

Bridge Mediated Electron Transfer: A Unified Description of the Thermally Activated and Superexchange Mechanisms

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Donor–acceptor electron transfer (D–A ET) through a linear molecular bridge is studied for the particular case of large electronic couplings among the molecular fragments inside the bridge. This makes it possible to choose a description in terms of extended bridge states, whereas the weak coupling of the bridge levels to the D and A centers guarantees the individuality of these terminal sites. Since fast vibrational relaxation within the D and A centers as well as within the system of bridge levels is provided, we can utilize our recently developed coarse graining description of ET (Petrov et al., *J. Chem. Phys.* **2001**, *115*, 7107). In particular, it is demonstrated that the whole ET process can be reduced to single-exponential kinetics for the electronic level populations characterized by an effective D–A transfer rate. This rate contains contributions from the overall superexchange and the overall thermally activated rate. The ratio of both contributions is calculated in the framework of the Song and Marcus model valid for a vibrational spectral density describing a single active vibrational mode. Taking reasonable parameters for the D–A ET reaction, it is demonstrated that the thermally activated mechanism can dominate the superexchange ET, even though the population of the bridge by the transferred electron is extremely small. And this dominance increases with increasing bridge length. Drawing the overall ET rate versus the number of bridge units, a novel behavior is predicted. First there is a strong decay of the rate up to a certain bridge length. But it is followed by a remarkable increase which is continued by a modest further increase or an independence on the bridge length. Furthermore, simple analytic expressions are given to decide which mechanism may work in a given experiment. Finally, it is underlined that ET pathways along hydrogen bonds or the key amino acids in proteins are extremely favorable for the thermally activated mechanism, while the pathways along covalent bonds are generally realized via the superexchange mechanism even at a small energy gap.

I. Introduction

Long-range donor–acceptor (D–A) electron transfer (ET) mediated by a molecular bridge represents one of the fundamental charge-transfer processes in systems of chemical and biological interest. This fact has been pointed out in dozens of textbooks and review articles (see, e.g., refs 1–11 and references therein). Concentrating on those D–A ET reactions where the population of the bridge by the transferred electron remains very small, the superexchange mechanism is supposed to be mainly responsible for the ET. Therefore, superexchange ET has been taken to model electron motion in proteins^{7,9,10} or to explain the formation of an elastic electron tunnel current through different types of molecular wires connecting, e.g., two microelectrodes.^{7,11}

However, long-range D–A ET is not determined exclusively by the superexchange mechanism (of D–A coupling via virtual states offered by bridging units). Already a decade ago it has been underlined by Mukamel that one has to choose a description that not only accounts for the superexchange mechanism but simultaneously for alternative ET mechanisms such as the sequential one.¹² The presented unifying description has been based on a certain projection operator technique, which

ends up with generalized rate equations for properly defined electronic level population. It is the great advantage of this approach that one may derive perturbation series for the rates, which graphical visualization leads to the concept of the so-called Liouville space pathway (see also refs 8, 13, 14). These pathways let one decide whether the respective contribution to the total rate expression refers to the superexchange mechanism or not.

A similar conclusion could be drawn in studying the photoinduced ET related to the charge separation in bacterial photosynthesis. Two mechanisms, the superexchange and the sequential one, have been suggested to contribute to the overall ET,^{15,16} and there are recent impressive experimental data on ET through DNA,^{17–22} which show the possible simultaneous presence of the superexchange and the sequential mechanisms and which demonstrate the dominance of the sequential mechanism with respect to the superexchange one if the length of the considered DNA strand is increased (see also refs 23–25).

Some of our own recent work touched the aspect of a unifying description of ET reactions (see refs 26, 27). In contrast to the mentioned projection operator technique of ref 12, we took an approach that starts from the density matrix defined for the set of electron-vibrational states referring to the entire ET system. Providing that the vibrational relaxation processes are fast in relation to characteristic times of the ET reaction a coarse-

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grained description could be introduced, ending up with rate equations for the total electronic level populations. The description given in refs 26 and 27 concentrated on nonadiabatic ET in assuming a sufficient weak intersite coupling. Studying the ET in dependence on the number of bridge units, it could be shown that the sequential mechanism works more efficient than the superexchange method if the bridge contains more than 5 up to 7 units. In this connection it is very important to underline that the sequential mechanism can dominate even at extremely small bridge populations (less than 10^{-5} to 10^{-10}).

However, if the electronic coupling between the bridge units becomes sufficiently large to form extended bridge states, the sequential mechanism of D–A ET is replaced by the so-called thermally activated mechanism. The strong intersite coupling may cover the D and A levels, too. But in the present studies we will assume that the coupling of the D and the A to the bridge levels remains small enough to let be the transition of the nonadiabatic type. Furthermore, providing a slow overall ET reaction compared to the vibrational relaxation within the bridge, again a coarse graining description can be taken leading to rate equations which, besides the D and A populations, only account for the total bridge population.

The importance of thermally activated ET through vacant bridge states has already been discussed by one of us (E.G.P.) years ago for bridging protein chains.^{28,29} A more recent discussion on thermally activated ET proceeding through a DNA strand is given in ref 30. The present paper is dedicated to a further discussion of this particular ET mechanism. Its efficiency will be compared with that of the superexchange mechanism in putting emphasis on the dependence of both mechanisms on the number of bridge units. Additionally, the fundamental difference to the sequential mechanism will be discussed. Our calculations based on reasonable ET parameters show that indeed the thermally activated mechanism can exceed the superexchange one, even at a very small bridge population. Furthermore, it is demonstrated that the influence of the thermally activated mechanism increases with increasing bridge length what is especially pronounced for strong bridge-internal electronic couplings. Drawing the overall ET rate versus the number of bridge units, a novel behavior is predicted. First there is a strong decay of the rate up to a certain bridge length. But it is followed by a remarkable increase which is continued by a modest further increase or an in dependence on the bridge length. For short bridges a fundamental difference of the dependence of the overall rate on the bridge length is obtained if the thermally activated mechanisms is compared with the sequential one.

To achieve a unified description of the different ET mechanisms becomes also necessary for the case of electron transmission through a molecular wire embedded between to microelectrodes. A recent description can be found in ref 31 where the contributions of the coherent (tunneling) and incoherent (activated) pathways to the temperature dependent transmission probability have been analyzed in concentrating on a steady-state regime and providing conditions that justify the application of the Redfield theory. However, a basic difference between the ET in a DBA system and through a molecular wire is related to the possible existence of an additional relaxation mechanism in the latter case caused by the presence of macroscopic electrodes. In the present paper, however, we will concentrate exclusively on the unifying description of ET reactions in DBA systems.

The paper is organized as follows. In the next section the ET model is introduced, the basic kinetic equations together

with all rate expressions are given, and finally the possible reduction to a single-exponential ET process is demonstrated. Some more technical aspects of the approach are put into the appendix. All concrete computations and estimations are given in section III. The paper ends with some concluding remarks in section IV.

II. Model and Theory

A comprehensive description of the ET process can be achieved in using the generalized master equation (GME) (cf., e.g., refs 8, 13, 32, 33) which governs the (reduced) electron-vibrational density operator $\rho(t)$ of the DBA system. However, if there is a hierarchy of interactions within the DBA system as well as between the system and the thermal environment, usually a hierarchy of time scales Δt results, reflecting the presence of different kinetic phases of the overall evolution process. Recently, for such a situation we presented a reduction scheme which started from the GME of the electron-vibrational density operator and ended up with a set of simple rate equations to model nonadiabatic bridge mediated long-range D–A ET.^{26,27} The electronic intersite couplings, V_{mn} , which are weak compared to the intrasite vibrational relaxation, result in strongly different characteristic transfer times. Within the shortest kinetic phase the thermal equilibrium is formed within the manifold $\{E_{m\alpha}\}$ of local vibrational energy levels belonging to the m th localization site of the transferred electron. The intrasite relaxation times $\{\tau_{m\alpha}\} \sim \tau_{\text{rel}}$ characterize this phase. They are all much smaller than the characteristic time τ_{ET} of the ET reaction, i.e., the condition $\tau_{\text{rel}} \ll \tau_{\text{ET}}$ indicates that the D–A ET proceeds on the background of fast intrasite relaxation processes. The given inequality enables one to describe the complex transfer process by introducing a coarse graining time scale $\Delta t \gg \tau_{\text{rel}}$. The ratio $\zeta_{m\alpha n\beta} = |V_{m\alpha n\beta}|^2 / [(E_{m\alpha} - E_{n\beta})^2 + (\hbar^2/4)(\tau_{m\alpha}^{-1} + \tau_{n\beta}^{-1})^2] \ll 1$ may serve as the small parameter of a perturbation expansion with respect to the coupling $V_{m\alpha n\beta}$ between local vibrational states $|m\alpha\rangle$ and $|n\beta\rangle$ (belonging to site m and n , respectively). Within this approach a reduced set of kinetic equations is derived including rates of sequential and superexchange ET.

If the electronic intersite couplings V_{mn} , however, become large compared to the couplings that describe the interaction with the thermal reservoir, the conditions $\zeta_{m\alpha n\beta} \ll 1$ will be violated. Therefore, the construction of a reduced set of kinetic equations has to be strongly modified. It is the goal of the present paper to show the details of this modification and to give an analysis of the different regimes of bridge-assisted D–A ET now valid for large intrasite couplings V_{mn} . The latter property is best accounted for in choosing the basis of extended electronic bridge states $|\mu\rangle$. They specify (in the adiabatic approximation) the *eigenstates* of the whole bridge. In contrast to the strong coupling between individual bridge units, the coupling to the D and the A levels should be weak. In particular the related ET step becomes much slower if the gaps between the D (A) level and the bridge levels are much larger than the respective electronic couplings V_{D1} and V_{NA} between these levels (cf, Figure 1). Such a parameter relation can be found in a number of DBA systems^{2–4} including electron transferring proteins.^{1,7,28} Consequently the whole DBA Hamiltonian can be written as

$$H_{\text{DBA}} = \sum_{m=D,A} H_m(Q)|m\rangle\langle m| + \sum_{\mu} \mathcal{H}_{\mu}(Q)|\mu\rangle\langle\mu| + \sum_{m=D,A} \sum_{\mu} (T_{\mu m}|m\rangle\langle\mu| + h.c.) + \sum_{\mu,\mu'} \theta_{\mu\mu'}(Q)|\mu\rangle\langle\mu'| \quad (1)$$

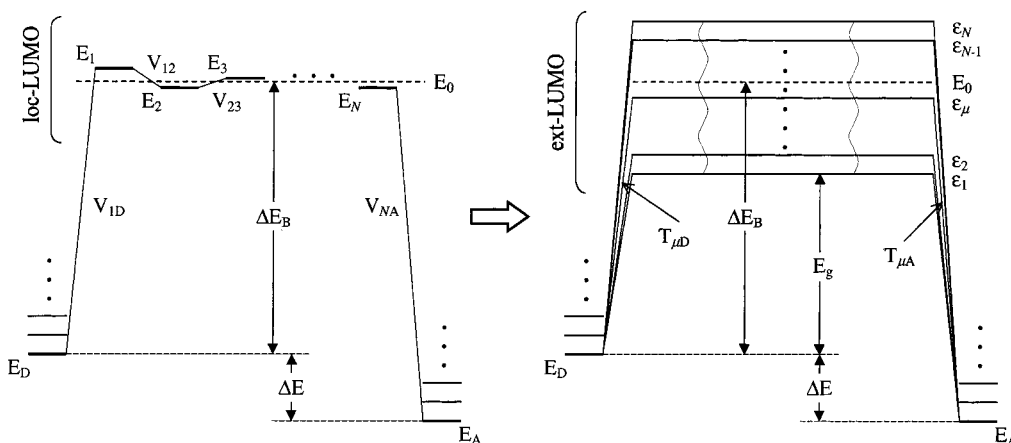


Figure 1. Energetic position of the local and extended bridge LUMO levels relative to the donor and acceptor electronic levels. E_0 gives the position of the local LUMO levels in a regular chain. Wavy lines indicate the relaxation between the extended LUMO levels.

Here the quantum numbers $\mu = 1, 2, \dots, N$ count the extended bridge levels characterized by the vibrational Hamiltonian $\mathcal{H}_\mu(Q)$. The $H_m(Q)$ ($m = D, A$) denote the vibrational Hamiltonian belonging to the D and the A. To all these vibrational Hamiltonians correspond vibrational manifolds, which lowest level will be denoted by ϵ_μ and E_m , respectively (cf. Figure 1).

The coupling of the D and A to the bridge levels is given by the quantities $T_{\mu D}$ and $T_{\mu A}$, respectively. If the bridge levels refer to a molecular chain with the first unit attached to the D and the last to the A, one obtains $T_{\mu D} = V_{1D}u_\mu(1)$ and $T_{\mu A} = V_{NA}u_\mu(N)$ where V_{1D} is the electronic coupling between the D and the first bridge unit and V_{NA} is the one between the last unit and the A. The $u_\mu(n)$ denote the elements of the transformation matrix which define the extended (adiabatic) states $|\mu\rangle$ via the local (diabatic) states $|n\rangle$. The relation of Hamiltonian, eq 1, to that given in the site representation (diabatic representation) is briefly outlined in Appendix A. Among the adiabatic bridge levels, nonadiabatic interactions become possible which are accounted for by the matrix $\theta_{\mu\mu'}$. At present there is no need to specify in detail the dependence of H_m , \mathcal{H}_μ , and $\theta_{\mu\mu'}$ on the vibrational coordinates. It is sufficient for our calculations to provide an independence of the couplings $T_{\mu m}$ on deviations around the equilibrium positions of the set Q of vibrational coordinates.

The kinetics of the considered ET process depends substantially on the relation between the characteristic time of the overall transfer process, τ_{ET} , and the characteristic times of vibrational relaxation within the states related to the D and A centers, $\tau_{rel}^{(m)}$ ($m = D, A$), and within the states related to the whole bridge, $\tau_{rel}^{(u)}$. These relaxation times are defined via the interaction of the DBA system, with vibrational modes forming a dissipative environment (thermal reservoir). For many molecular systems, vibrational relaxation proceeds on a time scale of 0.1 to 0.10 ps,³⁰ while τ_{ET} may be several orders of magnitude larger.^{7,9,10} Therefore, we provide the following inequality to be fulfilled

$$\tau_{ET} \gg \tau_{rel}^{(m)}, \tau_{rel}^{(u)} \quad (2)$$

This relation indicates that the kinetics of the D–A ET can be evaluated in the framework of a coarse-grained approximation leading to Pauli balance-like kinetic equations for the overall populations of the various electronic states. Concentrating on the case of nonadiabatic D–A ET, it has been explained in detail in our foregoing papers^{26,27} how to derive such kinetic equations and how to get the respective rate expression when starting from the basic electron vibrational density matrix. In which manner

this approach has to be modified to be applicable for the present case is briefly explained in Appendix B. Here we quote only the finally obtained rate equations valid for the populations P_m , ($m = D, A$), and P_μ , ($\mu = 1, 2, \dots, N$)

$$\begin{aligned} \dot{P}_D(t) &= - \left(\sum_\mu \kappa_{D\mu} + \kappa_{DA} \right) P_D(t) + \sum_\mu \kappa_{\mu D} P_\mu(t) + \kappa_{AD} P_A(t) \\ \dot{P}_\mu(t) &= - \left(\kappa_{\mu D} + \kappa_{\mu A} + \sum_{\mu' \neq \mu} \kappa_{\mu\mu'} \right) P_\mu(t) + \\ &\quad \sum_{\mu' \neq \mu} \kappa_{\mu'\mu} P_{\mu'}(t) + \kappa_{D\mu} P_D(t) + \kappa_{A\mu} P_A(t) \\ \dot{P}_A(t) &= - \left(\sum_\mu \kappa_{A\mu} + \kappa_{AD} \right) P_A(t) + \sum_\mu \kappa_{\mu A} P_\mu(t) + \kappa_{DA} P_D(t) \end{aligned} \quad (3)$$

The rate constants $\kappa_{D\mu}$ and $\kappa_{A\mu}$, as well as $\kappa_{\mu D}$ and $\kappa_{\mu A}$, characterize the ET from the D and the A, respectively, to the μ th bridge level as well as the reverse process. The direct transitions between the D and the A are accounted for by the forward superexchange rate κ_{DA} and the backward rate κ_{AD} . Transitions among different bridge levels are described by the rates $\kappa_{\mu\mu'}$. All ET rates except the last mentioned type read as follows (concerning $\kappa_{\mu\mu'}$ see the discussion below and Appendix B)

$$\kappa_{m\mu} = \frac{2\pi}{\hbar} |T_{m\mu}|^2 (FC)_{m\mu} \quad (4)$$

$$\kappa_{\mu m} = \frac{2\pi}{\hbar} |T_{m\mu}|^2 (FC)_{\mu m} \quad (5)$$

and

$$\kappa_{mn} = \frac{2\pi}{\hbar} |T_{AD}|^2 (FC)_{mn} \quad (6)$$

In the latter relation we have to identify m and n with D and A as well as with A and D. The square of the superexchange D–A coupling has the form

$$|T_{AD}|^2 = Re \sum_{\mu\mu'} \frac{T_{A\mu} T_{\mu D} T_{D\mu'} T_{\mu' A}}{\epsilon_{\mu\mu'} (\epsilon_\mu - E_D) (\epsilon_{\mu'} - E_A)} \quad (7)$$

To have a sufficient simple expression for the various Franck–Condon factors (FC) we provide the harmonic approximation

for every set of vibrational coordinates. In this case the electron vibrational coupling can be described by spectral densities for which we will utilize the Song–Marcus model^{35,36} in its simplest version (coupling to a single active vibrational mode with frequency ω_0). Finally, such a treatment leads to the well-known Jortner expression^{7,37} (which can be also derived in the framework of the spin-boson model^{8,38,39}):

$$(FC)_{ss'} = \frac{1}{\hbar\omega_0} \exp(-S_{ss'} \coth \hbar\omega_0/2k_B T) \times \left(\frac{1+n(\omega_0)}{n(\omega_0)} \right)^{v_{ss'}/2} I_{|v_{ss'}|}(2S_{ss'} \sqrt{n(\omega_0)(1+n(\omega_0))}) \quad (8)$$

Here, $s, s' = D, A, \mu$, $v_{ss'} \equiv \Delta E_{ss'}/\hbar\omega_0$, $S_{ss'} \equiv \lambda_{ss'}/\hbar\omega_0$ ($\Delta E_{ss'} = E_{s0} - E_{s'0}$ is the driving force and $\lambda_{ss'}$ is the reorganization energy of the $s \rightarrow s'$ ET reaction); furthermore, $n(\omega_0) = [\exp(\hbar\omega_0/k_B T) - 1]^{-1}$ denotes the Bose distribution, and $I_\nu(z)$ stands for the modified Bessel function.

Let us turn to the rates $\kappa_{\mu\mu'}$, which are responsible for relaxation processes among different bridge levels. Obviously, they determine the effective bridge relaxation time τ_B , which exceeds the characteristic times $\tau_{\text{rel}}^{(\mu)}$, what reflects the common observation that the vibrational relaxation within a single electronic bridge level (so-called intraterm relaxation) is faster than internal conversion-like relaxation processes between different levels (interterm relaxation caused by the nonadiabatic coupling).⁴⁰ Additionally to that, we will provide that the bridge interlevel relaxation is not the limiting process of the ET reaction, i.e., we set

$$\tau_{\text{ET}} \gg \tau_B \quad (9)$$

This inequality leads us to a further essential simplification of the D–A ET description. It is based on a second type of coarse-grained description that leads to kinetic equations valid on a time scale large compared to τ_B . At such a time scale the bridge-level populations $P_\mu(t)$ are in equilibrium to each other and vary only via an alteration of the overall bridge population

$$P_B(t) = \sum_{\mu=1}^N P_\mu(t) \quad (10)$$

Resulting from this, the bridge-level populations satisfy the relation $P_\mu(t)/P_{\mu'}(t) = \exp[-(\epsilon_\mu - \epsilon_{\mu'})/k_B T]$ and we can derive the following important relation

$$P_\mu(t) = W_B(\epsilon_\mu) P_B(t) \quad (11)$$

where

$$W_B(\epsilon_\mu) = \exp[-(\epsilon_\mu - \epsilon_1)/k_B T] / \sum_{\mu=1}^N \exp[-(\epsilon_\mu - \epsilon_1)/k_B T] \quad (12)$$

is the Boltzmann distribution of the bridge. Noting eq 11, the set of rate equations (eq 3) reduces to

$$\begin{aligned} \dot{P}_D(t) &= -(\kappa_{-1} + \kappa_3)P_D(t) + \kappa_1 P_B(t) + \kappa_{-3} P_A(t) \\ \dot{P}_B(t) &= -(\kappa_1 + \kappa_2)P_B(t) + \kappa_{-1} P_D(t) + \kappa_{-2} P_A(t) \\ \dot{P}_A(t) &= -(\kappa_{-2} + \kappa_{-3})P_A(t) + \kappa_2 P_B(t) + \kappa_3 P_D(t) \end{aligned} \quad (13)$$

with $\kappa_3 \equiv \kappa_{DA}$ and $\kappa_{-3} \equiv \kappa_{AD}$. Furthermore, we introduced the integral D(A)-bridge rate constants

$$\begin{aligned} \kappa_{-1} &= \sum_{\mu} \kappa_{D\mu} \\ \kappa_{-2} &= \sum_{\mu} \kappa_{A\mu} \end{aligned} \quad (14)$$

and the integral bridge-D(A) rate constants

$$\begin{aligned} \kappa_1 &= \sum_{\mu} \kappa_{\mu D} W_B(\epsilon_\mu) \\ \kappa_2 &= \sum_{\mu} \kappa_{\mu A} W_B(\epsilon_\mu) \end{aligned} \quad (15)$$

Taking the normalization condition

$$P_D(t) + P_B(t) + P_A(t) = 1 \quad (16)$$

the set of equations (eq 13) can be solved exactly to give (see also ref 26)

$$P_m(t) = P_m(\infty) + A_m e^{-K_1 t} + B_m e^{-K_2 t} \quad (m = D, B, A) \quad (17)$$

where K_1 and K_2 are the overall transfer rates. The prefactors A_m and B_m are determined by the rate constants as well as the initial conditions. Due to the presence of a large energy gap E_g between the D(A) level and the extended bridge levels (cf. Figure 1), the forward rate constants κ_1 and κ_2 strongly exceed the backward rate constants κ_{-1} and κ_{-2} . Also, due to a weak superexchange coupling between the D and A, κ_1 and κ_2 are much larger than the superexchange rate constants κ_3 and κ_{-3} . Therefore, it becomes an excellent approximation to set²⁶ $K_1 \approx \kappa_1 + \kappa_2$ and $K_2 \approx \kappa_3 + \kappa_{-3} + (\kappa_{-1}\kappa_2 + \kappa_{-2}\kappa_1)/(\kappa_1 + \kappa_2)$. As far as $K_1 \gg K_2$, the fast part of the ET process with characteristic transfer time $\tau_{1,\text{tr}} \equiv K_1^{-1}$ proceeds for times much less than $\tau_{2,\text{tr}} \equiv K_2^{-1}$. It is completed at $t \gg \tau_{1,\text{tr}}$, for which an intermediate population of the D, A, and B can be introduced

$$P_D(t \gg \tau_{1,\text{tr}}) = 1 - \frac{\kappa_{-1} + \kappa_3}{\kappa_1 + \kappa_2} \approx 1 \quad (18)$$

$$P_A(t \gg \tau_{1,\text{tr}}) = \frac{\kappa_3}{\kappa_1 + \kappa_2} \ll 1 \quad (19)$$

and

$$P_B(t \gg \tau_{1,\text{tr}}) = \frac{\kappa_{-1}}{\kappa_1 + \kappa_2} \ll 1 \quad (20)$$

Accordingly, the first part of the ET reaction does not result in any notable electron redistribution in the DBA system. As a result, the kinetics of D–A ET can be described by the rather simple single-exponential expression⁴¹

$$P_m(t) \approx (P_m(0) - P_m(\infty)) e^{-Kt} + P_m(\infty) \quad (m = D, A, B) \quad (21)$$

The overall transfer rate $K \equiv K_2$ can follow as

$$K \equiv \tau_{\text{ET}}^{-1} = k_f + k_b \quad (22)$$

It is given as a sum of the combined forward

$$\begin{aligned} k_f &\equiv k_f^{(\text{sup})} + k_f^{(\text{act})} \\ k_f^{(\text{sup})} &= \kappa_3 \\ k_f^{(\text{act})} &= \frac{\kappa_{-1}\kappa_2}{\kappa_1 + \kappa_2} \end{aligned} \quad (23)$$

and the combined backward

$$\begin{aligned} k_b &\equiv k_b^{(\text{sup})} + k_b^{(\text{act})} \\ k_b^{(\text{sup})} &= \kappa_{-3} \\ k_b^{(\text{act})} &= \frac{\kappa_{-2}\kappa_1}{\kappa_1 + \kappa_2} \end{aligned} \quad (24)$$

transfer rates. Both types of rates include the contributions $k_f^{(\text{sup})}$ and $k_b^{(\text{sup})}$ stemming from the superexchange mechanism of ET and the part $k_f^{(\text{act})}$ as well as $k_b^{(\text{act})}$ related to the activated ET mechanism.

III. Results and Discussion

To clearly demonstrate the efficiency of the thermally activated and the superexchange mechanisms of D–A ET, we will consider a sufficiently simple model of a regular chain-like bridge formed by N identical units. They are characterized by electronic energy levels E_0 and linked together by a common nearest-neighbor electronic intersite coupling V_0 (for the sake of clarity we put $V_0 > 0$). The eigenvalues of the electronic part of the bridge Hamiltonian (A1) as well as the transformation coefficients $u_\mu(n)$ have the well-known form

$$\begin{aligned} \epsilon_\mu &= \epsilon_\mu(N) = E_0 - 2V_0 \cos\left[\frac{\pi\mu}{N+1}\right] \\ u_\mu(n) &= \sqrt{\frac{2}{N+1}} \sin\left[\frac{\pi n\mu}{N+1}\right] \end{aligned} \quad (25)$$

Taking into consideration the definitions of $T_{\mu D}$ and $T_{\mu A}$, which specify the coupling of the D/A centers to the μ th bridge level in the Hamiltonian (1) and noting the expressions (4), (5), (8), and (15), one derives

$$\begin{aligned} \kappa_{1(2)} &= \frac{2\pi}{\hbar} \frac{|V_{1D(\text{NA})}|^2}{\hbar\omega_{1(2)}} \exp(-S_{1(2)} \coth \hbar\omega_{1(2)}/2k_B T) \\ &\quad \sum_{\mu=1}^N u_\mu^2(1(N)) W_B(\epsilon_\mu) \left(\frac{1 + n(\omega_{1(2)})}{n(\omega_{1(2)})} \right)^{\nu_{1(2)\mu}/2} \\ &\quad I_{|\nu_{1(2)\mu}|} (2S_{1(2)} \sqrt{n(\omega_{1(2)}) (1 + n(\omega_{1(2)}))}) \\ \kappa_3 &= \frac{2\pi}{\hbar} \frac{|T_{AD}(N)|^2}{\hbar\omega_3} \exp(-S_3 \coth \hbar\omega_3/2k_B T) \\ &\quad \left(\frac{1 + n(\omega_3)}{n(\omega_3)} \right)^{\nu_3/2} I_{|\nu_3|} (2S_3 \sqrt{n(\omega_3) (1 + n(\omega_3))}) \quad (26) \\ \kappa_{-1(-2)} &= \kappa_{1(2)} Z_B \exp(-\Delta E_{1(2)}/k_B T) \\ \kappa_{-3} &= \kappa_3 \exp(-\Delta E/k_B T) \end{aligned} \quad (27)$$

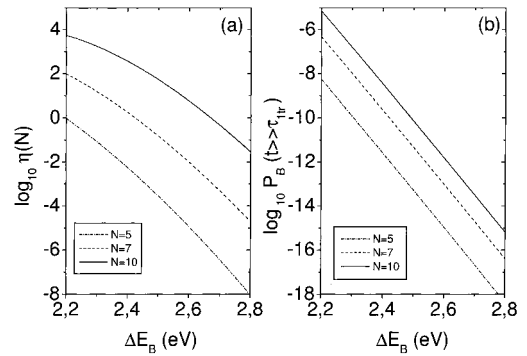


Figure 2. Relative contribution of the thermally activated and the superexchange mechanisms of D–A ET in dependence on the energy gap ΔE_B at room temperature $T = 298$ K and for a fixed number of bridge units N (part a), and the maximal integral bridge population $P_B(t \gg \tau_{lr})$ vs the energy gap ΔE_B (part b). The curves are calculated in using eqs 22–24 and 26–30 with $\lambda_1 = S_1 \hbar \omega_1 = 0.9$ eV, $\lambda_2 = S_2 \hbar \omega_2 = 1$ eV, $\lambda_3 = S_3 \hbar \omega_3 = 1.2$ eV, $\omega_1 = \omega_2 = 200$ cm^{-1} , $\omega_3 = 100$ cm^{-1} , $|V_{1D}| = |V_{NA}| = 0.02$ eV, and $\Delta E = 0.1$ eV at $V_0 = 1$ eV (a) and $V_0 = 2$ eV (b).

Here, $\Delta E_1 \equiv E_g = \epsilon_1 - E_D = \Delta E_B - 2V_0 \cos[\pi/(N+1)]$ and $\Delta E_2 = E_g + \Delta E = \epsilon_1 - E_A$ are the energy gaps for forward and backward ET transitions, respectively, while $\Delta E \equiv E_D - E_A$ is the driving force of the ET reaction and $\Delta E_D = E_0 - E_D \equiv \Delta E_B$ and $\Delta E_A = E_0 - E_A = \Delta E_B + \Delta E$ are the energy gaps at vanishing electronic intersite coupling (cf. Figure 1). Furthermore, we introduced in eq 26 $\nu_{1(2)\mu} \equiv (\epsilon_\mu - E_{D(A)})/\hbar\omega_{1(2)}$, $\nu_3 \equiv \Delta E/\hbar\omega_3$, and $S_j = \lambda_j/\hbar\omega_j$, where λ_j is the reorganization energy of the corresponding donor \rightarrow bridge ($j = 1$), acceptor \rightarrow bridge ($j = 2$), and donor \rightarrow acceptor, ($j = 3$), ET while ω_j denotes the active mode of each mentioned transition.

In line with eqs 23, 24, and 27, the overall transfer rate can be represented as $K = K^{(\text{act})} + K^{(\text{sup})} = (k_f^{(\text{sup})} + k_f^{(\text{act})}) [1 + \exp(-\Delta E/k_B T)]$. Therefore, to compare the efficiencies of the thermally activated and the superexchange mechanisms we introduce the ratio

$$\eta(N) = \frac{K^{(\text{act})}}{K^{(\text{sup})}} = \frac{k_f^{(\text{act})}}{k_f^{(\text{sup})}} = \frac{\kappa_{-1}}{\kappa_3} \frac{\kappa_2}{\kappa_1 + \kappa_2} \quad (28)$$

The dependence on the number N of bridge units is contained in the transfer rate $K^{(\text{act})}$ mainly via the factors $u_\mu^2(1(N))$ and $W_B(\epsilon_\mu)$ while it is located in the rate $K^{(\text{sup})}$ in the square of the effective D–A coupling $|T_{AD}(N)|^2$. Its analytic form follows from eqs 7 and 25 resulting in

$$\begin{aligned} |T_{AD}(N)|^2 &= |T_{AD}(1)|^2 \exp[-2\xi(N-1)] \\ |T_{AD}(1)|^2 &\equiv |V_{1D} V_{NA}|^2 / \Delta E_D \Delta E_A \end{aligned} \quad (29)$$

where the intersite decay constant $\xi = 1/2(\xi_D + \xi_A)$ is expressed via the partial decay constants

$$\xi_{D(A)} = \ln \left[\frac{2|V_0|}{\Delta E_{D(A)} - \sqrt{\Delta E_{D(A)}^2 - 4|V_0|^2}} \right] \quad (30)$$

For the condition $\Delta E \ll \Delta E_B$, the expressions ξ_D and ξ_A are equal to each other. Hence, the measured intersite decay constant reduces to the conventional form $\xi = \xi_D = \xi_A \approx \ln[2|V_0|/(\Delta E_B - \sqrt{\Delta E_B^2 - 4|V_0|^2})]$.^{7,28} Figure 2a demonstrates the relative importance of both mechanisms for a given number of bridge units and in dependence on the energy gap. It can be

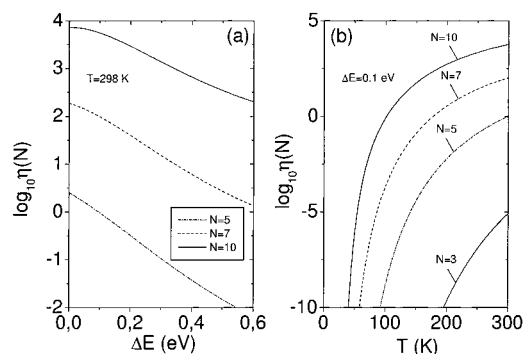


Figure 3. Relative contribution of the thermally activated and the superexchange mechanisms of D–A ET for a fixed number of bridge units N in dependence on the driving force of the ET reaction ΔE and at room temperature (part a), and in dependence on temperature for $\Delta E = 0.1$ eV (part b). The curves have been calculated in using eqs 26–30 with $V_0 = 1$ eV, $\Delta E_B = 2.2$ eV. All other parameters are identical with those used in Figure 2.

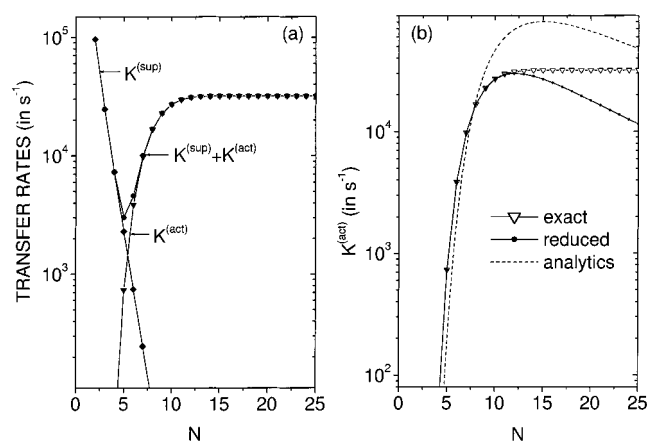


Figure 4. Formation of the overall D–A ET rate as the sum of superexchange and thermally activated transfer rates given by the general expressions of eqs 22–24 along with eqs 26 and 27 (part a), and comparison of the exact form for $K^{(act)}$ (see eq 26 for $\kappa_{1(2)}$) with the reduced form (the sum in eq 26 has been limited to the single term with $\mu = 1$), and the approximate analytic form eq 33 (part b). The curves are calculated using the same parameters as in Figure 2.

clearly seen that the influence of the activated mechanism on the overall transfer rate increases substantially with the number of bridge units. At realistic reorganization energies λ_j of the order of 1 eV and an energy gap $\Delta E_B \sim 1$ eV (cf. refs 1, 2, 4, 7), the thermally activated mechanism can exceed the superexchange one ($\log \eta(N) > 0$) if at $V_0 = 1$ eV the number of bridge units becomes larger than 7. It is very important that for the same parameters the maximum integral bridge population $P_B(t \gg \tau_{1tr})$ is rather small (e.g., at $V_0 = 1$ eV, $\Delta E_B = 2.6$ eV when $K^{(sup)}/K^{(act)} \approx 10^{-2}$, cf. Figure 2a, the population $P_B(t \gg \tau_{1tr})$ amounts about 10^{-11} , cf. Figure 2b).

The effect of the driving force of the D–A ET reaction is demonstrated in detail in Figure 3a. At a fixed number of bridge units, the contribution of the superexchange mechanism to the overall transfer rate K becomes more important for large ΔE . Nevertheless, even at $\Delta E = 0.3$ eV the thermally activated mechanism can dominate if $N > 7$.

Below we will discuss the influence of the bridge length on the overall ET rate. Figure 4a shows that the D–A transfer rate K , eq 22, is given as the sum of two contributions. The superexchange contribution reflects the exponential decrease of the transfer rate with increasing bridge length. In line with eqs 26 and 29 it can be represented by a simple analytic expression

$$K^{(sup)} = K_0^{(sup)} \exp[-2\xi(N-1)] \quad (31)$$

with $K_0^{(sup)}$ being the rate for $N = 1$. In contrast to the decrease of the superexchange rate, the thermally activated mechanism results in a rise (at small number of bridge units) and a saturation (at large N) of the rate $K^{(act)}$. Such a behavior is generally dictated by the dependence of the energy gap $E_g = \Delta E_B - 2V_0 \cos[\pi/(N+1)]$ on N as well as by the variability of the energetic distance between the nearest bridge energy levels $\epsilon_\mu - \epsilon_{\mu-1}$ (cf. Figure 1) with respect to N . If the number of bridge units increases, the gap reduces to a limiting value $E_g = \Delta E_B - 2V_0$ while the energetic distance mentioned before becomes so small that the condition $\exp[-(\epsilon_\mu - \epsilon_{\mu-1})/k_B T] \ll 1$ is satisfied for any pair of neighbored energy levels. Just this circumstance is responsible for the saturation of the thermally activated transfer rate with increasing bridge length as well as for the temperature effect, which is more pronounced for longer bridges, cf. Figure 3b.

The quantitative description of the crossover region between the two mechanisms of the D–A ET is a valuable tool for the analysis of experimental data. Due to the decreasing role of the superexchange mechanism and the increasing role of thermally activated ET (cf. Figure 4a) an overall D–A transfer rate K exhibits a nonmonotonic dependence on N with a minimum around 4–6 bridge units, i.e., in the vicinity of the crossover point $N = 5$. It is very important that just for such small number of bridge units an approximate analytic form of $K^{(act)}$ can be found if only the strict condition

$$\exp\{-[\epsilon_2(N) - \epsilon_1(N)]/k_B T\} \ll 1 \quad (32)$$

is satisfied for the bridge with a limited number of units. Indeed, at such a condition, only the very lowest bridge levels, Figure 1, are populated by the transferred electron and thus the main contribution to the rates κ_1 and κ_2 , eq 26 follows from the term $\mu = 1$ of the common sum. Figure 4b shows that up to $N = 12$ the exact and the reduced description (with the single term $\mu = 1$ in the sum) coincide with an extremely high accuracy. This behavior enables one to introduce an approximate analytic form for $K^{(act)}$ that can be applied for a qualitative analysis of the ET process taking place in a bridge with a small number of units. It reads (note $V_0 > 0$)

$$K^{(act)} \approx K_0^{(act)} \frac{2}{N+1} \sin^2 \left[\frac{\pi}{N+1} \right] \exp\{2V_0 \cos[\pi/(N+1)]/k_B T\} \quad (33)$$

The rate $K_0^{(act)}$ plays the role of certain parameter which can be estimated from the general (exact) formula at a concrete N . In Figure 4b $K_0^{(act)}$ has been estimated for $N = 7$ to achieve the best coincidence of the analytic form (eq 33) with the exact result, especially for the crossover region $4 \leq N \leq 10$. When the bridge number increases and thus $K^{(act)}$ saturates, the condition in eq 32 is no longer fulfilled. Therefore, the simple analytic expression, eq 33, does not hold. To evaluate $K^{(act)}$ one has to take the general expressions (eqs 23 and 26). Nevertheless, the analytic expressions eqs 31 and 33 for the transfer rates are suitable to analyze experimental data, especially in the vicinity of the crossover point.

Next let us estimate those conditions for which the crossover point can be observed. If the superexchange rate decreases with the D–A distance R according to $\exp(-\beta R)$ a distant-decay constant β is used as the main characteristic of the ET process.^{7,10} The constant β varies in a broad interval from 2 ≤

$\beta \leq 3 \text{ \AA}^{-1}$ for model compounds² and modified proteins⁴⁵ up to $0.9 \leq \beta \leq 1.15 \text{ \AA}^{-1}$ and $1.25 \leq \beta \leq 1.6 \text{ \AA}^{-1}$ for the β -sheet and α -helix regions in native proteins, respectively.¹⁰ For the DNA, β -values between 0.2 \AA^{-1} and 0.9 \AA^{-1} or between 1.2 \AA^{-1} and 1.6 \AA^{-1} have been reported.^{17–20,23}

Let a be the distance between the neighboring units in a regular bridge (in the case of a helical-bridge, the parameter a is the distance between the nearest turns). For example, we refer to a rigid peptide bridge given by a polyproline oligomer which has a through-bond distance per residue of $a = 4.2 \text{ \AA}$ ⁵¹ ($a = 3.1 \text{ \AA}$ for the shortest through-space distance), while a value $a_b = 1.4 \text{ \AA}$ corresponds to an average length of the covalent bond. When measuring the distance R in units of a one obtains $R = Na$ and thus $\exp(-2\xi N) = \exp(-\beta R)$ where $\xi = a\beta/2$. If an electron pathway is present along covalent bonds,^{9,42–44} the corresponding through-bond decay constant ξ_b is deduced from $\exp(-\xi N) = \exp(-\xi_b n_b)$, where $n_b = sN$ denotes the total number of covalent bonds forming the D–A pathway while s is the number of covalent bonds that are responsible for the ET within a single bridging unit. Consequently, $\xi = s\xi_b$, and thus the measured distant-decay constant β can be expressed via the calculated covalent bond-decay constant β_b as $\beta = \beta_b s(a_b/a)$. In Figure 4a, the intersite decay parameter is equal to $\xi = 0.88$. It means that, for example, at $a = 3.1 \text{ \AA}$ the distance-decay constant amounts the value of $\beta = 0.57 \text{ \AA}^{-1}$. If the ET occurs through covalent bonds with $s = 2$ bonds per bridge, then the covalent decay constant is given by $\beta_b = 0.63 \text{ \AA}^{-1}$ while $\xi_b = 0.44$. Both constants, $\beta = 0.57$ and $\beta_b = 0.63$, correspond to a rather slow decrease of superexchange transfer rate (compare the above given explanation for β). But even in this case the superexchange mechanism is already replaced at $N = 6–7$ by the mechanism of activated ET.

In molecular bridges where β exceeds 1 \AA^{-1} (for instance in peptides and proteins) the crossover point has to be shifted down to $N = 2–4$. The presence of the crossover point strongly depends on the relation between the energy gap E_g and the intersite coupling V_0 . Let ET occur at a small driving force so that $\Delta E \ll \Delta E_B$ and thus $\xi \approx \xi_D \approx \xi_A$. Then, in noting $\Delta E_B = 2V_0 + E_g$ (cf. Figure 1) and eq 30, we have the condition

$$2V_0 = E_g \frac{\gamma}{s-1-\gamma}$$

$$\gamma \equiv \frac{2 \exp(-\xi)}{1 + \exp(-2\xi)} \quad (34)$$

At any fixed decay parameter ξ (or $\beta = 2\xi/a$) the expressions gives a relation between the intersite electron coupling V_0 and the energy gap E_g . For $\beta = 1.3 \text{ \AA}^{-1}$ ($\xi \approx 2.02$) and $\beta = 1 \text{ \AA}^{-1}$ ($\xi \approx 1.55$), eq 34 yields $V_0 \approx 0.17E_g$ and $V_0 \approx 0.35E_g$, respectively. At room temperature, a thermally activated ET can be effective only if E_g does not exceed 0.3 eV. Let, for example, $E_g = 0.2 \text{ eV}$. Then, the crossover between the superexchange and activated ET becomes possible at $V_0 \approx 0.03 \text{ eV}$ ($\beta = 1.3 \text{ \AA}^{-1}$) and $V_0 \approx 0.07 \text{ eV}$ ($\beta = 1 \text{ \AA}^{-1}$). However, for such a very small electronic intersite coupling, the electron-vibrational interaction completely destroys the extended bridge states. The ET through the bridge takes place as a nonadiabatic reaction and a competition between the superexchange and the sequential ET mechanism results (for details see refs 23, 26, 27).

Now we will assume that the two decay constants $\beta = 1.3 \text{ \AA}^{-1}$ and $\beta = 1 \text{ \AA}^{-1}$ used above are related to ET reactions across covalent bonds.^{9,42–45} For the typical decay factor $\epsilon_b = \exp(-\xi_b) = 0.6$ it yields $\beta_b = 0.72 \text{ \AA}^{-1}$ ($\xi_b = 0.51$). (This means that distant decay constants $\beta = 1.3 \text{ \AA}^{-1}$ and $\beta = 1 \text{ \AA}^{-1}$ are formed

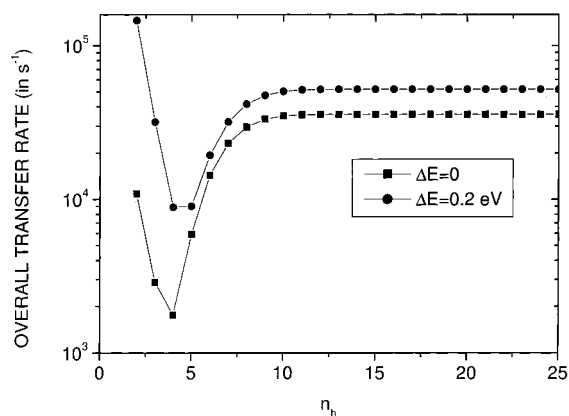


Figure 5. The dependence of the overall D–A transfer rate on the number of hydrogen bonds n_h and for a fixed driving force ΔE if the ET occurs along hydrogen bonds. The curves are calculated using the general expressions of eqs 22–27 for $V_0 = V_0^{(\text{hyd})} = 0.72 \text{ eV}$, $\Delta E_B = 1.64 \text{ eV}$, and $T = 298 \text{ K}$. All other parameters are identical with those used in Figure 2.

by $s = 4$ and $s = 3$ covalent bonds per single bridge unit, respectively.) Noting eq 34, we obtain $V_0^{(\text{cov})} = 3.65E_g$. Therefore, a crossover between the superexchange and thermally activated ET mechanism is only possible if an electronic pathway along covalent bonds exist where the inter-site coupling $V_0^{(\text{cov})}$ amounts values less than 1 eV. However, quantum chemical computations show that $V_0^{(\text{cov})} \approx 2.5 \text{ eV}$.⁴² This fact indicates that an activated ET mechanism is not realized in systems where the ET proceeds along covalent bonds.

Finally we will discuss the case where the bridge is formed via a hydrogen-bond network (the hydrogen bonds will be considered as specific covalent bonds^{9,10,42}). The corresponding coupling decay parameter can be estimated via the relation $\epsilon_h = \exp(-\xi_h) = \epsilon_b^2 \exp[-1.7(R - 2.8)]$, where R is measured in \AA .^{9,46} In the case of ET reactions along hydrogen bonds, a possible value of the distant-decay constant β may be positioned in a rather wide range around $1–2 \text{ \AA}^{-1}$.¹⁰ We will consider the situation where $\epsilon_h \approx \epsilon_b = 0.6$.^{9,46} Such a relation is valid if the effective tunneling length $R = a_h$ is equal to 2.51 \AA . At $\epsilon_h = 0.6$, one derives $\xi_h = 0.51$ and thus $\beta_h = 2\xi_h/a_h \approx 0.40 \text{ \AA}^{-1}$. The correspondence with the measured value β follows from the inequality $\beta = s_h\beta_h a_h/a$ where s_h is the number of hydrogen bonds that corresponds to an elementary length a along a linear bridge. In the case of a helical bridge, this length coincides with the distance between the nearest turns. The condition in eq 34, taken at $\xi = \xi_h = 0.6$, indicates that $V_0^{(\text{hyd})} \approx 3.67 E_g$. Thus, if the ET occurs along hydrogen bonds the crossover between the superexchange and thermally activated ET mechanism is possible for any $V_0^{(\text{hyd})} < 0.8 \text{ eV}$, provided that $E_g = \Delta E_B - 2V_0^{(\text{hyd})}$ does not exceed values of 0.2–0.25 eV. Figure 5 demonstrates the appearance of the crossover point for the case of ET along the hydrogen bonds. The crossover is shown to be take place at about $n_h = 4$ (i.e. $N \approx 2–3$ if the ET occurs along a helical-bridge).

IV. Conclusion

We consider it as the main result of our computations that bridge-mediated D–A ET can be described as a single-exponential kinetic process, independently on the number of bridging units. The corresponding overall transfer rate (eq 22) includes the contribution of the thermally activated and the superexchange mechanisms of ET (cf. eqs 23 and 24). The derivation of the set of kinetic equations (eq 13) and the

corresponding solution (eqs 21–24) has been based only on the fundamental inequalities of eqs 2 and 9. In particular, these equations do not depend on the concrete interaction of the DBA system with the heat bath. However, the given single-exponential (coarse-grained) description is valid only if the overall bridge population (eq 20) becomes very small (less than 10^{-4}). Such a small bridge population can be achieved if the extended bridge-states couple weakly to the D and A states, i.e., if the coupling matrix elements V_{1D} and V_{NA} are small compared to the intrabridge couplings $V_{n,n\pm 1}$ as well as to the energy gaps $E_n - E_{D(A)}$ (cf. Figure 1). Furthermore, the D-level has to be positioned below the lowest extended bridge level.

As already stated, there does not exist the general possibility to get the exact solution for the ET reaction as a single exponential kinetic process which appears to be independent of the number of electron-vibrational levels in the DBA system and which is valid at any time t . Therefore, the recently published results of refs 47–49 on a unified description of bridge-assisted D–A ET have to be considered to be incorrect since they are based on the assumption of a single exponent valid in the whole time region $0 \leq t \leq \infty$.

Realistic conditions for DBA-ET have been given where the thermally activated ET mechanism becomes much more effective than the superexchange one, even if the bridge population is of the order of 10^{-5} to 10^{-11} (cf. Figure 2). We consider this as a novel result since within the conventional approach thermally activated D–A ET (or sequential ET in the case of nonadiabatic reactions) is taken into account only if the transferred electron populates the bridge levels with a sufficiently high probability (0.1 to 0.01). The thermally activated mechanism is especially important for long bridges. For such systems the overall ET rate is dictated by the different dependence on the number N of bridge units of the rate of thermally activated ET and of the rate referring to the superexchange ET. The given analytic formula (eq 33) offers a good opportunity to estimate for a given ET experiment whether the thermally activated or the superexchange ET mechanism dominates. This can be achieved by comparing the N -dependence on the basis of the expressions given in eqs 31 and 33. It is only necessary to remember that eq 33 for $K^{(\text{act})}$ is valid if the condition of eq 32 is fulfilled (e.g., for $V_0 = 1$ eV, it works up to $N = 10$).

If one remembers that the superexchange and the sequential ET rates, $K^{(\text{sup})}$ and $K^{(\text{seq})}$, drop with the rise of the bridge length as $\exp(-\xi N)$ and N^{-1} , respectively while the rate of activated ET $K^{(\text{act})}$ increases up to its saturation value (cf. refs 5, 23, 26), there is an excellent possibility to clarify which type of ET takes place in a given system. In particular, one can specify the mechanisms of distant D–A ET in complex molecular systems such as DNA strands or proteins. In the case of the DNA, it has already been stressed that just the sequential mechanism is responsible for long-range ET.^{21–23,25,30,50} Considering peptide-mediated D–A ET as measured in ref 51, it could be also interpreted in the framework of the superexchange and sequential mechanisms.^{26,27} Note that the interplay of the sequential (incoherent) and superexchange (coherent) ET mechanism is valid for small ratios $\zeta_{m\alpha, n\beta}$ (see the discussion at the beginning of Section II). Since the most effective transitions occur at $E_{m\alpha} \approx E_{n\beta}$, the inequality $\zeta_{m\alpha, n\beta} \ll 1$ roughly reduces to the simple condition $|V_{mn}|/\hbar \ll \tau_{\text{rel}}^{-1}$. In contrast, if the relation $|V_{mn}|/\hbar \gg \tau_{\text{rel}}^{-1}$ is valid for all bridge units, then N specific coherent ET channels through the extended bridge levels are formed. Just these coherent channels are responsible for the mechanism of activated D–A ET studied in the present paper.

Each channel contributes via thermal activation of an electron from the D(A) center. As a result, strong electronic intersite couplings in the bridge can provide an effective thermally induced coherent ET through the bridge, even though the overall electronic population of the bridge remains small. If $N > 5-7$, the rate of activated transfer $K^{(\text{act})}$ becomes independent of the number of bridge units reflecting the predominance of the specific thermally induced coherent mechanism of ET compared with the superexchange (pure coherent) ET. Thus, for $|V_{mn}| \gg \hbar\tau_{\text{rel}}^{-1}$ the combined action of the sequential (incoherent) and superexchange mechanism of D–A ET is replaced by the interplay between the thermally activated coherent and purely coherent superexchange mechanism of ET.

Concentrating on ET reactions in proteins, we demonstrated that if the main ET pathway in proteins is associated with the electron motion along covalent bonds, the superexchange mechanism dominates, even for a small energy gap between the donor level and the lowest extended bridge level (of the order 0.2 eV). If, however, the pathway is determined by ET along specific hydrogen bonds, then the crossover from superexchange to thermally activated transfer takes place already at a number of four hydrogen bonds. The mentioned considerations also indicated that the condition for activated D–A ET can be fulfilled in α -helical and β -strand structures if the ET occurs along hydrogen bonds. But thermally activated ET can also take place along the key amino acid residues. This statement is supported by the results of quantum-chemical calculation on the electronic couplings.⁵²

Therefore, our central conclusion is that the specification of electron pathways through complex macromolecular structures requires the comparison of three different types of ET mechanisms, the superexchange mechanism, the sequential mechanism, and the mechanism of thermally activated coherent ET. Possibly the sequential mechanism can become important for small intersite couplings (V_0 in the order of 0.01–0.1 eV), while the activated mechanism dominates the ET reaction if V_0 lies in the range of 0.1 eV up to 1 eV. In both cases, the energy gap E_g should not be larger than 0.3 eV to allow for thermal activation of coherent channels at room temperature.

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Appendix A: Diabatic vs Adiabatic Representation

In Section II we introduced the ET Hamiltonian, eq 1, which gives the basis for all following considerations. Here, we will concentrate on the bridge part of eq 1 and briefly indicate how to obtain this Hamiltonian. The site representation (diabatic representation) uses the LUMO levels of the localized bridge units with energies E_n ($n = 1, 2, \dots, N$), where N denotes the number of units within the bridge. To be more concrete, we consider a DBA complex where the intrabridge gaps $\Delta E_n \equiv E_n - E_{n+1}$ are small compared with interbridge electronic couplings $V_{n,n\pm 1}$ (cf. Figure 1). Large intersite electronic couplings can be found, for example along covalent bonding ($V_{n,n\pm 1}^{(\text{cov})} > 2$ eV) and hydrogen bridges ($V_{n,n\pm 1}^{(\text{hyd})} < 1$ eV).^{42–44} The supposed inequality $|\Delta E_n| \ll |V_{n,n\pm 1}|$ indicates that just the extended LUMO levels give the most adequate representation to study ET through the bridge (cf. the discussions in refs 5, 23, 28, 29). These levels can be understood as adiabatic states of the whole bridge, leading to adiabatic potential energy surface (PES) as introduced in Section II. Of course sophisticated

quantum-chemical methods have to be applied to calculate these adiabatic PES. In such quantum-chemical framework the derivation, which will be given in the following, corresponds to a simple Hückel approach where the bridge energies ϵ_μ and the bridge states $|\mu\rangle$ are found from a diagonalization of the bridge Hamiltonian (electronic part). Consequently, we have the following one-to-one correspondence:

$$H_B^{(el)} = \sum_{n,n'} [E_n \delta_{n,n'} + V_{nn'} (\delta_{n',n+1} + \delta_{n',n-1})] |n\rangle \langle n'| \equiv \sum_{\mu} \epsilon_{\mu} |\mu\rangle \langle \mu| \quad (A1)$$

which is established by the unitary transformation $|\mu\rangle = \sum_n u_{\mu}(n) |n\rangle$ (for the case of a bridge with N identical units and identical electronic couplings between the neighboring units, the $u_{\mu}(n)$ have the well-known form given in eq 25).

Next we briefly indicate how the electron-vibrational coupling is affected by this transformation. To do this we include vibrational degrees of freedom but neglect any vibrational modulation of the electronic intersite coupling. Therefore, to get the complete bridge Hamiltonian H_B the energies E_n in eq A1 have to be replaced by the vibrational Hamiltonian $H_n = T_{\text{vib}} + U_n(Q)$ with the kinetic energy operator T_{vib} and the PES $U_n(Q) = U_n^{(0)} + \sum_j \hbar \omega_j (Q_j - Q_j^{(n)})^2/4$ written here in a representation of dimensionless normal-mode oscillator coordinates ($Q_j^{(n)}$ denotes the replacement of vibrational mode j).

To establish a connection to the bridge part of the ET Hamiltonian, eq 1, we proceed as follows. First we split off the PES according to $U_n(Q) = U_n^{(0)} + \sum_j \hbar \omega_j Q_j^{(n)2}/4 - \sum_j \hbar \omega_j Q_j^{(n)} Q_j/2$ what enables us to introduce the site energies $E_n = U_n^{(0)} + \sum_j \hbar \omega_j Q_j^{(n)2}/4$ and a reference vibrational Hamiltonian $H_{\text{vib}} = T_{\text{vib}} + \sum_j \hbar \omega_j Q_j^2/4$. Using the electronic states $|\mu\rangle$ the bridge Hamiltonian can be written in the following form

$$H_B = \sum_{\mu,\mu'} \{ \delta_{\mu,\mu'} (\epsilon_{\mu} + H_{\text{vib}}) + \sum_j \hbar \omega_j g_j(\mu,\mu') Q_j \} |\mu\rangle \langle \mu'| \quad (A2)$$

where the electron vibrational coupling constant has been introduced according to $g_j(\mu,\mu') = -\sum_m u_{\mu}^*(m) u_{\mu'}(m) Q_j^{(m)}/2$. Their separation into those parts being diagonal with respect to the electronic quantum numbers and those being off-diagonal offers the possibility of a second type of notation for the bridge Hamiltonian. A simple rearrangement of the part of eq A2 being diagonal with respect to the electronic quantum numbers suggests the introduction of a new type of PES $U_{\mu}(Q) = \epsilon_{\mu} - \sum_j \hbar \omega_j g_j^2(\mu,\mu) + \sum_j \hbar \omega_j (Q_j + 2g_j(\mu,\mu))^2/4 \equiv U_{\mu}^{(0)} + \sum_j \hbar \omega_j (Q_j + Q_j^{(\mu)})^2/4$. This finally gives the Hamiltonian, eq A2 in the new form

$$H_B = \sum_{\mu,\mu'} \{ \delta_{\mu,\mu'} H_{\mu} + (1 - \delta_{\mu,\mu'}) \sum_j \hbar \omega_j g_j(\mu,\mu') Q_j \} |\mu\rangle \langle \mu'| \quad (A3)$$

with vibrational Hamiltonian $H_{\mu} = T_{\text{vib}} + U_{\mu}(Q)$ and vibrationally induced interlevel coupling represented by the last term of eq A3. This Hamiltonian may serve as a certain approximation for the more general one introduced in eq 1. If one follows this line, one can identify \mathcal{H}_{μ} and the nonadiabatic coupling of eq 1 with H_{μ} and the interlevel coupling $g_j(\mu,\mu')$, respectively. In particular, one can study in an easy way how the extended states change with an increase of the number of bridge units. The whole derivation seems to be consistent and has been used in the literature (see, e.g., ref 23). Nevertheless, it is based on an expansion of vibrational coordinates around equilibrium

positions that refer to the diabatic and not the adiabatic states. Therefore, the equilibrium positions $Q_j^{(\mu)}$ obtained via the introduction of extended states might be incorrect.

For an application in the next appendix we give the electron-vibrational representation of the DBA-Hamiltonian, eq 1 (or of its approximate version, eq A3). This representation is based on the vibrational eigenstates $|\chi_{m\alpha}\rangle$ and $|\chi_{\mu\alpha}\rangle$ of the Hamiltonian $H_m(Q)$ and $H_{\mu}(Q)$, respectively. The related eigenenergies are denoted as $E_{m\alpha_m}$ for the D and A site, and $\epsilon_{\mu\alpha_{\mu}}$ for the bridge states. Accordingly, one can introduce a zero-order part H_0 of the DBA-Hamiltonian, eq 1, a part V_{tr} which is responsible for transitions into and out of the bridge state, and a part V_{rel} which is responsible for intrabridge relaxation processes. Therefore, we write

$$H_{\text{DBA}} = H_0 + V_{\text{tr}} + V_{\text{rel}} \quad (A4)$$

The first part simply reads

$$H_0 = \sum_{m=D,A} \sum_{\alpha_m} E_{m\alpha_m} |\chi_{m\alpha_m}\rangle \langle \chi_{m\alpha_m}| + \sum_{\mu} \sum_{\alpha_{\mu}} \epsilon_{\mu\alpha_{\mu}} |\chi_{\mu\alpha_{\mu}}\rangle \langle \chi_{\mu\alpha_{\mu}}| \quad (A5)$$

The transfer part has the following form

$$V_{\text{tr}} = \sum_{m=D,A} \sum_{\alpha_m} \sum_{\mu} \sum_{\alpha_{\mu}} \langle T_{m\alpha_m \mu\alpha_{\mu}} \rangle |m\rangle \langle \chi_{\mu\alpha_{\mu}}| + hc \quad (A6)$$

For the relaxational part we obtain

$$V_{\text{rel}} = \sum_{\mu,\mu'} \sum_{\alpha_{\mu},\beta_{\mu'}} \theta_{\mu\alpha_{\mu} \mu'\beta_{\mu'}} |\chi_{\mu\alpha_{\mu}}\rangle \langle \chi_{\mu'\beta_{\mu'}}| \quad (A7)$$

The electron-vibrational matrix elements introduced in the two foregoing expressions directly follow as the vibrational matrix elements of $T_{\mu m}$ and $\theta_{\mu\mu'}$, respectively.

To derive kinetic equations for the electronic level populations we use the density matrix approach together with an introduction of a coupling of the given electron-vibrational DBA system to an additional thermal bath. The respective coupling induces vibrational relaxation within the electron-vibrational level of the D and A as well within the bridge states and is written ($s = D, A, \mu$ counts the whole set)

$$V_{\text{SB}} = \sum_s \sum_{\alpha_s, \beta_s} (1 - \delta_{\alpha_s, \beta_s}) \Phi_{\alpha_s, \beta_s}^{(s)} |\chi_{s\alpha_s}\rangle \langle s| \langle \chi_{s\beta_s}| \quad (A8)$$

Appendix B: Electron-Vibrational Density Matrix Equations and Coarse Graining Approximation

The aim of the following appendix is to briefly explain how to derive the set of kinetic equations (eq 3) for the overall donor, acceptor, and μ th bridge populations $P_D(t) = \sum_{\alpha_D} \rho_{D\alpha_D} D_{\alpha_D}(t)$, $P_A(t) = \sum_{\alpha_A} \rho_{A\alpha_A} A_{\alpha_A}(t)$, and $P_{\mu}(t) = \sum_{\alpha_{\mu}} \rho_{\mu\alpha_{\mu}} \mu_{\alpha_{\mu}}(t)$, respectively (more details can be found in refs 26 and 27 where the same approach has been applied to the case of nonadiabatic ET). As indicated in the given expressions for the populations, they should be defined via diagonal elements of the DBA electron-vibrational density matrix (remember $s, s' = D, A, \mu$)

$$\rho_{s\alpha_s s'\alpha_{s'}}(t) = \langle s\alpha_s | \rho(t) | s'\alpha_{s'} \rangle \quad (B1)$$

(for notational details see the second part of the foregoing appendix). The respective equations of motion are obtained from the GME for the reduced density operator $\rho(t)$ of an open

quantum system interacting with a heat bath. The derivation of the GME has been well documented in various textbooks (see, e.g., refs 8, 13, 32) and reads in the present notation

$$\begin{aligned} \dot{\rho}_{s\alpha s'\beta}(t) = & -i\omega_{s\alpha s'\beta}\rho_{s\alpha s'\beta}(t) - \frac{i}{\hbar} \sum_{k\xi} (T_{s\alpha k\xi} \rho_{k\xi s'\beta}(t) - \\ & T_{k\xi s'\beta} \rho_{s\alpha k\xi}(t)) - (1 - \delta_{s,s'}) \frac{1}{2} (\tau_{s\alpha}^{-1} + \tau_{s'\beta}^{-1}) \rho_{s\alpha s'\beta}(t) - \\ & \delta_{s,s'} \delta_{\alpha,\beta} \sum_{\alpha'} (w_{\alpha \rightarrow \alpha'}^{(s)} \rho_{s\alpha s\alpha'}(t) - w_{\alpha' \rightarrow \alpha}^{(s)} \rho_{s\alpha' s\alpha}(t)) \quad (\text{B2}) \end{aligned}$$

This type of equation is sufficient since non-Markovian contributions are of no interest for the time scale of distant ET. The quantity $\tau_{s\alpha}^{-1}$ defines the inverse lifetime of the state $|s\alpha\rangle$ and reads

$$\tau_{s\alpha}^{-1} = \sum_{\alpha'} w_{\alpha' \rightarrow \alpha}^{(s)} \quad (\text{B3})$$

The rates

$$\begin{aligned} w_{\alpha \rightarrow \alpha'}^{(s)} = & e^{\hbar\omega^{(s)}_{\alpha\alpha'}/k_B T} W_{\alpha' \rightarrow \alpha}^{(s)} = \\ & \frac{1}{\hbar^2} \sum_{-\infty}^{\infty} d\tau e^{-i\omega^{(s)}_{\alpha\alpha'}\tau} \langle e^{-iH_T\tau/\hbar} \Phi^{\omega^{(s)}_{\alpha\alpha'}} e^{iH_T\tau/\hbar} \Phi^{\omega^{(s)}_{\alpha\alpha'}} \rangle \quad (\text{B4}) \end{aligned}$$

characterize the relaxation between the vibrational states $|s\alpha\rangle$ and $|s\alpha'\rangle$, which belong to the same electronic level and which are separated by the transition energy $E_{s\alpha} - E_{s\alpha'} = \hbar\omega_{\alpha\alpha'}^{(s)}$. The quantities $\Phi_{\alpha\alpha'}^{(s)}$, eq A8, contain the bath degrees of freedom and, thus, define the coupling of DBA vibrational states to the heat bath. In eq B4, the bracket $\langle \dots \rangle$ denotes the thermal average with respect to the equilibrium state of the thermal (heat) bath (the respective Hamiltonian is denoted as H_T). If $s = D, A$ then $\tau_{D(A)\alpha}$ defines the characteristic time of relaxation within the diabatic level, $\tau_{\text{rel}}^{(D,A)}$, while at $s = \mu$, $\tau_{\mu\alpha}$ specifies a relaxation time $\tau_{\text{rel}}^{(\mu)}$ within the μ th adiabatic level of the bridge. In line with the basic inequality of eq 2, the ET proceeds on the background of fast intraterm relaxation. As a result, a quasi-equilibrium distribution within the D and A centers, as well as within each adiabatic bridge term μ , is generated in the course of the distant D–A ET reaction. Noting the definition of the density matrix elements, eq B1, one can state that at $t \gg \tau_{\text{rel}}^{(D,A)}$, $\tau_{\text{rel}}^{(\mu)}$, all off-diagonal matrix elements related to a given site D(A) or a given adiabatic bridge term μ vanish while the diagonal matrix elements, i.e., the partial site populations $\rho_{s\alpha s\alpha}(t)$, describe a thermal equilibrium (Boltzmann) distribution versus the states $|s\alpha\rangle$. Accordingly we can set

$$\rho_{s\alpha s'\beta}(t) = \delta_{\alpha,\beta} W(E_{s\alpha}) P_s(t) \quad (\text{B5})$$

where the $P_s(t)$ denotes the above-mentioned integral populations. Furthermore, we introduced the Boltzmann distribution for the vibrational states of electronic level s

$$W(E_{s\alpha}) = \exp(-E_{s\alpha}/k_B T) / \sum_{\alpha'} \exp(-E_{s\alpha'}/k_B T) \quad (\text{B6})$$

Equation B5 reflects the main assumption of the chosen coarse-grained description based on the strong inequality of eq 2. According to the fast intersite relaxation, the site populations $\rho_{D(A)\alpha D(A)\alpha}(t)$ and the populations of any extended bridge state $\rho_{\mu\alpha\mu \mu\alpha}(t)$ vary only via an alteration of the integral site population $P_{D(A)}(t)$ and $P_{\mu}(t)$, respectively. If one inserts the

factorized distribution (eq B5) into eq B2, it results in the following equations for the integral populations (details of the derivation can be found in ref 26)

$$\dot{P}_s(t) = -\frac{i}{\hbar} \sum_{\alpha} \sum_{k\xi} (T_{s\alpha k\xi} \rho_{k\xi s\alpha}(t) - T_{k\xi s\alpha} \rho_{s\alpha k\xi}(t)) \quad (\text{B7})$$

The equations for the off-diagonal elements $\rho_{s\alpha s'\beta}(t)$, ($s \neq s'$) follow from the GME (eq B2) according to

$$\begin{aligned} \dot{\rho}_{s\alpha s'\beta}(t) = & -\frac{1}{\hbar} (i\Delta E_{s\alpha s'\beta} + \Gamma_{s\alpha s'\beta}) \rho_{s\alpha s'\beta}(t) - \\ & \frac{i}{\hbar} \sum_{k\xi} (T_{s\alpha k\xi} \rho_{k\xi s'\beta}(t) - T_{k\xi s'\beta} \rho_{s\alpha k\xi}(t)) \quad (\text{B8}) \end{aligned}$$

where we changed from the transition frequencies and inverse lifetimes to transition energies $\Delta E_{s\alpha s'\beta} \equiv \hbar\omega_{s\alpha s'\beta}$ and the level broadening $\Gamma_{s\alpha s'\beta} \equiv (\hbar/2)(\tau_{s\alpha}^{-1} + \tau_{s'\beta}^{-1})$. The characteristic times for the change of the off-diagonal elements ($s \neq s'$), $\tau_{(D(A)\mu)}$, and $\tau_{\mu\mu'}$, largely exceed the characteristic times of intralevel relaxation processes, $\tau_{\text{rel}}^{(D,A)}$ and $\tau_{\text{rel}}^{(\mu)}$. Therefore, we can neglect in eq B8 the time derivative of $\rho_{s\alpha s'\beta}(t)$ in comparison to the first term on the right-hand side. It follows

$$\begin{aligned} \rho_{s\alpha s'\beta}(t) = & \frac{1}{\Delta E_{s\alpha s'\beta} - i\Gamma_{s\alpha s'\beta}} \sum_{k\xi} (T_{k\xi s'\beta} \rho_{s\alpha k\xi}(t) - T_{s\alpha k\xi} \rho_{k\xi s'\beta}(t)) \quad (\text{B9}) \end{aligned}$$

Equations B7 and B9, along with relation B5, offer the basis for a coarse-grained description of bridge-mediated ET if strong electronic intrabridge coupling is present. The small interlevel coupling matrix elements $T_{s\alpha s'\beta}$ (at $s \neq s'$) are responsible for interstate transitions and thus just these small couplings define the specificity of the procedure to derive the closed set of equations for the integral populations $P_s(t)$. The equations are obtained in two steps. First one has to iterate eq B9 to get density matrix elements that are diagonal with respect to the index s . And second one uses an expression similar to eq B5 to replace a density matrix element such as $\rho_{s\alpha s'\beta}(t)$ by the integral population $P_s(t)$ and the thermal distribution $W(E_{s\alpha})$. It results an iteration procedure characterized by small parameters such as $|T_{s\alpha s'\beta}|^2 / (\Delta E_{s\alpha s'\beta}^2 + \Gamma_{s\alpha s'\beta}^2)$; details can be found in ref 26. The perturbation expansion leads to the set of Pauli-like kinetic equations (eq 3) with the interlevel rate constants defined by eqs 4–8. A similar form can be derived for the transfer rates $\kappa_{\mu\mu'}$, which describe the transitions between the adiabatic terms μ and μ' of the bridge. It is only necessary to define the corresponding coupling matrix elements $T_{\mu\alpha \mu'\beta} = \langle \mu\alpha | \theta | \mu'\beta \rangle$ via the operator of nonadiabaticity θ , eq A7 (see also, e.g., refs 8 and 40).

References and Notes

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