtained for different time instants from the numerical solution of the set of the first-order differential equations arising from the substitution of eq 12 into eq 13 as discussed in Section III.2. Subsequently, the survival probability and the CT rate were calculated from eqs 16 and 17, respectively.

A similar computational procedure can be used for theoretical studies of CT in D-B-A systems with torsional disorder. However this requires information about the potential $U_{\text{tor}}(\theta)$ describing the rotation of two adjacent structural subunits relative to each other. In the present work, we exploit the data on $U_{\text{tor}}(\theta)$ obtained earlier for fluorene bridges from electronic structure calculations at the MP2 level.⁵² In the case where torsional disorder is static, this enables one to sample the θ values from the distribution given by eq 11 and to set up the tight-binding Hamiltonian using the dependence of the charge transfer integral on the torsion angle calculated previously for bifluorene ($V \approx V_0 \cos \theta$ with $V_0 = 0.43$ eV).

In the cases where the disorder is taken to be dynamic, the values of the torsion angles were propagated in time by assuming that the subunits in the bridge undergo rotational

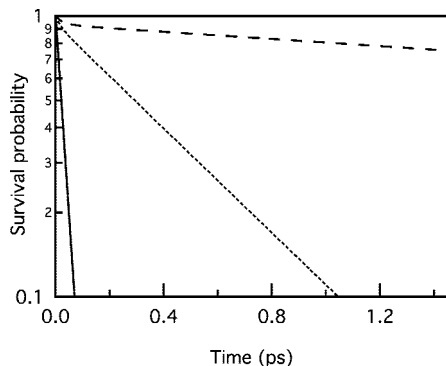


Figure 2. Survival probability as a function of time for D-B-A systems containing 3 (solid line), 4 (dotted line), and 5 (dashed line) subunits. All curves were calculated for the D-B-A system with the energy gap $\Delta\varepsilon$ between the donor and the equienergetic bridge equal to 1.2 eV. The value of the charge transfer integral V was taken to be equal to 0.3 eV.

diffusion on the rotational potential energy profile discussed above. During a small time step Δt , the change in the angles is given by⁸⁴

$$\Delta\theta_i = -\frac{D_{\text{rot}}}{k_B T} \frac{\partial U_{\text{tot}}(\theta_i)}{\partial \theta_i} \Delta t + \Delta\theta_{\text{dif}} \quad (18)$$

The first term in eq 18 describes the rotational drift due to the torsion potential resulting from interaction of a given subunit with right and left neighbors, while the second term accounts for the random diffusive rotation. The value of the latter term is calculated according the relation $\Delta\theta_{\text{dif}} = (24D_{\text{rot}}\Delta t)^{1/2}\chi$ with χ being a uniformly distributed random number in the interval $[-1/2, 1/2]$, so that the mean squared value of $\Delta\theta_{\text{dif}}$ is given by

$$\langle \Delta\theta_{\text{dif}}^2 \rangle = 2D_{\text{rot}}\Delta t \quad (19)$$

with $D_{\text{rot}} = 1/(2\tau_{\text{rot}})$ and τ_{rot} the diffusional rotation time of the molecular subunits. The values of τ_{rot} for different molecules can be obtained from results of molecular simulations or can be measured by variety of techniques.⁸⁷

For the migration-controlled CT, which is the process of our primary interest here, the characteristic time τ in eqs 14 and 15 should be much less than τ_{CT} and hence will have no influence on the time evolution of the survival probability. However, the value of this parameter is important from the computational point of view. In all calculations the value of τ was chosen within the femtosecond time range. This choice is dictated by a compromise between the need for a reasonable duration of computer simulations and the necessity to satisfy the condition $\tau \ll \tau_{\text{CT}}$ that allows the process of CT to be considered as migration-controlled. As has been shown in a series of additional calculations, variations of τ within the range mentioned above do not affect the obtained numerical results in accordance with our expectations. This verifies that the time evolution of the CT process is indeed governed by the motion of charge carriers from D to A rather than by their trapping on the acceptor site.

The data presented below were obtained by averaging eq 16 over 300 realizations with different initial torsion angles. To study the effect of dynamic fluctuations associated with changes in electronic coupling between neighboring sites of the D-B-A system, the rotation time τ_{rot} was varied from 0.1 up to 500 ps. The values of other parameters involved in calculations are given in the text.

IV. Results and Discussion

We first consider reference results obtained for static ordered systems and then compare these results with the time evolution

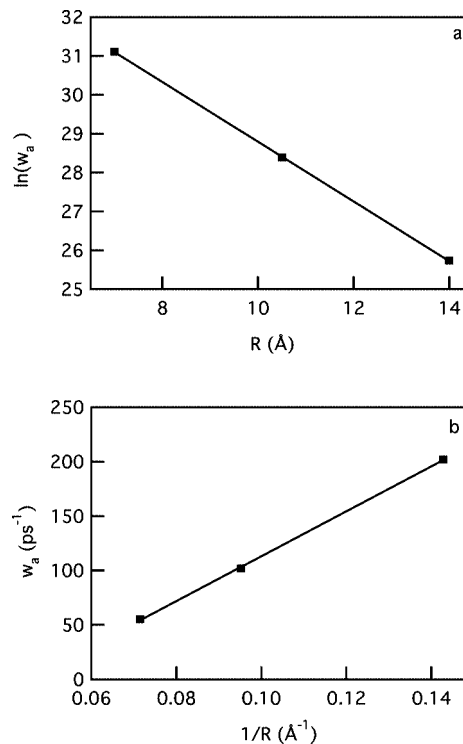


Figure 3. Distance dependencies for the rate coefficient for charge transfer in D-B-A systems. The distance dependence in panel (a) was calculated from data presented in Figure 2 taking the value of the intersite distance equal to 3.5 Å. The dependence in panel (b) was obtained for zero energy gap taking the same value of the charge transfer integral V as in Figure 2.

of the same process for systems with static disorder or dynamic fluctuation. The comparison enables us to establish the specific disorder effects on the CT kinetics as discussed in Sections IV.2 and IV.3.

IV.1 One D-B-A Systems without Disorder. In the absence of disorder, the bridge connecting the donor and the acceptor includes only equienergetic sites with electronic coupling between nearest neighbors uniquely determined by a single time-independent value, V , of the charge transfer integral. As can be seen from the data presented in Figure 2, in this case the survival probability $P(t)$ obtained from eq 16 decreases with time following the exponential law with the well-defined time-independent rate coefficient w_a .

The numerical results plotted in Figure 2 also demonstrate that the process slows down as the distance, R_{DA} , between D and A becomes larger. One generally expects that for a mechanism of coherent tunneling,^{2-4,8-10}

$$w_a = w_0 \exp(-\beta R_{\text{DA}}) \quad (20)$$

where w_0 is the pre-exponential factor and β is the so-called falloff parameter. This distance dependence is consistent with our numerical results, but only if the ratio of the energy gap, $\Delta\varepsilon$, between the donor and the equienergetic bridge to the value of the charge transfer integral, V , is substantially larger than 1; see Figure 3a. In the opposite situation, when $\Delta\varepsilon/V \ll 1$, the rate of the charge arrival turns out to be proportional to $1/R_{\text{DA}}$ as is evident from Figure 3b (and expected on the basis of a time scale argument⁸⁸).

Two distinct functional forms found numerically for the dependence of w_a on R_{DA} at large and small values of the ratio $\Delta\varepsilon/V$ suggest that two extremes for the mechanism of CT should be considered within the simple tight-binding model formulated

TABLE 1: Examples of Molecular Bridges with Known Values of Intramolecular Drift Mobility μ_{im} of Charge Carriers, Charge Transfer Integral V , and Minimal Mobility $\mu^* = e\hbar/(4mV)$ of Charges for Band Transport Estimated from the Ioffe–Frohlich–Sewell Criterion⁹⁰

bridge subunit	μ_{im} , cm ² V ⁻¹ s ⁻¹	V , eV	μ^* , cm ² V ⁻¹ s ⁻¹
fluorene	>0.7 ^a	0.39 ^a	0.7
phenylene vinylene	68 ^b	0.43 ^b	0.7
dialkoxyphenyl	<0.01 ^c	0.37 ^c	0.8
ladder phenyl	600 ^d	0.79 ^d	0.4
adenine:thymine base pair in DNA A-tracts	9×10^{-4e}	4×10^{-3f}	72
	4×10^{-5g}		

^a Data of ref 53. ^b Data of ref 52. ^c Grozema, F. C.; Siebbeles, L. D. A., unpublished. ^d Prins, P.; Grozema, F. C.; Schins, J. M.; Patil, S.; Scherf, U.; Siebbeles, L. D. A. *Phys. Rev. Lett.* **2006**, *96*, 146601. ^e Takada, T.; Kawai, K.; Cai, X.; Sugimoto, A.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 1125–1129; ^f Data of ref 55. ^g Data of ref 86.

in the previous section. One extreme is the single-step tunneling of a charge from D to A without physical occupation of the bridge (see, e.g., refs 2–4, 6, 9, 10). This mechanism is operative if the energy splitting of bridge states due to their electronic coupling does not reduce the gap $\Delta\epsilon$ significantly, so that the inequality $\Delta\epsilon/V \gg 1$ holds.

However, if $\Delta\epsilon/V \ll 1$, other regimes of CT are feasible. Since now the gap $\Delta\epsilon$ effectively vanishes, electrons or holes can be transferred from D to A through long bridges undergoing motion in a tight-binding band.⁸⁹ On the basis of the Ioffe–Frohlich–Sewell criterion,⁹⁰ one can expect that this mechanism prevails when the width of tight-binding band, $4V$, exceeds the scattering width \hbar/τ_{scatt} with τ_{scatt} standing for the characteristic time of charge relaxation induced by the scattering on intramolecular vibrations and by the presence of diagonal or off-diagonal disorder in the system. Note that the relaxation time for particles with charge e and mass m can be expressed in terms of the intramolecular drift mobility of charge carriers μ_{im} as $\tau_{scatt} = (m/e)\mu_{im}$. Therefore the Ioffe–Frohlich–Sewell criterion implies that band transport along the bridge will dominate if $\mu_{im} > \mu^* = e\hbar/(4mV)$. The values of μ_{im} , V , and μ^* available for several bridges with molecular subunits are listed in Table 1. As follows from the data presented in this table, μ_{im} is large than μ^* for fluorine, phenylene vinylene, and ladder phenyl bridges. Thus, based on the Ioffe–Frohlich–Sewell criterion we conclude that CT through these bridges can proceed via a mechanism involving bandlike charge transport in the weak scattering limit. In this limit the time spent on the bridge by a moving charge should be proportional to the distance between D and A and hence

$$w_a \sim 1/R_{DA} \quad (21)$$

in qualitative agreement with the computational results shown in Figure 3b.

By contrast, $\mu_{im} < \mu^*$ for dialkoxyphenyl bridge and a stack of adenine:thymine in the DNA hairpin conjugates. For these and other bridges with relatively slow intramolecular drift mobility, effects of polaronic on-site coupling become so significant that a charge will be temporarily localized on a bridge subunit and will move toward the acceptor in the incoherent regime of sequential hopping. This regime as well as the crossover between tunneling and hopping received much attention,^{28,40,91} particularly in the context of CT in DNA,^{4,29,92a–g} and is not considered here.

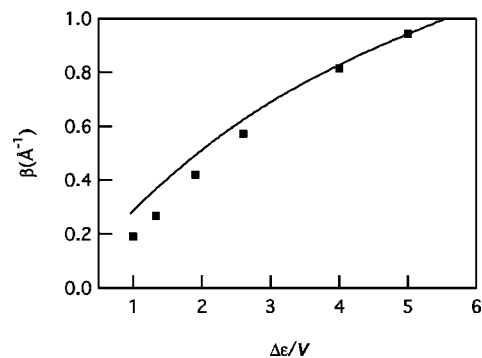


Figure 4. The dependence of the falloff parameter β on the ratio of the energy gap between the donor and the equienergetic bridge, $\Delta\epsilon$, to the value of the charge transfer integral, V , for static uniform bridge without disorder. The curve shown by a solid line was obtained from eq 22. Points correspond to the results of numerical calculations.

The ratio $\Delta\epsilon/V$ not only indicates whether coherent tunneling or other mechanisms of CT considered above prevails in a given D-B-A system, but also determines the falloff parameter β in eq 20 that describes the rate coefficient for the charge arrival on the acceptor site in the tunneling regime. For the latter mechanism, earlier theoretical studies^{4,29} provide the following relation between β and $\Delta\epsilon/V$

$$\beta = \frac{2}{a} \ln \left[\frac{\Delta\epsilon}{2V} + \left(1 + \frac{\Delta\epsilon^2}{(2V)^2} \right)^{1/2} \right] \quad (22)$$

where a is the distance between neighboring structural subunits. This relation reduces to the expression for β which has been derived earlier by Onuchic and Beratan⁹³ and by Evenson and Karplus⁹⁴ within the tight-binding scheme in the case $\Delta\epsilon/V \gg 1$.

According to the results in Figure 4, the dependencies of β versus $\Delta\epsilon/V$ obtained from eq 22 and calculated numerically within the framework of the tight-binding approximation are close to each other and, as expected, become the same as $\Delta\epsilon/V$ becomes large. On the basis of these results, we conclude that β monotonically increases with $\Delta\epsilon/V$ for all values for which the coherent tunneling mechanism of CT is expected to occur. Furthermore, the data in Figure 4 enable us to specify the lower limit, β_{min} , for the values of the falloff parameter imposed by the crossover between tunneling and other mechanisms at $\Delta\epsilon/V \approx 1$. To find this limit, either $\Delta\epsilon$ in eq 22 should be set equal to V or the β value should be calculated numerically for $\Delta\epsilon/V = 1$. The analytical estimation based on eq 22 for the regular 1D chain with $a = 3.5 \text{ \AA}$ gives $\beta_{min} = 0.27 \text{ \AA}^{-1}$, while the numerical procedure yields $\beta_{min} = 0.19 \text{ \AA}^{-1}$. The higher β_{min} value obtained from eq 22 as compared with the result of numerical calculations is not surprising since the analytical expression for the falloff parameter can be derived only in the limit of infinitely long chains.^{4,29} As has been shown earlier,²⁹ eq 22 overestimates β for finite chains, thus providing less accurate result for β_{min} as compared to the result of numerical calculations.

The above estimate can be used as a guideline in distinguishing between tunneling and other mechanisms of intramolecular CT in D-B-A systems on the basis of experimentally determined β values. The experimental data on the distance dependence of intramolecular charge transfer rates that are available for different bridges yield β values ranging from 0.06 \AA^{-1} for polyene-bridged binuclear complexes⁹⁵ up to 1.47 \AA^{-1} for a stack of adenine (A):thymine (T) connecting acridinium and guanine (G) in DNA.⁹⁶ For D-DNA-A systems, the experimental

β values were found to vary from 0.02⁹⁷ to 1.47 Å⁻¹ (see ref 96) depending on the nucleobase sequence in the interior of the DNA duplex. Our estimation of the lower limit β_{\min} of the falloff parameter in eq 20 suggests that these seemingly controversial results can be explained by different mechanisms of intramolecular CT in systems with large and small β values.⁹² On the basis of this estimation, a large β ($> 0.96/a$ (Å) $\approx 0.2-0.3$ Å⁻¹) exceeding β_{\min} can be attributed to the tunneling regime of the process. By contrast, a smaller experimental value of the falloff parameter ($< 0.96/a$ (Å) $\approx 0.2-0.3$ Å⁻¹) can be evidence in favor of incoherent charge motion along the bridge. Certainly, this is true only if experimental data ensure that the measured rate coefficient of CT and the CT efficiency exponentially decrease with the bridge length; otherwise, β is not a proper parameter for the description of incoherent charge transfer.^{92a}

It should be noted that both experiment^{92b,d} and theory^{92d-f} show that for sufficiently long bridges the incoherent hopping mechanism of CT can exhibit exponential distance dependence, as does single-step coherent tunneling (see eq 12). The falloff parameters for these two mechanisms have, however, distinct physical interpretations. While β in eq 20 is a measure of electronic coupling between D and A (cf. eq 22), the falloff parameter, β_h , for multistep incoherent hopping mechanism reflects either an asymmetry in the hopping rates in forward (toward A) and backward (toward D) directions^{92h} or the competition of hopping and different channels for the charge depopulation of the bridge.^{92d-f} For these reasons, parameters β and β_h can also differ in their values. As has been explained above, β for a single-step tunneling transfer between D and A must not be less than 0.2–0.3 Å⁻¹. For incoherent hopping, contrastingly, no lower limit exists, so that β_h can have much smaller value. A typical example of the D-B-A triads in which the incoherent CT process exhibits a weak exponential distance dependence with $\beta_h < 0.1$ Å⁻¹ is the system involving a guanine radical cation G⁺ (a hole donor), the hole trap triple GGG (an acceptor), and a long sequence with m repeating AT pairs between G bases ($m = 1, 2, \dots$) serving as a bridge.^{92b,d} In such systems (as well as in many other D-DNA-A assemblies) a hole hops between neighboring G bases with the rate coefficient k_h and in addition is able to react with surrounding water with the rate k_r at each hopping step.¹⁵ Kinetic analysis^{92d-f} of this situation shows that both the efficiency and the rate coefficient of hole transfer between G⁺ and GGG drop exponentially as the bridge length increases, with the falloff parameter β_h given by

$$\beta_h = \frac{1}{a(m+1)} \left(\frac{k_r}{k_h} \right)^{1/2}$$

Note that in typical experiments k_h must be larger than k_r in order to allow a charge to be transferred from D to A through long bridges. As a consequence, β_h can indeed be much smaller than the minimal value $\beta_{\min} \approx 1/a$ of the falloff parameter β for the tunneling regime of CT. For example, for sequences of alternating AT and GC base pairs with $m = 2$ and $a = 3.4$ Å, the ratio $k_h/k_r = 8.9$ (for details, see ref 92f) and therefore β_h turns out to be less than β_{\min} by almost a factor of 10.

Another example of the reaction channel competitive with sequential hopping is the depopulation of the bridge due to reverse charge transitions from the first bridge site to D (with the rate coefficient $k_{1,D}$) and from the last bridge site to A (with the rate coefficient $k_{N,A}$). Analysis of the kinetics of CT along bridges with equal rate coefficients, k_{hs} , of hopping steps shows^{92i,j} that

$$w_a = \frac{k_{hs} \exp\left(-\frac{\Delta\varepsilon}{k_B T}\right)}{\frac{k_{N,A}}{k_{1,D}} + \frac{k_{hs}}{k_{1,D}} + N - 1}$$

Since usually $k_{hs} > k_{1,D}$, this equation can be rewritten as

$$w_a = \frac{k_d \exp\left(-\frac{\Delta\varepsilon}{k_B T}\right)}{1 + \frac{k_d}{k_{hs}} N} \quad (23)$$

where $k_d = k_{N,A}k_{1,D}/(k_{N,A} + k_{1,D})$ is the effective depopulation rate coefficient. For $k_d N/k_{hs} \ll 1$, the latter result can be transformed to the exponential function of N using the Taylor expansion of eq 23. As a result, the distance dependence of w_a for the hopping mechanism of CT again becomes identical in form to eq 20 derived for the tunneling regime of the process, although pre-exponential factors and falloff parameters in these two cases are, of course, distinct. In particular, for incoherent sequential hopping the exponential decrease of w_a with increasing bridge length is not adequately described by the falloff parameter β given by eq 22. Instead, this dependence is characterized by the parameter $\beta_h = k_d/(ak_{hs}) \cong \beta_{\min}k_d/k_{hs}$ which can be less than β_{\min} as long as $k_d/k_{hs} < 1$. This together with our estimations of β_{\min} implies that small β values ($< 0.2 - 0.3$ Å⁻¹) deduced from experimental dependencies of the CT efficiency or the rate coefficients on the bridge length can not be attributed to the tunneling mechanism of charge transfer in D-B-A systems. On the basis of theoretical results obtained, we thus conclude that the measured distance dependence of w_a enables one to distinguish between single-step tunneling and multistep hopping but only if experiments are performed within a wide range of bridge lengths (up to $R_{DA} \cong a(1 + k_{hs}/k_d)$).

IV.2. Two D-B-A Systems with Static Torsional Disorder. Theoretical analysis of the effect of static disorder on various physical and chemical processes goes back to pioneering works of Mott.⁹⁸ As has been shown using various methods,⁹⁹ this type of disorder can strongly affect different incoherent thermally activated rate processes in polymers, glasses and biological molecules.^{74,75,100,101} On the basis of the results obtained, one can expect that static disorder may also cause significant changes in the kinetics of coherent CT processes. Indeed, our calculations show that in the particular case of static torsional disorder associated with variations in the values of the charge transfer integral V along the chain, the time evolution of the survival probability becomes essentially nonexponential. Several examples of such nonexponential behavior are given in Figure 5a, where the dependence P versus t is shown for different degrees of disorder expressed in terms of the mean-square deviation, σ_V , of V from the average.¹⁰² As follows from the data presented in this figure, the survival probability for systems with static torsional disorder exhibits a fast nonexponential decay at short times, which gradually slows down as t increases, but does not approach an exponential asymptote within the entire time range investigated (see examples in Figure 5b). On the basis of these results, we conclude that in the presence of static disorder, the rate coefficient for the charge arrival on the acceptor (defined by eq 17 as a slope of the decay curve) becomes time-dependent. Hence, contrary to the completely ordered system, the kinetics of CT in D-B-A assemblies with static torsional disorder can not be characterized by a constant rate coefficient.

The nonexponential time evolution of the survival probability is a direct consequence of the static torsional disorder present

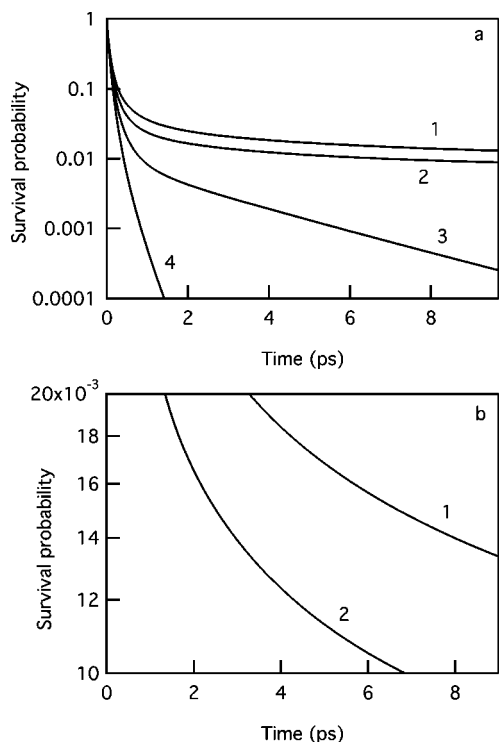


Figure 5. Time evolution of the survival probability for the four-site D-B-A system with a different degree of static torsional disorder. All decay curves in panel (a) were calculated for the equienergetic fluorene bridge ($V_0 = 0.43$ eV) separated from a donor by the energy gap equal to 0.6 eV. The mean-square deviation σ_V of the charge transfer integral with the average value of 0.3 eV is $3.61 \cdot 10^{-2}$ eV² (1), $3.28 \cdot 10^{-2}$ eV² (2), $2.89 \cdot 10^{-2}$ eV² (3), $2.44 \cdot 10^{-2}$ eV² (4). These values were obtained using the angular dependence of the charge transfer integral and torsion angles sampled from the Boltzmann distribution (see eq 11) at temperatures of 298, 250, 200, and 150 K, respectively. The angular dependence of the charge transfer integral and the torsion potential in eq 11 were taken from ref 52. The long-time tails of curves 1 and 2 are plotted in panel (b) on the enlarged logarithmic scale to show that the decay remains nonexponential for times larger than 2 ps.

in the 1D chain modeling the D-B-A system. This manifests itself as variations in the value of charge transfer integrals along the chain and, more importantly, as differences in the V values among different chains. A certain number of chains in the ensemble exist with a sequence of large charge transfer integrals that is favorable for rapid CT between D and acceptor sites. This group of chains is responsible for the fast initial decay of the survival probability in Figure 5a. In other groups with distinct realizations of disorder, the charge transfer integrals are smaller on average and therefore the process of intramolecular CT occurs on a longer time scale. For example, calculations performed for torsional disorder with $\sigma_V = 3.28 \cdot 10^{-2}$ eV² show that a fast initial decay of the survival probability is due to the transfer of charges from the donor to the acceptor on the time scale $0 \leq t < 0.1$ ps along the chains with the root-mean-square (rms) value of transfer integral $\sqrt{\langle V^2 \rangle} = 0.34$ eV. The further decrease of $P(t)$ can be attributed to CT proceeding within the time intervals $0.1 \text{ ps} \leq t < 0.2 \text{ ps}$, $0.2 \text{ ps} \leq t < 0.4 \text{ ps}$, and $t \geq 0.4$ ps along chains with smaller rms values, which were found to be 0.32, 0.29, and 0.27 eV, respectively. As a result, we infer that in the presence of static torsional disorder intramolecular CT in D-B-A systems proceeds on many coexisting time scales. This gives rise to a distribution of the CT rates within the ensemble and to strongly nonexponential kinetics of the process characterized by a time-dependent rate coefficient. Such features are typical for the dispersive kinetics

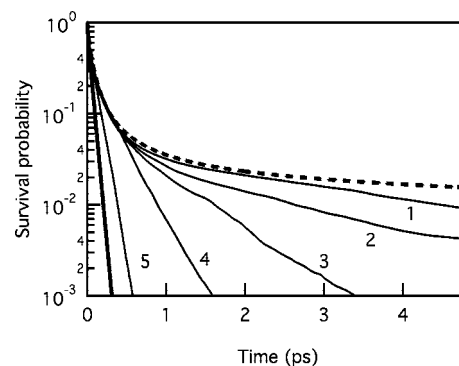


Figure 6. Survival probability as a function of time for the four-site D-B-A system with dynamic torsional disorder. The rotational diffusion times for adjacent molecular subunits of the bridge were 500 (1), 100 (2), 10 (3), 1 (4), and 0.1 ps (5). The bold solid line corresponds to the decay calculated for the ordered static chain with a charge transfer integral equal to the rms value of 0.30 eV, obtained by time averaging. The dashed line shows the decay for the bridge with static torsional disorder (curve 1 in Figure 5). For all decay curves, the energy gap between a donor and the equienergetic fluorene bridge with $V_0 = 0.43$ eV is equal to 0.6 eV.

known so far only for rate processes described classically (for review, see, e.g., refs 74 and 75).

IV.3 D-B-A Systems with Dynamic Fluctuations of Torsion Angles. Strictly speaking, static disorder discussed in the previous section exists only at temperatures that are sufficiently low to suppress the rotational diffusive motion of bridge structural subunits. Typically these temperatures are less than the freezing point, T_f , of the solvent used in experiment. If, however, $T > T_f$, disorder becomes dynamic rather than static due to significant variations of the torsion angle between the building blocks of the bridge because of rotational diffusion. Such dynamic variations can affect the values of the charge transfer integral and, hence, the electronic coupling between neighboring sites, thus leading to the breakdown of the Condon approximation (see Section II).

To investigate the kinetics of CT in D-B-A systems in which the Condon approximation ceases to be valid, we calculated the survival probability $P(t)$ as a function of time for four-site chains (D, A, and two bridge sites) with different degrees of dynamic torsional disorder characterized by the rotational diffusion time, τ_{rot} . The data in Figure 6 obtained for τ_{rot} ranging from 0.1 up to 1000 ps show that all transients describing the time evolution of the survival probability in the presence of dynamic fluctuations lie between two curves. One curve shown by the bold solid line describes the dependence of P versus t for the ordered static chain with a charge transfer integral equal to the rms value of 0.30 eV, obtained by time averaging. The other depicted by the dashed line corresponds to the analogous dependence for the chain containing static disorder only. If fluctuations occur on a time scale exceeding $\tau_{\text{rot}} = 0.1$ ps, the decay curves exhibit a nonexponential time behavior and asymptotically coincide with the results obtained in the limit of static disorder as $\tau_{\text{rot}} \rightarrow \infty$. The latter finding suggests that in the case where migration of electrons or holes in the absence of disorder is much faster than variations of the torsion angle, the dynamic fluctuations are too slow to affect the charge motion along the bridge. Hence in the slow fluctuation limit, electrons or holes will experience only static torsional disorder while migrating from D to A. This resembles the situation which arises in optical absorption spectroscopy if the medium surrounding molecules is slower than relevant molecular processes and can be regarded frozen on the experimental time scale. In such static

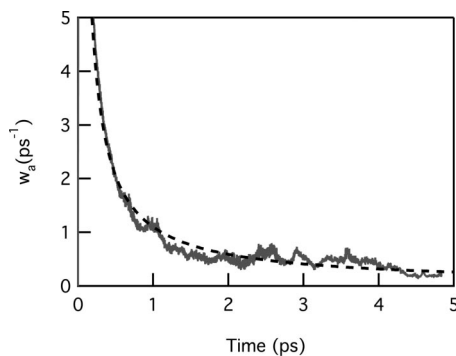


Figure 7. Time dependence of the rate coefficient for the charge arrival on the acceptor in the four-site DBA system with dynamic torsional disorder. The curve in gray is the result of numerical differentiation of the decay curve 2 in Figure 6. The dashed line was obtained from eq 16 with $\omega_0 = 2.6 \text{ ps}^{-1}$ and $\alpha = 0.1$.

limit each molecule sees a slightly different local configuration of the surrounding medium and therefore experiences a slightly different interaction with the local environment. Then the absorption line shape can be obtained by summing (integrating) over the contribution of various configurations.^{36,99i} As a result, the observed many-molecule spectrum shows the broad absorption profile. The line shape in this case is called inhomogeneous and the broadening is referred to as inhomogeneous broadening. As follows from the results obtained, similar inhomogeneous broadening effect occurs for CT process in the slow fluctuation limit. In the latter case, however, different bridge configurations cause the deviation of the survival probability decay from a simple monoexponential kinetic law rather than the occurrence of the inhomogeneously broadened line shape in optical spectra of molecules.

For much faster fluctuations of torsion angle with $\tau_{\text{rot}} \leq 0.1$ ps, our simulations show that the shape of the calculated decay curve $P(t)$ is close to exponential within the time window studied. Now, fluctuations of torsion angle become so fast that a charge moves along the bridge with the time-averaged conformation, for which the V value is determined by the mean torsion angle and remains the same along the entire bridge length (see Section II). This self-averaging of electronic coupling gives rise to the monoexponential kinetics of CT in the case where fluctuations are relatively fast. The analogy of this effect with the homogeneous broadening of the spectral line is fairly close.^{36,99i} Indeed, this broadening arises in the case where fluctuations in the environment are faster than the molecular-photon processes leading to absorptions. Therefore, as far as the radiation field is concerned, all molecules on the average appear identical and the ensemble-averaged line shape is the same as what would be observed by monitoring a single molecule.

The data in Figure 6 together with eq 17 enable one to calculate numerically the time dependence of the rate coefficient w_a for bridges with different degrees of dynamic torsional disorder. A typical example of this dependence obtained for the D-B-A system with the energy gap $\Delta\varepsilon = 0.6 \text{ eV}$ and the rotation time $\tau_{\text{rot}} = 100 \text{ ps}$ is depicted in Figure 7 by the curve shown in gray. A dashed line plotted in the same figure demonstrates that the rate coefficient for the charge arrival decreases with t following the power law

$$w_a = \omega_0^\alpha t^{\alpha-1} \quad 0 < \alpha \leq 1 \quad (24)$$

For the example in Figure 7, the values of the fitting parameters ω_0 and α in eq 24 are equal to 2.6 ps^{-1} and 0.1 , respectively.

TABLE 2: Values of Parameters ω_0 and α Used to Fit Equation 24 to the Numerical Values of the Charge Arrival Rate Coefficient w_a Deduced from Decay Curves Shown in Figure 6

τ_{rot} , ps	ω_0 , ps^{-1}	α
100	2.60	0.10
10	4.90	0.33
1	5.39	0.75
0.1	12.04	0.96

The same equation also describes the time behavior of the rate coefficient when the rotation time is smaller than 100 ps. However the values of ω_0 and α in eq 24 should be distinct from those mentioned above to get a reasonable fit for each τ_{rot} (see Table 2). The data presented in this table show that both ω_0 and α decrease with τ_{rot} and that $\alpha \rightarrow 1$ in the fast fluctuation limit. As a consequence, if fluctuations are fast, w_a becomes independent of time and approaches the constant value $w_a = \omega_0$ dictated by time self-averaging of the charge transfer integral. A very similar result has been obtained by Büttiker and Landauer⁷⁶ for tunneling transmission through a barrier evolving with time. According to their theoretical findings, at high modulation frequencies a particle tunnels through an effective time-independent barrier with the time-averaged height.

As has been shown in Section II in the presence of dynamic torsional disorder the Condon approximation does not hold because of changes in the magnitude of electronic coupling with the torsion angle. In the limit where τ_{rot} is much larger than the characteristic time of CT in the absence of static or dynamic disorder, τ_{CT} , variations of torsion angle are too slow to cause dynamic fluctuations of electronic coupling during the CT process. However the configuration averaging of the survival probability leads to nonexponential time evolution of the CT process (see Section II). For faster fluctuations, the breakdown of the Condon approximation also gives rise to the complex kinetic behavior of CT process. According to our theoretical results, in both cases non-Condon effects are kinetic and include the occurrence of time scale invariance and nonexponential decay transients. Consequently, the concept of constant rate coefficient is no longer valid. Instead, intramolecular CT in the tunneling regime is characterized by a time-dependent rate coefficient (see eq 24) and the kinetics of the process become dispersive.

In the opposite limit where $\tau_{\text{rot}} \ll \tau_{\text{CT}}$, kinetics of intramolecular CT becomes monoexponential due to the self-averaging of electronic coupling. Accordingly, a moving charge sees a bridge with the same time-averaged electronic coupling $\sqrt{\langle V^2(t) \rangle}$ for all pairs of adjacent subunits and the rate coefficient w_a turns out to be time-independent. In the case where fluctuations are so fast that $\tau_{\text{rot}} \ll \tau_{\text{CT}}$, additional simulations, however, show that the decay rate of the monoexponential transients is slightly different from the w_a value calculated for the above-mentioned ordered bridge with the time averaged electronic coupling. This suggests that in contrast to the situations of “frozen” ($\tau_{\text{rot}} \ll \tau_{\text{CT}}$) and slow ($\tau_{\text{rot}} \approx \tau_{\text{CT}}$) fluctuations, the breakdown of the Condon approximation in the fast fluctuation limit manifests itself only as static corrections to the rate coefficient calculated for the ordered bridge mentioned above. The magnitude of this correction is proportional to the ratio $\sigma_V / \langle V^2(t) \rangle$ in accord with earlier analytical results.^{70,103}

Thus, as follows from the above analysis, the transition from dispersive to monoexponential kinetic behavior of the CT process occurs as τ_{rot} becomes much less than τ_{CT} . By virtue of eq 20, the characteristic time τ_{CT} for the tunneling regime of

charge motion exponentially increases with the length of the bridge and, hence, with the number of bridge subunits, n_{br} . Therefore it might be expected that for $n_{br} \gg 4$, the decay curves would always be monoexponential, even if these curves are dispersive for shorter bridges. However for such long bridges, coherent tunneling ceases to be a dominant mechanism of CT and charge carriers move from D to A via incoherent sequential hopping.²⁹ For this reason, our results can not be extended to the D-B-A systems with more than 4 or 5 bridges subunits.

It is worth noting that nonmonoexponential transients attributed to the process of intramolecular CT were reported for a variety of D-B-A systems studied by different time-resolved spectroscopy techniques. In particular, decay curves that do not follow a single exponential kinetic law were reported for "harpooning" semiflexibly bridged donor-acceptor systems,¹⁰⁴ σ -bridged triads comprising a vinylanthracene donor and a dicyanovinyl acceptor¹⁰⁵ as well as for a porphyrin-base molecular wire bridging ferrocene (a hole acceptor) and fullerene (a hole donor).⁸⁰ In addition, similar decay profiles were observed for a number of D-DNA-A assemblies^{78,79,81,106,107} and for a series of helical peptides connecting an electron donor (an indole group) and an acceptor moiety (pyrene attached to N-terminus).¹⁰⁸ Experimental decay curves for these systems are often fitted with the sum of several exponentials with different time constants or with a single exponential as long as the fitting procedure is restricted only to one particular narrow time window. For example, Kurzawa et al.¹⁰⁵ found that the fluorescent transients used to obtain information about the formation and decay of the CT state in vinylanthracene donor- σ -bridge-dicyanovinyl acceptor compounds can be described with the sum of three exponentials with different time decay constants. Fiebig, Barton, Zewail and their co-workers¹⁰⁷ reported that femtosecond transient absorption of DNA assemblies also exhibits three components. According to the interpretation proposed,¹⁰⁰ two of these components with the decay time constants 5 and 75 ps can be ascribed to the charge motion from the electron donor (7-deazaguanine) to the acceptor (tethered ethidium) along two types of trajectories, one being favorable and the other unfavorable for CT. The third component with a decay time constant 100 ps was attributed to the slow molecular rotations including that of the whole DNA duplex.

In connection with the interpretation of the experimental results mentioned above, it should be emphasized that nonmonoexponential kinetics of CT alone can not be considered as a convincing evidence of multistep mechanism of the process. This becomes evident from the results of our theoretical analysis which clearly shows the possibility of nonmonoexponential kinetic patterns even in the case of a single step intramolecular CT. For the same reasons, a successful fit of experimental transients with the sum of a few exponentials distinct in their time decay constants does not necessarily imply that there is one-to-one correspondence between values of these constants and time scales of the assumed elementary steps of the CT process. As follows from our results, CT in D-B-A systems can exhibit time scale invariance due to static or dynamic torsional disorder, thus proceeding in one single step, but on many coexisting time scales.

V. Summary and Conclusions

A simple tight-binding model for studying effects of static and dynamic torsional disorder on the kinetics of charge transfer in donor-bridge-acceptor systems is proposed. Using this model, the process of intramolecular charge transfer from donor to acceptor was simulated without postulating a priori the existence

of a constant rate coefficient. The systems studied can be distinguished by the type of the bridge involved. They contain (i) flat rigid linkers with electronic coupling that does not vary along their length, (ii) inflexible bridges with disorder resulted from static variations of the torsion angle (and, hence, electronic coupling) along their length, and (iii) dynamic bridges in which electronic coupling can fluctuate in time due to the torsional motion of adjacent structural subunits relative to each other. In all three cases the investigated bridges were short enough to allow an electron or a hole to be irreversibly transferred from donor to acceptor site via quantum mechanical tunneling.

For perfectly ordered bridges (i), the survival probability exponentially decreases with time, so that the kinetics of charge transfer over a given distance can be characterized by a time-independent rate coefficient. In the tunneling regime this rate coefficient drops with the bridge length following the familiar exponential length dependence. We show that the values of the falloff parameter characterizing the length dependence of the rate coefficient should not exceed the reciprocal of the mean intersite distance. This implies that typically the lower limit for this parameter is 0.2–0.3 Å⁻¹.

By contrast, the numerical results obtained for bridges (ii) enable us to conclude that static torsional disorder gives rise to the time scale invariance of the charge transfer process. Accordingly, the survival probability exhibits nonexponential decay with time. On the basis of these results we infer that generally kinetics of intramolecular charge transfer through bridges with static torsional disorder should not be characterized by a certain value of the rate constant, but must be actually described in terms of the time-dependent rate coefficient.

The latter conclusion equally pertains to bridges (iii). In these bridges torsional disorder causes dynamic fluctuations of electronic coupling between two neighboring molecular subunits. From the performed analysis of the computer simulation data, two types of the resultant non-Condon effects were distinguished. When torsion motion and CT in the absence of disorder occur on comparable time scales the non-Condon effect can be considered as kinetic. In this case, the intramolecular charge transfer proceeding via quantum tunneling exhibits time scale invariance and nonmonoexponential (dispersive) temporal behavior. As a consequence, the rate coefficient for charge arrival on the acceptor is not constant for a given donor-bridge-acceptor system, but decreases with time following the power law with a negative exponent.

For much faster torsion motion, the above-mentioned features typical for dispersive kinetics vanish due to self-averaging of electronic coupling and the decay curves become monoexponential. In this fast fluctuation limit the non-Condon effect is static because now the breakdown of the Condon approximation manifests itself as a static correction to the time-independent rate coefficient for the ordered bridge with the same time-averaged electronic coupling for all pairs of adjacent subunits. Thus the applicability of the concept of constant rate coefficient to the kinetic description of the tunneling regime of charge transfer through short bridges with torsionally induced fluctuations of electron coupling is restricted to the special case where such fluctuations are much faster than charge motion between donor and acceptor in the absence of static or dynamic disorder.

On the basis of theoretical results obtained, we conclude that even a single-step rate process can show nonmonoexponential kinetic patterns. Therefore experimental observations of nonexponential transients do not necessarily signify that the mechanism of charge transfer involves a sequence of elementary processes with different constant rate coefficients.

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References and Notes

- Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.
- Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148–13168.
- Bixon, M.; Jortner, J. *Adv. Chem. Phys.* **1999**, *106*, 35–208.
- Berlin, Y. A.; Kurnikov, I. V.; Beratan, D.; Ratner, M. A.; Burin, A. L. *Top. Curr. Chem.* **2004**, *237*, 1–36.
- Matyushov, D. V.; Voth, G. A. *Rev. Comp. Chemistry* **2002**, *18*, 147–210.
- Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668–6697.
- Weiss, E. A.; Wasielewski, M. R.; Ratner, M. A. *Top. Curr. Chem.* **2005**, *257*, 103–133.
- Kuznetsov, A. M. *Charge Transfer in Physics, Chemistry and Biology*; Gordon & Breach: New York, 1995.
- Kuznetsov, A. M.; Ulstrup, J. *Electron Transfer in Chemistry and Biology*; Wiley: Chichester, 1999.
- Balzani, V.; Piotrowiak, P.; Rodgers, M. A. J.; Mattay, J.; Astruc, D.; Gray, H. B.; Winkler, J.; Fukuzumi, S.; Mallouk, T. E.; Haas, Y.; de Silva, A. P.; Gould, I., Eds.; *Electron Transfer in Chemistry*; Wiley-VCH Verlag GmbH: Weinheim, 2001; Vols. 1–5.
- Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461.
- Schuddeboom, W.; Ktjnen, B.; Verhoeven, J. W.; Staring, E. G. J.; Rikken, G. L. J. A.; Oevering, H. *Chem. Phys. Lett.* **1991**, *179*, 73–78.
- Ratner, M. A.; Jortner, J. In *Molecular Electronics*; Ratner, M. A., Jortner, J., Eds.; Blackwell: Oxford, UK, 1997; pp 5–72, and references therein.
- Lindsay, S. M.; Ratner, M. A. *Adv. Mater.* **2007**, *19*, 23–31.
- See, e.g., reviews published in *Top. Curr. Chem.*; Schuster, G. B., Ed.; Springer: Berlin, 2004; Vols. 236 and 237 and references therein.
- Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395–410.
- Warman, J. M.; De Haas, M. P.; Verhoeven, J. W.; Paddon-Row, M. N. *Adv. Chem. Phys.* **1999**, *106*, 571–601.
- Wegewijs, B.; Verhoeven, J. W. *Adv. Chem. Phys.* **1999**, *106*, 221–264.
- Sikes, H. D.; Smalley, J. F.; Dudek, S. P.; Cook, A. R.; Newton, M. D.; Chidsey, C. E. D.; Feldberg, S. W. *Science* **2001**, *291*, 1519–1523.
- Walters, K. A.; Kim, Y.-J.; Hupp, J. T. *J. Electroanal. Chem.* **2003**, *554–555*, 449–458.
- Hviid, L.; Verhoeven, J. W.; Brouwer, A. M.; Paddon-Row, M. N.; Yang, J. X. *Photochem. Photobiol. Sci.* **2004**, *3*, 246–251.
- Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 5577–5584.
- Goldsmith, R. H.; Sinks, L. E.; Kelley, R. F.; Betzen, L. J.; Liu, W. H.; Weiss, E. A.; Ratner, M. A.; Wasielewski, M. R. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 3540–3545.
- Davis, W. B.; Ratner, M. A.; Wasielewski, M. R. *Chem. Phys.* **2002**, *281*, 333–346.
- Isied, S. S.; Ogawa, M. Y.; Wishart, J. F. *Chem. Rev.* **1992**, *92*, 381–394.
- Giese, B.; Amaudrut, J.; Köhler, A.-K.; Spormann, M.; Wessely, S. *Nature* **2001**, *412*, 318–320.
- Davis, W. B.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 7877–7886.
- Petrov, E. G.; May, V. *J. Phys. Chem. A* **2001**, *105*, 10176–10186.
- Berlin, Y. A.; Burin, A. L.; Ratner, M. A. *Chem. Phys.* **2002**, *275*, 61–74.
- The latter term is more precise since actually k_{CT} is not a constant and includes all parameters that affect the CT rate except for concentration which is explicitly taken into account. For this reason, k_{CT} hereinafter is referred to as a rate coefficient.
- Kulzer, F.; Kettner, R.; Kummer, S.; Basché, Th. *Pure Appl. Chem.* **1997**, *69*, 743–748.
- Bai, C.; Wang, C.; Xie, X. S.; Wolynes, P. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 11075–11076.
- Moerner, W. E. *J. Phys. Chem. B* **2002**, *106*, 910–927.
- Barkai, E.; Jung, Y. J.; Silbey, R. *Annu. Rev. Phys. Chem.* **2004**, *55*, 457–507.
- Levine, R. D. In *Molecular Relaxation Processes*; Academic Press: London, 1966.
- For various applications of the Condon approximation in optical spectroscopy and their theoretical analysis, see: Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York-Oxford, 1995.
- Newton, M. D. *Chem. Rev.* **1991**, *91*, 767–792.
- (a) Schatz, G. C.; Ratner, M. A. *Quantum Mechanics in Chemistry*; Prentice Hall: Englewood Cliffs, N. J., 1993. (b) See, e.g., Levich, V. G.; *Theoretical Physics: an Advanced Text*; North-Holland: Amsterdam, 1970; Vol. 3.
- Ratner, M. A.; Madhukar, A. *Chem. Phys.* **1978**, *30*, 201–215.
- Medvedev, E. S.; Stuchebrukhov, A. A. *J. Chem. Phys.* **1997**, *107*, 3821–3831.
- Daizadeh, I.; Medvedev, E. S.; Stuchebrukhov, A. A. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 3703–3708.
- Newton, M. D. *Int. J. Quantum Chem.* **2000**, *77*, 255–263.
- Toutounji, M. M.; Ratner, M. A. *J. Phys. Chem.* **2000**, *104*, 8566–8569.
- Voityuk, A. A.; Siriwong, K.; Rösch, N. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5421–5425.
- Troisi, A.; Orlandi, G. *Chem. Phys. Lett.* **2001**, *344*, 509–518.
- Voityuk, A. A.; Rösch, N. *J. Phys. Chem. B* **2002**, *106*, 3013–3018.
- Pourtois, G.; Beljonne, D.; Cornil, J.; Ratner, M. A.; Brédas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 4436–4447.
- Newton, M. D. *Theor. Chem. Acc.* **2003**, *110*, 307–321.
- Troisi, A.; Ratner, M. A.; Zimmt, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 2215–2224.
- (a) Jones, G. A.; Carpenter, B. K.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1998**, *120*, 5499–5508. (b) Jones, G. A.; Paddon-Row, M. N.; Carpenter, B. K.; Piotrowiak, P. *J. Phys. Chem. A* **2002**, *106*, 5011–5021.
- Grozema, F. C.; van Duijnen, P. Th.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. *J. Phys. Chem. B* **2002**, *106*, 7791–7795.
- Prins, P.; Grozema, F. C.; Siebbeles, L. D. A. *J. Phys. Chem. B* **2006**, *110*, 14659–14666.
- Prins, P.; Grozema, F. C.; Galbrecht, F.; Scherf, U.; Siebbeles, L. D. A. *J. Phys. Chem. C* **2007**, *111*, 11104–11112.
- Berlin, Y. A.; Burin, A. L.; Siebbeles, L. D. A.; Ratner, M. A. *J. Phys. Chem. A* **2001**, *105*, 5666–5678.
- Senthilkumar, K.; Grozema, F. C.; Guerra, C. F.; Bickelhaupt, F. M.; Lewis, F. D.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. *J. Am. Chem. Soc.* **2005**, *127*, 14894–14903.
- Kumar, K.; Lin, Z.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 243–244.
- Castner, E. W.; Kennedy, D.; Cave, R. J. *J. Phys. Chem. A* **2000**, *104*, 2869–2885.
- Napper, A. M.; Read, I.; Waldeck, D. H.; Kaplan, R. W.; Zimmt, M. B. *J. Phys. Chem. A* **2002**, *106*, 4784–4793.
- Marin, T. W.; Homoelle, B. J.; Spears, K. G. *J. Phys. Chem. A* **2002**, *106*, 1152–1166.
- Kurnikov, I. V.; Zusman, L. D.; Kurnikova, M. G.; Farid, R. S.; Beratan, D. N. *J. Am. Chem. Soc.* **1997**, *119*, 5690–5700.
- Peskin, U.; Edlind, A.; Bar-On, L.; Galperin, M.; Nitzan, A. *J. Chem. Phys.* **1999**, *111*, 7558–7566.
- Milischuk, A.; Matyushov, D. V. *J. Chem. Phys.* **2003**, *118*, 5596–5606.
- Xie, Q.; Archontis, G.; Skourtis, S. S. *Chem. Phys. Lett.* **1999**, *312*, 237–246.
- Miller, N. E.; Wander, M. C.; Cave, R. J. *J. Phys. Chem. A* **1999**, *103*, 1084–1093.
- Balabin, I. A.; Onuchic, J. N. *Science* **2000**, *290*, 114–117.
- Galperin, M.; Nitzan, A. *J. Chem. Phys.* **2001**, *115*, 2681–2694.
- (a) Skourtis, S. S.; Archontis, G.; Xie, Q. *J. Chem. Phys.* **2001**, *115*, 9444–9462. (b) Teklos, A.; Skourtis, S. S. *Chem. Phys.* **2005**, *319*, 52–58. (c) Skourtis, S. S.; Balabin, I. A.; Kawatsu, T.; Beratan, D. N. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 3552–3557. (d) Nishioka, H.; Kimura, A.; Yamato, T.; Kawatsu, T.; Kakitani, T. *J. Phys. Chem. B* **2005**, *109*, 15621–15635.
- Troisi, A.; Orlandi, G. *J. Phys. Chem. B* **2002**, *106*, 2093–2101.
- Jones, G. A.; Paddon-Row, M. N.; Carpenter, B. R.; Piotrowiak, P. *J. Phys. Chem. A* **2002**, *106*, 5011–5021.
- Troisi, A.; Nitzan, A.; Ratner, M. A. *J. Chem. Phys.* **2003**, *119*, 5782–5788.
- Jang, S.; Newton, M. D. *J. Chem. Phys.* **2005**, *122*, 024501.
- (a) Hammes-Schiffer, S. *J. Phys. Chem. A* **1998**, *102*, 10443–10454. (b) Marx, D.; Hutter, J. In *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; J. von Neumann Institute for Computing: Jülich, 2000. (c) Doltsinis, N. L.; Marx, D. *J. Theor. Comp. Chem.* **2002**, *1*, 319–349.

- (73) Grozema, F. C.; Siebbeles, L. D. A. *Int. Rev. Phys. Chem.* **2008**, 27, 87–138.
- (74) Scher, H.; Shlesinger, M. F.; Bendler, J. T. *Phys. Today* **1991**, 44, 26–34.
- (75) Plonka, A. *Dispersive Kinetics*; Kluwer Academic Publishers: Dordrecht, 2001 and references therein.
- (76) Büttiker, M.; Landauer, R. *Phys. Rev. Lett.* **1982**, 49, 1739–1742.
- (77) Azbel, M. Ya.; Malomed, B. A. *Phys. Rev. Lett.* **1993**, 71, 1617–1620.
- (78) Lewis, F. D.; Zhu, H.; Daublain, P.; Fiebig, T.; Raytchev, M.; Wang, Q.; Shafirovich, V. *J. Am. Chem. Soc.* **2006**, 128, 791–800.
- (79) Valis, L.; Wang, Q.; Raytchev, M.; Buchvarov, I.; Wagenknecht, H.-A.; Fiebig, T. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 10192–10195.
- (80) Winters, M. U.; Dahlstedt, E.; Blades, H. E.; Wilson, C. J.; Frampton, M. J.; Anderson, H. L.; Albinsson, B. *J. Am. Chem. Soc.* **2007**, 129, 4291–4297.
- (81) Wagenknecht, H.-A.; Fiebig, T. In *Charge Transfer in DNA: From Mechanism to Application*; Wagenknecht, H.-A., Ed.; Wiley-VCH: New York, 2005, pp 197–223.
- (82) (a) Fedorov, M. V. *J. Phys. B* **1977**, 10, 2573–2582. (b) Sukharev, M. E.; Charron, E.; Suzor-Weiner, A.; Fedorov, M. V. *Int. J. Quantum Chem.* **2004**, 99, 452–459.
- (83) See Berlin, Y. A. *Chem. Phys.* **1996**, 212, 29–39, and references therein.
- (84) Risken, H. *The Fokker-Planck Equation*; Springer: Berlin, 1984, Sec. 8.3.
- (85) Agmon, N.; Rabinovich, S. J. *Phys. Chem.* **1992**, 97, 7270–7286.
- (86) Lewis, F. D.; Zhu, H.; Daublain, P.; Cohen, B.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2006**, 45, 7982–7985.
- (87) See, e.g. Schwartz, M.; Duan, D.; Berry, R. J. *J. Phys. Chem. A* **2005**, 109, 8637–8641, and references therein.
- (88) Nitzan, A.; Jortner, J.; Wilkie, J.; Burin, A. L.; Ratner, M. A. *J. Phys. Chem. B* **2000**, 104, 5661–5665.
- (89) Kittel, C. *Introduction to Solid State Physics*, 7th ed.; John Wiley: New York, 1996.
- (90) Gutman, F.; Lyons, L. E. *Organic Semiconductors*; John Wiley: New York, 1966.
- (91) (a) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1989**, 134, 323–354. (b) Reimer, J. R.; Hush, N. S. *J. Photochem. Photobiol. A* **1994**, 82, 3146. (c) Felts, A. K.; Pollard, W. T.; Friesner, R. A. *J. Phys. Chem.* **1995**, 99, 2929–2940. (d) Pollard, W. T.; Felts, A. K.; Friesner, R. A. *Adv. Chem. Phys.* **1996**, 93, 77–134. (e) Skourtis, S. S.; Mukamel, S. *Chem. Phys.* **1995**, 197, 267–388. (f) Okada, A.; Chernyak, V.; Mukamel, S. *J. Phys. Chem. A* **1998**, 102, 1241–1251. (g) Segal, D.; Nitzan, A. *Chem. Phys.* **2001**, 268, 315–335. (h) Nitzan, A.; Ratner, M. *Science* **2003**, 300, 1384–1389. (i) Petrov, E. G.; Shevchenko, Ye. V.; May, V. *Chem. Phys.* **2003**, 288, 269–279. (j) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, 126, 5577–5584. (k) Mühlbacher, L.; Ankerhold, J.; Escher, C. *J. Chem. Phys.* **2004**, 121, 12696–12707. (l) Weiss, E. A.; Katz, G.; Goldsmith, R. H.; Wasielewski, M. R.; Ratner, M. A.; Kosloff, R.; Nitzan, A. *J. Chem. Phys.* **2006**, 124, 074501.
- (92) (a) Jortner, J.; Bixon, M.; Langenbacher, T.; Michel-Beyerle, M. E. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, 95, 12759–12765. (b) Giese, B.; Wessely, S.; Spormann, M.; Lindemann, U.; Meggers, E.; Michel-Beyerle, M. E. *Angew. Chem., Int. Ed. Engl.* **1999**, 38, 996–998. (c) Ratner, M. A. *Nature* **1999**, 397, 480–481. (d) Bixon, M.; Giese, B.; Wessely, S.; Langenbacher, T.; Michel-Beyerle, M. E.; Jortner, J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, 96, 11713–11716. (e) Berlin, Y. A.; Burin, A. L.; Ratner, M. A. *J. Phys. Chem. A* **2000**, 104, 443–445. (f) Berlin, Y. A.; Burin, A. L.; Ratner, M. A. *J. Am. Chem. Soc.* **2001**, 123, 260–268. (g) Bixon, M.; Jortner, J. *Chem. Phys.* **2002**, 281, 393–408. (h) Berlin, Y. A.; Ratner, M. A. To be submitted. (i) Nitzan, A. *Israel J. Chem.* **2002**, 42, 163–166. (j) Berlin, Y. A.; Ratner, M. A. *Radiat. Phys. Chem.* **2005**, 74, 124–131.
- (93) Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, 109, 6771–6778.
- (94) Evenson, J. W.; Karplus, M. *J. Chem. Phys.* **1992**, 96, 5272–5278.
- (95) Benniston, A. C.; Goulle, V.; Harriman, A.; Lehn, J.-M.; Marczinke, B. *J. Phys. Chem.* **1994**, 98, 7798–7804.
- (96) Fukui, K.; Tanaka, K.; Fujitsuka, M.; Watanabe, A.; Ito, O. *J. Photochem. Photobiol., B* **1999**, 50, 18–27.
- (97) Henderson, P. T.; Jones, D.; Hampikian, G.; Kan, Y.; Schuster, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, 96, 8353–8358.
- (98) Mott, N. F.; Davis, E. A. *Electronic Processes in Non-crystalline Materials*, 2nd edition; Oxford University Press: New York, 1979; and references therein.
- (99) For review, see, e.g., (a) Alexander, S.; Bernasconi, J.; Orbach, R.; Schneider, W. R. *Rev. Mod. Phys.* **1981**, 53, 175–198. (b) Druger, S. D.; Nitzan, A.; Ratner, M. A. *J. Chem. Phys.* **1983**, 79, 3133–3142. (c) Shklovskii, B. I.; Efros, A. L. *Electronic Properties of Doped Semiconductors*; Springer Verlag: Berlin, 1984. (d) Zharikov, A. A.; Temkin, S. I.; Burshtein, A. I. *Chem. Phys.* **1986**, 103, 1–10. (e) *Dynamic Processes in Condensed Molecular Systems*; Klafter, J.; Jortner, J.; Blumen, A., Eds.; World Scientific: Singapore, 1989. (f) Bouchaud, J. P.; Georges, A. *Phys. Rep.* **1990**, 195, 127–293. (g) Haus, J.; Kehr, K. W. *Phys. Rev. B* **1987**, 36, 5639–5642. (h) Haus, J.; Kehr, K. W. *Phys. Rep.* **1987**, 150, 263–406. (i) Nitzan, A. *Chemical Dynamics in Condensed Phases. Relaxation, Transfer, And Reactions in Condensed Molecular Systems*; Oxford University Press: Oxford, 2006; and references therein.
- (100) *Charge Transport in Disordered Solids with Applications in Electronics*; Baranovski, S., Ed.; Wiley: Chichester, 2006; and references therein.
- (101) (a) Berlin, Y. A.; Fischer, S. F.; Chekunaev, N. I.; Goldanski, V. I. *Chem. Phys.* **1995**, 200, 369–385. (b) Berlin, Y. A.; Burin, A. L. *Chem. Phys. Lett.* **1996**, 257, 665–673. (c) Berlin, Y. A.; Burin, A. L.; Fischer, S. F. *Chem. Phys.* **1997**, 220, 25–41. (d) van de Craats, A. M.; Siebbeles, L. D. A.; Bleyl, I.; Haarer, D.; Berlin, Y. A.; Zharikov, A. A.; Warman, J. M. *J. Phys. Chem. B* **1998**, 102, 9625–9634. (e) Berlin, Y. A.; Siebbeles, L. D. A.; Zharikov, A. A. *Chem. Phys. Lett.* **1999**, 305, 123–131. (f) Berlin, Y. A.; Burin, A. L.; Siebbeles, L. D. A.; Ratner, M. A. *J. Phys. Chem. A* **2001**, 105, 5666–5678. (g) Berlin, Y.; Burin, A.; Friedrich, J.; Köhler, J. *Phys. Life Rev.* **2006**, 3, 262–292; *ibid.* **2006**, 4, 6489.
- (102) Note that at $\Delta\epsilon/\langle V \rangle = 2$ calculations for disordered D-B-A systems are time-consuming and become impractical at larger $\Delta\epsilon/\langle V \rangle$ values. This can be easily understood since to obtain reliable data on the effect of disorder on the CT kinetics, computer simulations should be performed within the time window in which the survival probability, $P(t)$, drops at least by one order of magnitude. Furthermore, the duration of calculations strongly increases with the width, Δt , of this window, which, in turn, rapidly increases with the falloff parameter β and, hence, with $\Delta\epsilon/\langle V \rangle = \Delta\epsilon/V$ (see Figure 4). As a consequence, for $\Delta\epsilon/\langle V \rangle \gg 1$ the width Δt becomes so large that our computational facilities do not allow us to calculate the time dependence $P(t)$ for reasonable time. That is why up to now we can simulate the decay transients for the D-B-A systems with torsional disorder only in the case where $\Delta\epsilon/\langle V \rangle$ does not exceed two (see examples on Figures 5 and 6), while for ordered systems numerical results are available for larger values $\Delta\epsilon/\langle V \rangle = \Delta\epsilon/V$ (see Figures 2 and 3).
- (103) Bixon, M.; Jortner, J. *Russ. J. Electrochem.* **2003**, 1, 5–10.
- (104) Lauteslager, X. Y.; van Stokkum, I. H. M.; van Ramesdonk, H. J.; Brouwer, A. M.; Verhoeven, J. W. *J. Phys. Chem. A* **1999**, 103, 653–659.
- (105) Kurzawa, J.; Schneider, S.; Bübler, J.; Gleiter, R.; Clark, T. *Phys. Chem. Chem. Phys.* **2004**, 6, 3811–3823.
- (106) Brun, A. M.; Harriman, A. *J. Am. Chem. Soc.* **1992**, 114, 3656–3660.
- (107) Wan, C.; Fiebig, T.; Kelley, S. O.; Treadway, C. R.; Barton, J. K.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, 96, 6014–6019.
- (108) Jones, G., II; Zhou, X.; Vullev, V. I. *Photochem. Photobiol. Sci.* **2003**, 2, 1080–1087.