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A Unified Description of Superexchange and Sequential Donor−Acceptor Electron Transfer Mediated by a Molecular Bridge

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To describe nonadiabatic bridge-assisted donor−acceptor (D−A) electron transfer (ET) kinetic equations for the electronic site, populations are presented that simultaneously account for the sequential as well as the superexchange transfer mechanism. The derivation of the kinetic equations is based on the precondition of fast intrasite vibrational relaxation, which is used to introduce a coarse-grained kinetic description. If the electron hopping across the bridge units is fast compared to the overall D−A ET, the number of kinetic equations can be reduced additionally. A set remains that covers only the donor, acceptor, and the integral bridge populations, independently on the number of bridging units. The case of a small bridge population is studied in detail. In such a situation, the D−A ET process can be described by single-exponential kinetics with a transfer rate that is the sum of the overall sequential and superexchange rate. The ratio of these overall rates is analyzed in the framework of the Song and Marcus model for the vibrational spectral function. If the reorganization energy of the D−A ET amounts to about 1 eV the sequential mechanism can dominate the superexchange ET, even though the population of the bridge by the transferred electron is of the order of 10^{-4} to 10^{-10}. The dominance of the sequential ET mechanism increases not only with increasing bridge length but also with increasing frequency of the ET reaction coordinate. Finally, the whole approach is applied to earlier experiments on D−A ET through a peptide bridge formed by proline oligomers of varying length.[39] The measured fast decrease of the overall transfer rate with an increase of the bridge length for short oligomers (trimers and tetramers) followed by a much weaker decrease for larger oligomers can be completely reproduced.

I. Introduction

Originally proposed by McConnell,[1] the superexchange mechanism of distant donor−acceptor (D−A) electron transfer (ET) mediated by a bridging molecular chain has received constant interest during the past decades. The concept could be successfully applied to the analysis of ET reactions in chemical as well as biological systems (see, e.g., the overviews[2−7] and the textbooks[8−10]). It has been already realized in the late seventies that the superexchange type of ET occurs in combination with thermally activated[8,11−14] or hopping[15−20] ET. Such a theoretical conclusion has been supported by recent experiments where DNA fragments act as the bridging system.[21−24] To evaluate the contribution of each mechanism, and in this manner to specify the details of bridge-assisted ET (oxidation−reduction reactions), one needs an approach that simultaneously accounts for all ET mechanisms.

First results in this direction have been published by Mukamel in the late eighties[18,19] (see also the more recent description[10,14,17,20]). Within this approach so-called Liouville space pathways could be introduced that correspond either to the superexchange or to the sequential mechanism of D−A ET. Therefore, these pathways allow for a classification of the various rate expressions and lead to a universal form of the corresponding ET rates. An alternative derivation of such general ET rates has been given in an approach where properly defined reduced density matrix equations are solved numerically. The respective density matrix describes ultrafast ET by incorporating into the description a very restricted number (1...3) of active vibrational coordinates. The latter can be understood as reaction coordinates of the ET and are coupled to passive coordinates that form a heat bath[13,15,25−30] (see also the various contributions in ref 31). Unfortunately, the numerical solution of the density matrix equations becomes practically impossible if one tries to treat systems with more than 3 or 4 active vibrational coordinates. A further attempt to derive ET rates has been given in the framework of the path integral technique applied to the spin-boson model.[32] But these treatments are restricted to systems with a small number of electronic states (at least two in the case of the standard spin-boson model).

However, a solution of the mentioned reduced density matrix equations becomes possible if the ET is not of the ultrafast type. This would be the case if the characteristic time of the ET reaction, τ_{ET}, becomes larger than the characteristic time of (intrasite) vibrational relaxation, τ_{rel}, i.e.,

$$\tau_{\mathrm{ET}} \gg \tau_{\mathrm{rel}} \tag{1}$$

It is just this type of ET reaction we will exclusively concentrate on in the present paper. In particular, inequality (1) suggests a coarse-grained description of bridge-mediated D−A ET. According to the coarse-graining procedure, the huge set of density matrix equations for the whole DBA system is reduced to a dramatically smaller set of Pauli-like equations for the electronic level populations (integral site populations) $P_m(t)$. Since the

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characteristic time τ_{rel} is typically of the order of 0.1−10 ps,[20,25] the coarse-grained description is valid for those ET systems where the rate constants do not exceed values of $10^{11}$to 10^{13} s^{-1}. Such a situation is typical for nonadiabatic bridge-mediated ET where the electronic couplings between neighboring sites are too small to form an electronic band covering the whole bridging system.

As shown in the subsequent considerations, inequality (1) paves the way for a correct description of D−A ET across a bridge with an arbitrary number of bridging units and with each single unit characterized by a complicated vibrational structure. A characterization of the relative importance of the superexchange and the sequential ET mechanism for bridges with a rather large number of units becomes possible. For appropriate chosen energetic parameters it can be shown that the sequential mechanism may strongly dominate the superexchange one. Especially for systems with a large number of bridging units, this dominance can be demonstrated even though the population of the bridge by the transferred electron is very small (of the order of 10^{-4} to 10^{-10} depending on the energy gap and the various coupling parameters). In this manner the results of[18,19] are generalized to D−A ET reactions mediated by a molecular bridge with an arbitrary number of units. In particular, our approach avoids the use of certain projection operators that fix the considered type of vibrational distribution from the very beginning.

The paper is organized as follows. In the next section the basic ideas to derive the kinetic equations for the overall electronic site-populations are given with the hint on Appendix A where the collection of technical details can be found. The assumption of fast intrabridge hopping processes is used in section III to obtain an effective three-site system where the whole bridge acts, beside the D and A, as a third effective site. This simplification is valid for an arbitrary number of bridge units and enables us to present an analytical expression for the ET rate. A discussion of the dependence on the various parameters entering the ET rate-expressions is given in section IV together with an application to ET experiments on DA systems where the bridge is given by polypeptide chains of varying length. Our conclusion are presented in section V.

II. Rate Equation Approach

Let us start with the standard model for bridge-mediated ET (cf. Figure 1a) where the D and the A are interconnected by a linear molecular chain of N bridging units B. Each unit and the D and the A are characterized by a set of local electron-vibration states $|m\alpha\rangle$ with corresponding energies $E_{m\alpha}$. Here, m labels the sites of the whole ET system ($m = D$, 1, 2,...,N, A, Figure 1b), and α counts the respective vibrational levels.

As it has been mentioned in the introductory section, the coarse-grained approach is based on inequality (1), which is valid for the case of *nonadiabatic* bridge-mediated D−A ET. This type of ET is characterized by a weak coupling between electron-vibrational states $|m\alpha\rangle$ of site m and the states $|n\beta\rangle$ of site n.

$$V_{m\alpha\ n\beta} = V_{mn}\langle\chi_{m\alpha}|\chi_{n\beta}\rangle \tag{2}$$

The quantity V_{mn} denotes the electronic intersite coupling matrix element (cf. Figure 1b) whereas $\langle\chi_{m\alpha}|\chi_{n\beta}\rangle$ is the overlap integral between the corresponding vibrational wave functions. Relation (1) indicates that the ET occurs on the background of fast intrasite relaxation processes. For the time $t \sim \tau_{\mathrm{rel}}$, these processes establish a Boltzmann distribution among the electron-vibration states $|m\alpha\rangle$ of each mth site. As a consequence, specific relations can be established among the elements of the density matrix $\rho_{m\alpha\ n\beta}(t)$ of the whole DBA system. This type of density matrix we have to deal with is defined as

$$\rho_{m\alpha\ n\beta}(t) = \langle m\alpha|\rho(t)|n\beta\rangle \tag{3}$$

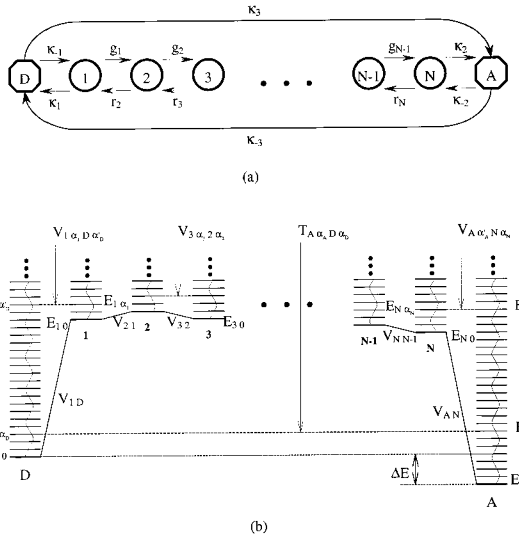

Figure 1. Linear molecular DBA nanostructure composed of N bridging units. Part a: The sequential (g_n and r_n) and superexchange (κ_3 and κ_{-3}) rate constants are indicated only. Part b: The ET occurs as the result of the off-diagonal couplings $V_{m\alpha_m\ n\alpha_n} = V_{mn}\langle\chi_{m\alpha_m}|\chi_{n\alpha_n}\rangle$ between the energy levels $E_{n\alpha_n} \approx E_{m\alpha_m}$ related to neighboring sites n and m, ($n, m = D$, 1, 2,...$N - 1$, A) and as a result of the superexchange coupling $T_{A\alpha_A\,D\alpha_D}$ between the separated donor and acceptor centers.

where $\rho(t)$ denotes the reduced statistical operator of the ET system. It has been already discussed in ref 33 that for ET processes for which eq 1 is valid, the various elements of the density matrix reach particular values. All off-diagonal elements $\rho_{m\alpha\ m\beta}(t)$ related to a single site m vanish, whereas the diagonal elements, i.e., the populations $P_{m\alpha}(t) \equiv \rho_{m\alpha\ m\alpha}(t)$ obey Boltzmann's relation $P_{m\alpha}(t)/P_{m\beta}(t) = \exp[-(E_{m\alpha} - E_{m\beta})/k_{\mathrm{B}}T]$. This behavior can be cast into the following expression:

$$\rho_{m\alpha\ m\beta}(t) = \delta_{\alpha,\beta}W(E_{m\alpha})P_m(t) \tag{4}$$

where we introduced the complete electronic site population (integral population),

$$P_m(t) = \sum_{\alpha} \rho_{m\alpha\ m\alpha}(t) \tag{5}$$

and the Boltzmann equilibrium distribution functions of site m,

$$W(E_{m\alpha}) = \frac{1}{Z_m}\exp(-E_{m\alpha}/k_{\mathrm{B}}T),\ Z_m = \sum_{\alpha'}\exp(-E_{m\alpha'}/k_{\mathrm{B}}T) \tag{6}$$

Relation (4) underlines the main property of the chosen coarse-grained description. According to a fast intrasite relaxation, the populations $P_{m\alpha}(t)$ vary only via an alteration of the total site populations $P_m(t)$ caused by the weak intersite couplings (2). The respective time scale, as well as that for the change of the intersite off-diagonal elements $\rho_{m\alpha\ n\beta}(t)$, coincides with the characteristic time τ_{ET} of the ET reaction.

The resulting set of coarse-grained equations follows from the generalized master equation (written out in tetradic representation via the elements (3)[10,13,15,17]) by taking into consideration the property (4). Within this set of equations, the integral site populations are coupled to the intersite off-diagonal elements

$$\dot{P}_m(t) = -(i/\hbar)\sum_{\alpha}\sum_{k\xi}(V_{m\alpha\,k\xi}\rho_{k\xi\,m\alpha}(t) - V_{k\xi\,m\alpha}\rho_{m\alpha\,k\xi}(t)) \quad (7)$$

$$\dot{\rho}_{m\alpha\,n\beta}(t) = -\frac{i}{\hbar}[(\Delta E_{m\alpha\,n\beta} - i\Gamma_{m\alpha\,n\beta})\rho_{m\alpha\,n\beta}(t) + \sum_{k\xi}(V_{m\alpha,k\xi}\rho_{k\xi\,n\beta}(t) - V_{k\xi,n\beta}\rho_{m\alpha\,k\xi}(t))] \quad (8)$$

Here, we introduced transition energies $\Delta E_{m\alpha\,n\beta} = E_{m\alpha} - E_{n\beta}$ and a respective energy broadening $\Gamma_{m\alpha\,n\beta} = (\hbar/2)(\tau_{m\alpha}^{-1} + \tau_{n\beta}^{-1})$ defined via the inverse lifetimes $\tau_{m\alpha}^{-1}$ and $\tau_{n\beta}^{-1}$ of those states involved in the transition. The lifetimes directly describe the fast intrasite relaxation processes and thus $\tau_{m\alpha} \sim \tau_{\mathrm{rel}}$. In concentrating on the much slower ET process proceeding on a time-scale τ_{rel}, one can neglect the time derivative of $\rho_{m\alpha\,n\beta}(t)$ in comparison to the first term of the right-hand side. It follows that

$$\rho_{m\alpha\,n\beta}(t) = \frac{1}{\Delta E_{m\alpha\,n\beta} - i\Gamma_{m\alpha\,n\beta}}\sum_{k\xi}(V_{k\xi\,n\beta}\rho_{m\alpha\,k\xi}(t) - V_{m\alpha\,k\xi}\rho_{k\xi\,n\beta}(t)) \quad (9)$$

Equations 7 and 9, along with relation (4), constitute the basis for an appropriate description of nonadiabatic bridge-mediated ET. It is easy to see from eq 9 that the coarse-grained description is characterized by the smallness of the parameters

$$\frac{|V_{m\alpha\,n\beta}|^2}{\Delta E^2_{m\alpha n\beta} + \Gamma^2_{m\alpha n\beta}} \ll 1 \quad (10)$$

These parameters can be attributed to the various steps of the iteration procedure necessary to derive the closed set of equations for the site populations $P_m(t)$. All details of the derivation together with concrete expressions for the different types of rates can be found in Appendix A (in particular, see eqs A10−A12).

III. Overall D−A ET Rates

The subsequent analysis of the D−A ET will be based on the standard type of kinetic eqs A10−A12, which will be written here as (note n, $m = D, 1, 2, ...N, A$)

$$\dot{P}_n(t) = -\sum_{m\neq n}(\kappa_{n\to m}P_n(t) - \kappa_{m\to n}P_m(t)) \quad (11)$$

Obviously, they are of such a type to guarantee probability conservation, i.e., the site populations satisfy

$$P_D(t) + P_B(t) + P_A(t) = 1 \quad (12)$$

where $P_B(t) = \sum_{n=1}^{N} P_n(t)$ denotes the integral bridge population.

If the ET proceeds between the neighboring sites (cf. Figure 1a), the rate constants in eq 11 coincide with sequential transfer rates

$$\kappa_{D\to 1} = \kappa_{D\to 1}^{(\mathrm{seq})} \equiv \kappa_{-1}$$

$$\kappa_{A\to N} = \kappa_{A\to N}^{(\mathrm{seq})} \equiv \kappa_{-2} \quad (13)$$

$$\kappa_{1\to D} = \kappa_{1\to D}^{(\mathrm{seq})} \equiv \kappa_1$$

$$\kappa_{N\to A} = \kappa_{N\to A}^{(\mathrm{seq})} \equiv \kappa_2 \quad (14)$$

$$\kappa_{n\to n+1} = \kappa_{n\to n+1}^{(\mathrm{seq})} \equiv g_n \quad (15)$$

and

$$\kappa_{n\to n-1} = \kappa_{n\to n-1}^{(\mathrm{seq})} \equiv r_n \quad (16)$$

If m and n in the rate expressions of eq 11 do not belong to neighboring sites, they express the superexchange transfer rates according to

$$\kappa_{n\to m} = \kappa_{n\to m}^{(\mathrm{sup})} \quad (17)$$

Concrete expressions for the rates are listed in Appendix A, eqs A17 and A18.

The solution of the set (11) leads to $N + 2$ different transfer rates that completely specify the ET reaction. The number of rates can be drastically reduced if an ET reaction is considered where the energy gap $\Delta E_{n\,D(A)} \equiv E_{n0} - E_{D(A)0}$ is large compared to the bridge internal energy gaps $\Delta E_{n\,n'} \equiv E_{n0} - E_{n'0}$, ($n$, $n' = 1, 2, ...N$). In such a case the bridge interior rate constants $\kappa_{n\to n'}$ significantly exceed the rate constants $\kappa_{n\to D(A)}$ and $\kappa_{D(A)\to n}$. Accordingly, the D−A ET occurs on the background of much faster hopping processes within the bridging with characteristic time τ_{hop}. This behavior can be reflected by the inequality

$$\tau_{\mathrm{rel}} \ll \tau_{\mathrm{hop}} \ll \tau_{\mathrm{ET}} \quad (18)$$

which leads us to a second type of coarse-grained description, valid on a time scale τ_{ET}. On this time scale, according to the fast hopping processes within the bridge the alteration, of the bridge-internal site populations $P_n(t)$, ($n = 1, 2, ...N$) is exclusively determined by an alternation of the total bridge population $P_B(t)$. Bearing in mind the ratio $P_m(t)/P_n(t) = Z_m/Z_n$ (Z_m is the partition function, cf. eq 6) valid at $t \gg \tau_{\mathrm{hop}}$, we see that

$$P_m(t) = \frac{Z_m}{Z}P_B(t),\ Z = \sum_{m=1}^{N} Z_m \quad (19)$$

Introducing this expression into the set of eqs 11, we obtain a reduced set of kinetic equations

$$\dot{P}_D(t) = -(\chi_{-1} + \kappa_3)P_D(t) + \chi_1 P_B(t) + \kappa_{-3}P_{\mathrm{A}}(t)$$

$$\dot{P}_B(t) = -(\chi_1 + \chi_2)P_B(t) + \chi_{-1}P_D(t) + \chi_{-2}P_A(t)$$

$$\dot{P}_A(t) = -(\chi_{-2} + \kappa_{-3})P_A(t) + \chi_2 P_B(t) + \kappa_3 P_D(t) \quad (20)$$

with effective transfer rates

$$\chi_1 = \frac{Z_1}{Z}\kappa_1 + \frac{1}{Z}\sum_{n=2}^{N} Z_n\kappa_{n\to D}^{(\mathrm{sup})}$$

$$\chi_2 = \frac{Z_N}{Z}\kappa_2 + \frac{1}{Z}\sum_{n=1}^{N-1} Z_n\kappa_{n\to A}^{(\mathrm{sup})} \quad (21)$$

and

$$\chi_{-1} = \kappa_{-1} + \sum_{n=2}^{N}\kappa_{D\to n}^{(\mathrm{sup})}$$

$$\chi_{-2} = \kappa_{-2} + \sum_{n=1}^{N-1} \kappa_{A\to n}^{(\mathrm{sup})} \tag{22}$$

The superexchange transfer rates

$$\kappa_3 \equiv \kappa_{D\to A}^{(\mathrm{sup})},\ \kappa_{-3} \equiv \kappa_{A\to D}^{(\mathrm{sup})} \tag{23}$$

are defined by eqs (A16) and (A18) with $n = D$, $j = A$ and $n = A$, $j = D$, respectively. Taking the initial conditions $P_D(0) = 1$, $P_A(0) = 0$, and $P_B(0) = 0$ the following analytical solution of the rate eqs 20 is obtained

$$P_D(t) = \frac{a_1\chi_1 + d_2\chi_2}{K_1K_2}\left[1 - \frac{1}{K_1 - K_2}(K_1 \mathrm{e}^{-K_2t} - K_2\mathrm{e}^{-K_1t})\right] + \frac{1}{K_1 - K_2}[(a_1 + \chi_1)(\mathrm{e}^{-K_2t} - \mathrm{e}^{-K_1t}) + K_1\mathrm{e}^{-K_1t} - K_2\mathrm{e}^{-K_2t}]$$

$$P_A(t) = \frac{a_2\chi_1 + d_1\chi_2}{K_1K_2}\left[1 - \frac{1}{K_1 - K_2}(K_1 \mathrm{e}^{-K_2t} - K_2\mathrm{e}^{-K_1t})\right] + \frac{a_2 + \chi_2}{K_1 - K_2}(\mathrm{e}^{-K_2t} - \mathrm{e}^{-K_1t})$$

$$P_B(t) = 1 - P_D(t) - P_A(t) \tag{24}$$

The two overall transfer rates,

$$K_{1,2} = \frac{1}{2}(a_1 + d_1 \pm \sqrt{(a_1 - d_1)^2 + 4a_2d_2}) \tag{25}$$

with

$$a_1 \equiv \chi_2 + \chi_{-2} + \kappa_{-3}, \quad a_2 \equiv \kappa_3 - \chi_2,$$

$$d_1 \equiv \chi_1 + \chi_{-1} + \kappa_3, \quad d_2 \equiv \kappa_{-3} - \chi_1 \tag{26}$$

give a complete description of the coarse-grained D−A ET kinetics.

The solution (24) indicates that the coarse-grained bridge-assisted ET is generally characterized by double exponential kinetics. However, at large energy gaps $\Delta E_{n\,D(A)}$ the rate constants χ_{-1} and χ_{-2} (as well as κ_{-3} and κ_3) become small compared to the rate constants χ_1 and χ_2. As a result, the overall transfer rates reduce to the expression

$$K_1 \approx a_1 + d_1 \approx \chi_1 + \chi_2 \tag{27}$$

and expression

$$K_2 \approx \frac{a_1d_1 - a_2d_2}{a_1 + d_1} \approx \kappa_3 + \kappa_{-3} + \frac{\chi_1\chi_{-2} + \chi_2\chi_{-1}}{\chi_1 + \chi_2} \tag{28}$$

with $K_1 \gg K_2$. It follows from the solution of eq 24 that the largest population of the bridge is reached within time interval $K_1^{-1} \ll t \ll K_2^{-1}$. The respective value is given by the ratio

$$P_B^{(\mathrm{max})} = \frac{\chi_{-1}}{\chi_1 + \chi_2} \tag{29}$$

If $\chi_{-1} \ll \chi_1 + \chi_2$, the maximal population $P_B^{(\mathrm{max})}$ becomes negligibly small so that the transferred electron populates mainly either the donor or acceptor site. A detailed inspection of the solution (24) indicates that at $\chi_{-1},\chi_{-2} \ll \chi_1,\chi_2$, when $K_1 \gg K_2$, the D−A ET appears at $t \gg K_1^{-1}$ where only the small overall transfer rate K_2 specifies the D−A ET. Thus, the condition $P_B^{(\mathrm{max})} \ll 1$, which corresponds completely to inequality $K_1 \gg K_2$, can be taken as the condition for the single-exponential D−A ET process. Now, the D−A ET is described by

$$P_n(t) \simeq (P_n(0) - P_n(\infty))\mathrm{e}^{-Kt} + P_n(\infty),\ (n = D, A, B) \tag{30}$$

where the overall D−A ET rate

$$K = \tau_{\mathrm{ET}}^{-1} \equiv K_2 = k_{\mathrm{f}} + k_{\mathrm{b}} \tag{31}$$

can be represented as the sum of the combined forward transfer rate

$$k_{\mathrm{f}} \equiv \kappa_3 + \frac{\chi_{-1}\chi_2}{\chi_1 + \chi_2} \tag{32}$$

and the combined backward rate

$$k_{\mathrm{b}} \equiv \kappa_{-3} + \frac{\chi_{-2}\chi_1}{\chi_1 + \chi_2} \tag{33}$$

Such a structure of the forward and backward transfer rates is well known from the case of a bridge with a single unit only (cf. refs 8, 34). Here, a generalization is given for the case of an arbitrary number of bridging units. Just this result becomes especially important for a comparison of the bridge-mediated sequential and superexchange mechanisms of D−A ET.

IV. Results and Discussion

The combined forward and backward transfer rates introduced at the end of the foregoing section contain contributions that result from pure superexchange (rate constants κ_3 and κ_{-3}) as well as from the superposition of the sequential and superexchange mechanisms of ET (transfer rates $\chi_{1(2)}$ and $\chi_{-1(-2)}$). In the following we will analyze the ET in D−A complexes where the energy gaps $\Delta E_{n\,D}$ and $\Delta E_{n\,A}$ largely exceed the bridge internal energy gaps $\Delta E_{n\,n'}$, (n, $n' = 1, 2,...N$). For such a case it becomes possible to show that the sequential rate constants κ_1, κ_2 and κ_{-1}, κ_{-2} give the main contribution to the transfer rates χ_1, χ_2 and χ_{-1}, χ_{-2}, respectively. Correspondingly, the combined transfer rates (eq 32) and (eq 33) reduce to the expression

$$k_{\mathrm{f(b)}} = \kappa_{\mathrm{f(b)}}^{(\mathrm{seq})} + \kappa_{\mathrm{f(b)}}^{(\mathrm{sup})} \tag{34}$$

with the sequential component

$$\kappa_{\mathrm{f(b)}}^{(\mathrm{seq})} \equiv \frac{\kappa_{-1(-2)}(Z_{\mathrm{N(1)}}/Z)\kappa_{2(1)}}{(Z_1/Z)\kappa_1 + (Z_{\mathrm{N}}/Z)\kappa_2} \tag{35}$$

and the superexchange component

$$\kappa_{\mathrm{f(b)}}^{(\mathrm{sup})} \equiv \kappa_{3(-3)} \tag{36}$$

of forward (backward) D−A ET rates.

Because it is the purpose of this paper to compare the sequential and superexchange mechanism of bridge-assisted D−A ET in dependence on the number of bridging units and because the D−A ET can be described by single-exponential kinetics, we rewrite the overall transfer rate as

$$K = K^{(\mathrm{seq})} + K^{(\mathrm{sup})} \tag{37}$$

Here, we set

$$K^{(\mathrm{seq})} \equiv \kappa_{\mathrm{f}}^{(\mathrm{seq})} + \kappa_{\mathrm{b}}^{(\mathrm{seq})} \tag{38}$$

and

$$K^{(\mathrm{sup})} \equiv \kappa_{\mathrm{f}}^{(\mathrm{sup})} + \kappa_{\mathrm{b}}^{(\mathrm{sup})} \tag{39}$$

Furthermore, we introduce the ratio

$$\eta(N) = K^{(\mathrm{seq})}/K^{(\mathrm{sup})} \tag{40}$$

which is well suited to characterize the relative efficiency of both discussed ET mechanisms.

To have somewhat more concrete results at hand, we use the rate constants as introduced in eqs A17 and A18, with the Franck Condon factor specified according to eq A22. The latter is based on the use of the spectral function localized at a single vibration with frequency ω_0 (Song−Marcus model,[35,36] for details see Appendix A2). We obtain

$$\kappa_1 = \frac{2\pi}{\hbar}\frac{|V_{1D}|^2}{\hbar\omega_0}\, \mathrm{e}^{-S_{1D}\coth\hbar\omega_0/2k_{\mathrm{B}}T}\left(\frac{1+n(\omega_0)}{n(\omega_0)}\right)^{\nu_{1D}/2} \times I_{|\nu_{1D}|}(2S_{1D}\sqrt{n(\omega_0)(1+n(\omega_0))})$$

$$\kappa_2 = \frac{2\pi}{\hbar}\frac{|V_{NA}|^2}{\hbar\omega_0}\, \mathrm{e}^{-S_{NA}\coth\hbar\omega_0/2k_{\mathrm{B}}T}\left(\frac{1+n(\omega_0)}{n(\omega_0)}\right)^{\nu_{NA}/2} \times I_{|\nu_{NA}|}(2S_{NA}\sqrt{n(\omega_0)(1+n(\omega_0))})$$

$$\kappa_3 = \frac{2\pi}{\hbar}\frac{|T_{DA}(N)|^2}{\hbar\omega_0}\, \mathrm{e}^{-S_{DA}\coth\hbar\omega_0/2k_{\mathrm{B}}T}\left(\frac{1+n(\omega_0)}{n(\omega_0)}\right)^{\nu_{DA}/2} \times I_{|\nu_{DA}|}(2S_{DA}\sqrt{n(\omega_0)(1+n(\omega_0))}) \tag{41}$$

where n denotes the Bose distribution, I_ν is the modified Bessel function and $T_{DA}(N)$ gives the DA superexchange matrix element (all other parameters have been explained in the appendix). The reverse rates simply follow from

$$\kappa_{-1} = \kappa_1 \exp(-\Delta E_{1D}/k_{\mathrm{B}}T)$$
$$\kappa_{-2} = \kappa_2 \exp(-\Delta E_{NA}/k_{\mathrm{B}}T)$$
$$\kappa_{-3} = \kappa_3 \exp(-\Delta E/k_{\mathrm{B}}T) \tag{42}$$

with the driving force $\Delta E \equiv E_{D0} - E_{A0}$ of the D−A ET reaction (cf. Figure 1b).

An easy consideration of the dependence of $\eta(N)$, eq 40 becomes possible for a regular bridge with identical bridge units. In this case, all partition functions Z_m coincide, and we have $Z = NZ_0$ where $Z_0 \equiv Z_1 = Z_2 = ... = Z_N$. Noting this property and bearing in mind relations (42), we can reduce the ratio (40) to

$$\eta(N) = \frac{\kappa_{-1}}{\kappa_3}\frac{1}{1 + \kappa_1/\kappa_2} \tag{43}$$

The number N of bridge units is only contained in the superexchange rate constant κ_3. In line with the general expression, eq A16, the square of the superexchange D−A coupling reads

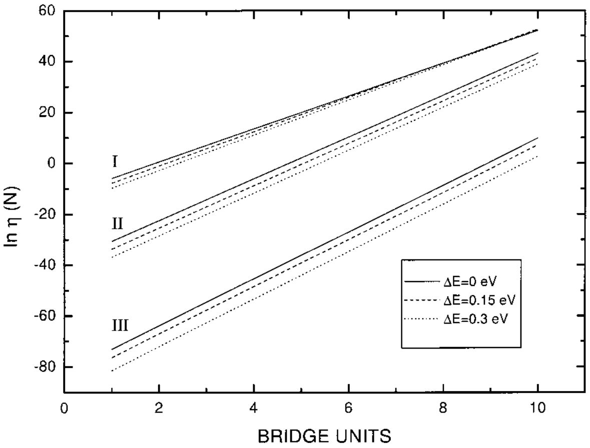

Figure 2. Relative contribution of the sequential and the superexchange mechanism of D−A ET in dependency on the number of bridge units N at various driving forces ΔE and energy gaps. I: $\Delta E_D = 0.5$ eV, II: $\Delta E_D = 1.2$ eV, III: $\Delta E_D = 2.0$ eV. The curves are calculated in using eqs 46, 41, 42, and 44 with $\lambda_{1D} = S_{1D}\hbar\omega_0$=0.9 eV, $\lambda_{NA} = S_{NA}\hbar\omega_0$=1 eV, $\lambda_{DA} = S_{DA}\hbar\omega_0$=1.2 eV, $|V_{1D}| = |V_{NA}| = 0.04$ eV, $|V_B| = 0.02$ eV, $\omega_0 = 100$ cm^{-1} and $T = 300$ K.

$$|T_{DA}(N)|^2 = |T_{DA}(1)|^2\, \zeta^{2(N-1)}$$
$$\left(\left|T_{DA}(1)\right|^2 \equiv \frac{|V_{NA}|^2|V_{1D}|^2}{\Delta E_D \Delta E_A}, \quad \zeta \equiv \frac{|V_B|}{\sqrt{\Delta E_D \Delta E_A}} \ll 1\right) \tag{44}$$

Here, $\Delta E_D \equiv \Delta E_{1D} = \Delta E_{2D} = ... = \Delta E_{ND}$, $\Delta E_A = \Delta E_{1A} = \Delta E_{2A} = ...\Delta E_{NA} = \Delta E_D + \Delta E$, and the quantity $V_B \equiv V_{n\,n+1}$ gives the electronic coupling between the nearest-neighbor bridge units of the regular bridge.

According to expressions (41), (42), and (44), one can use eq 43 to evaluate the efficiency of each ET mechanism in dependence on the various parameters (electron couplings, gaps, driving force of ET reaction, vibration frequencies, number of bridge units, and temperature). Analogously, one can estimate the bridge population (eq 29), which reads

$$P_B^{(\max)} = \frac{\kappa_{-1}}{\kappa_1}\frac{1}{1 + \kappa_2/\kappa_1} \tag{45}$$

Below, we will focus on the influence of the bridge length on the ET that represents the most interesting effect. Therefore we will vary the gap ΔE_D, the driving force ΔE, as well as the frequency ω_0 and use ratio (43) in the form

$$\eta(N) = \eta_0\, \zeta^{-2(N-1)}, \quad \left(\eta_0 \equiv \frac{\kappa_{-1}}{\tilde{\kappa}_3}\frac{1}{1 + \kappa_1/\kappa_2}\right) \tag{46}$$

Note that the quantity $\tilde{\kappa}_3$ follows from κ_3, eq 41, if one replaces $|T_{DA}(N)|^2$ by $|T_{DA}(1)|^2$.

Figure 2 shows the contribution assigned to the sequential and the superexchange mechanism of distant D−A ET for various values of the energy gap and the driving force. The most striking feature is the substantial increase of the part of the overall transfer rate related to the sequential mechanism with the increase of the number of bridge units. For common values of the reorganization energies, $\lambda_{lk} = S_{lk}\hbar\omega_0 \sim 1$ eV and the energy gap $\Delta E_D \sim 1$ eV (cf. refs 3−5, 7, 34), the sequential mechanism exceeds the superexchange one ($\ln \eta(N) > 0$) if the number of bridge units becomes larger than 5 or 7 (see the set II of lines in Figure 2). More precisely, for $\Delta E_D = 0.5$ eV

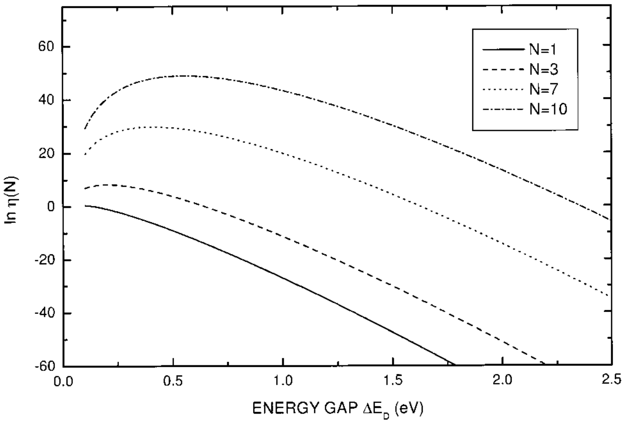

Figure 3. Relative contribution of the sequential and the superexchange mechanism of bridge-assisted DA-ET in dependency on the energy gap and for different numbers of bridge units. The curves are calculated in using eqs 46, 41, 42, and 44 with $\lambda_{1D} = S_{1D}\hbar\omega_0$=0.9 eV, $\lambda_{NA} = S_{NA}\hbar\omega_0 = 1$ eV, $\lambda_{DA} = S_{DA}\hbar\omega_0 = 1.2$ eV, $\Delta E = 0$, $|V_{1D}| = |V_{NA}| = 0.04$ eV, $|V_B| = 0.02$ eV, $\omega_0 = 1000$ cm^{-1} and $T = 300$ K.

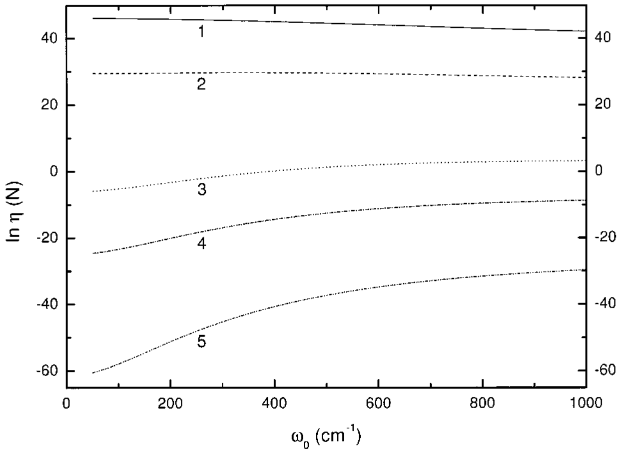

Figure 4. Relative contribution of the sequential and the superexchange mechanism of bridge-assisted DA-ET in dependency on the vibrational frequency ω_0 at a fixed number $N = 10$ of bridging units and for different energy gap (curves 1, 2, 3, 4, and 5 for $\Delta E_D = 1$, 1.5, 2.2, 2.5, and 3.0 eV, respectively). The curves are calculated using eqs 46, 41, 42, and 44 with $\lambda_{1D} = S_{1D}\hbar\omega_0 = 0.9$ eV, $\lambda_{NA} = S_{NA}\hbar\omega_0 = 1$ eV, $\lambda_{DA} = S_{DA}\hbar\omega_0 = 1.2$ eV, $\Delta E = 0.2$ eV, $|V_{1D}| = |V_{NA}| = 0.04$ eV, $|V_B| = 0.02$ eV, and $T = 300$ K.

only the sequential mechanism is responsible for ET at room temperature (the set I of lines in Figure 2) while at $\Delta E_D = 2$ eV the sequential mechanisms becomes important for $N > 12$.

The influence of the energy gap is demonstrated in Figure 3 in detail. For a fixed number of bridge units, the relative contribution of the superexchange mechanism to the formation of the overall transfer rate K increases with increasing ΔE_D.Nevertheless, even at $\Delta E_D = 1.5$ eV, the sequential mechanism can dominate at $N > 5-6$. It is very important to note that the sequential mechanism works effectively at very small bridge populations. An estimation based on eq 45 with $\Delta E_D = 0.8$ eV, $T = 300$ K, and $N = 6$ gives a value of $P_B^{(\max)} \sim 10^{-10}$. But, even at a rather small energy gap, $\Delta E_D = 0.21$ eV, which is typical for photoinduced D−A ET in DNA,[14,21] the integral bridge population remains small ($P_B^{(\max)} \sim 10^{-4}$) to guarantee a description of long-range D−A ET by a single effective transfer rate.

Figure 4 illustrates the frequency dependence of ratio (46). The influence of ω_0 becomes more significant for larger energy gaps ΔE_D. For $N = 10$, the sequential mechanism dominates if $\Delta E_D < 2$ eV. However, for $\Delta E_D = 2.2$ eV, the superexchange mechanism is more efficient if $\omega_0 < 400$ cm^{-1}, while the sequential mechanism exceeds the superexchange if $\omega_0 > 400$ cm^{-1}.

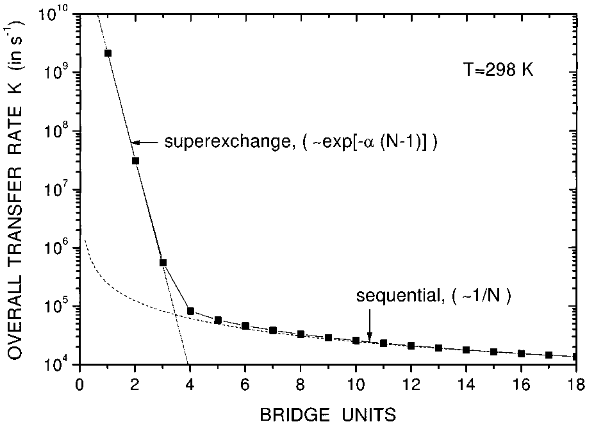

Figure 5. The overal transfer rate of distant D−A ET versus the number of bridging units. The limiting stage of the sequential ET is given by the hopping across the bridge. Calculations are based on a numerical solution of the set of kinetic eqs 11, 41, 42, and 47 with parameters $\omega_B = \omega_0 = 50$ cm^{-1}, $\lambda_{1D} = S_{1D}\hbar\omega_0 = 0.8$ eV, $\lambda_{NA} = S_{NA}\hbar\omega_0 = 0.6$ eV, $\lambda_{DA} = S_{DA}\hbar\omega_0 = 1$ eV, $\lambda_B = S_B\hbar\omega_B = 0.6$ eV, $\Delta E = 0.25$ eV, $\Delta E_D = 0.35$ eV, $|V_{1D}| = |V_{NA}| = 0.05$ eV, $|V_B| = 0.055$ eV, and $T = 298$ K.

So far the D−A ET has been analyzed with the supposition of fast hopping transitions between the bridge units. Following from inequality (18), a further coarse-grained description could be used, finally resulting in an analytic form for the overall D−A transfer rate. However, if bridge-internal hopping transitions are the limiting step of the ET, the derivation of analytical expressions for the ET rates becomes impossible and one has to apply numerical methods to solve the complete set of kinetic equations (eq 11). To explore the typical features of this case we will consider a regular bridge where all intersite rate constants coincide ($\kappa_{n\to n\pm1} = g_n = r_n$). In analogy to eq 41, we set

$$\kappa_B \equiv \kappa_{n\to n\pm1} = \frac{2\pi}{\hbar}\frac{|V_B|^2}{\hbar\omega_B}\,\mathrm{e}^{-S_B\coth\hbar\omega_B/2k_\mathrm{B}T}\left(\frac{1+n(\omega_B)}{n(\omega_B)}\right)^{\nu_{DA}/2} \times I_{|\nu_B|}(2S_B\sqrt{n(\omega_B)(1+n(\omega_B))}) \quad (47)$$

The supposition of slow hopping across the bridge is guaranteed by

$$\kappa_B \ll \kappa_1,\kappa_2 \quad (48)$$

Figure 5 displays the crossover from the predominance of the superexchange mechanism to that of the sequential mechanism with the increase of the bridge length. The superexchange ET rate decreases according to the factor

$$\exp[-\alpha(N-1)] = \exp[-\beta(R-R_0)] \quad (49)$$

where N is the number of bridging units and $R - R_0 = a(N - 1)$ denotes the total distance the transferred electron has to overcome along the bridge. The decay constant $\beta = \alpha/a$ depends strongly on the bridge constant a and the intersite decay parameter α. In the present case of nonadiabatic D−A ET, the latter is defined via ζ, eq 44, as $\alpha = -2\ln\zeta$, which gives here $\alpha = 4.2$. Consider, for example a bridge formed by a polypeptide structure for which $a \approx 4-4.2$ Å per residue (through-bond distance), then the decay factor amounts to $\beta \approx 1$ Å^{-1}, which is typical for an idealized α-helix structure.[37]

In contrast, the part of the transfer rate referring to the sequential mechanism is proportional to N^{-1}. It is just this distance dependence that has been described recently in ref 38 for relatively large bridging systems. However, the same behavior, $K^{(\text{seq})} \sim N^{-1}$, is valid in the case of a short regular bridge, provided the ET across the bridge is the limiting step of the overall D−A ET process. A detailed inspection of the solution of the rate eqs 11 shows that at a small total bridge population ($P_B^{(\max)} < 10^{-3}$) for which the inequality

$$\kappa_{-1},\kappa_{-2}, \ll \kappa_1,\kappa_2 \tag{50}$$

is fulfilled, the nonadiabatic D−A ET can always be characterized by a single-exponential time dependence. The corresponding overall transfer rate contains contributions from the superexchange and the sequential ET mechanism. The crossover region (with respect to an increasing N) between these two mechanisms is mainly determined by the energy gap ΔE_D, the driving force ΔE, the reorganization energies λ_{mn}, and the intrasite bridge coupling V_B. A weak dependence, however, is obtained with respect to the couplings V_D and V_A. (In Figure 5, the crossover region is found for bridges with $N = 4...5$.)

There exists a further case of interest characterized by inequality (48), i.e., by slow hopping transitions inside the bridge. This type of bridge-mediated ET will be related below to experimental results on ET reactions through D−A complexes interconnected by a rigid peptide bridge of proline oligomers with different lengths.[39] We will concentrate on two types of ET reactions, first on Ru(II) → Co(III), and second on Os(II) → Ru(III). In all measurements, the D and A have been interconnected by oligomers with up to six proline units.

As the main experimental result it could be demonstrated (at room temperature conditions) that the ET rate decreases drastically with an increase of the number of proline units up to $N = 2...4$. Afterward, a further increase of N only leads to a slightly decrease of the rate (cf. Figure 6). From the perspective of all preceding discussions of this paper, such a behavior should be explainable as the transition from the dominance of the superexchange mechanism to that of the sequential one. And indeed, the nice agreement of our numerical calculations with the measurements of ref 39 as presented in Figure 6 justify this conjecture. All parameters taken for the computations are given in the caption to Figure 6. Although the D and A are different in both studied examples the bridge units are not. For that reason the same intersite bridge coupling $V_B \approx 0.076$ eV and identical reorganization energies $\lambda_B = 1.35$ eV haven been taken for both examples. Of course, there remains a certain arbitrariness with respect to the choice of the parameters, in particular with respect to the transfer couplings V_{1D} and V_{NA}. Because they do not alter essentially the general form of the N-dependence of the ET rate, we have put $V_{1D} \approx V_{NA}$ for the sake of simplicity. Unfortunately, only a restricted amount of experimental data is available on the N-dependence at $N > 4$, which avoids a more extended fit of all parameters.

As can be seen in both parts of Figure 6, we also addressed the question of the related β-values of the ET. It is very important to note that the superexchange decay parameters, α = 4.2 (β =1 Å^{-1}) for Ru(II) → Co(III) ET and α = 4.6 (β = 1.1 Å^{-1}) for Os(II) → Ru(III) ET, are defined via the same bridge internal parameters V_B and λ_B. In which manner the given set of ET parameters has to be changed if structural and energetic disorder is taken into account will be the subject of a separate study[40] (see also the discussion of disorder influence on the conductivity of molecular wires in refs 41, 42). Nevertheless, the main experimental findings of ref 39 could be explained in a natural way and with reasonable values for all involved parameters, indicating in particular that the ET in proline oligomers proceeds as a nonadiabatic reaction.

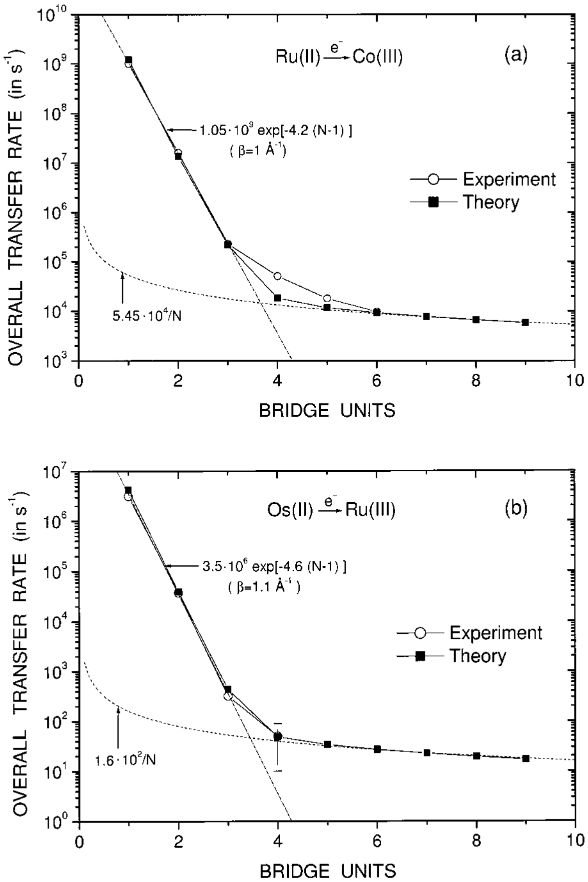

Figure 6. Comparison with the experimental data of ref 39 (T = 298 K) for the D−A ET system (a) $[(\text{bpy})_2\text{Ru(II)L}\cdot(\text{Pro})_n\text{Co(III)}(\text{NH}_3)_5]^{3+}$ and the D−A ET system (b) $[(\text{NH}_3)_5\text{Os(II)i}(\text{Pro})_n\text{Ru(III)}(\text{NH}_3)_5]^{4+}$. Theoretical results follow from the solution of the set of eqs 11 with rate constants according to eqs 41, 42, and 47. The fit is reached with the parameters $|V_B| = 0.076$ eV, $\lambda_B = S_B\hbar\omega_B = 1.35$ eV, $\omega_B = \omega_0 = 50$ cm^{-1}, and $\lambda_{1D} = S_{1D}\hbar\omega_0 = 0.8$ eV, $\lambda_{NA} = S_{NA}\hbar\omega_0 = 1.8$ eV, $\lambda_{DA} = S_{DA}\hbar\omega_0 = 3.05$ eV, $\Delta E = 1.7$ eV, $\Delta E_D = 0.21$ eV, $|V_{1D}| = |V_{NA}| = 0.06$ eV (case a), and $\lambda_{1D} = 0.9$ eV, λ_{NA}=1 eV, $\lambda_{DA} = 2.9$ eV, $\Delta E = 1.35$ eV, $\Delta E_D = 0.36$ eV. $|V_{1D}| = |V_{NA}| = 0.03$ eV (case b).

V. Conclusions

In the present paper we gave a unifying theory of bridge-mediated D−A ET utilizing a coarse-grained approximation of the dynamics of the transferred electron. This approximation describes the ET on the background of fast intrasite relaxation and is based on the smallness of the intersite electron couplings. Consequently the ET proceeds in the nonadiabatic regime. Within our approach, the huge set of electron-vibrational density matrix equations can be reduced to the set of $N + 2$ kinetic equations, eq 11, governing the redistribution of the site populations. The two types of rate constants contained in the rate equations are originated by the sequential as well as the superexchange mechanism of ET reactions.

In most cases of nonadiabatic bridge-assisted D−A ET, the energy gaps between the terminal bridging units and the donor and the acceptor strongly overcome the energy gaps among the bridging units themselves. The resulting small population $P_B(t)$

of the complete bridge makes it possible to characterize the overall ET process by a single-exponential time dependency. A detailed description has been given for the case of fast hopping transitions within the bridge. In this case, an additional reduction of the $N + 2$ coupled rate equations to the set of three equations for $P_D(t)$, $P_A(t)$, and $P_B(t)$, eq 20 referring to the D, A, and total bridge population, respectively, became possible. Interestingly, an exact solution, eq 24, can be derived describing the D−A ET as a double-exponential process. It reduces to a single-exponential ET if the bridge population becomes small enough.

We consider it as a main result of our studies that the nonadiabatic bridge-assisted D−A ET can be described by single-exponential kinetics. The description is independent of the number N of bridging units, and the related overall transfer rate K is obtained as the sum of sequential and superexchange transfer rates, eqs 30 and 34−36. Accordingly, an illuminative analysis becomes possible, which characterizes the efficiency of the sequential and the superexchange mechanisms in dependence on various ET parameters, including the energy gaps, the reorganization energies, the driving force of the ET reaction, the temperature, and the bridge length. To compare the efficiency of both ET mechanisms, the ratio has been introduced between the overall sequential and the overall superexchange transfer rates, eq 40. For our numerical analysis we used the Song and Marcus model for the vibrational spectral function dominated by a single active vibrational mode.[35] The model leads to concrete expressions for the sequential and the superexchange rate constants, eqs 41 and 42. Furthermore, it allows to study the various regimes of D−A ET via an estimation of the ratio of transfer rates, eq 46. We have been able to demonstrate that at room temperature the D−A ET is dominated by the sequential mechanism if the number of bridge units exceeds 5. This result is valid even for an extremely small total bridge population, $P_B^{(\max)} \sim 10^{-10}$. We consider this as a novel insight into the mechanisms of bridge-mediated ET. So far, the standard treatment of nonadiabatic bridge-assisted D−A ET concentrated on the superexchange mechanism if the bridge population becomes small.

Therefore, we would like to underline as our final conclusion that the sequential mechanism of D−A ET must be be taken into consideration if one deals with long-range ET pathways. This is especially important for ET reactions that proceed in complex three-dimensional bridging systems, as they can be found, for example, in proteins. Our main conclusion is supported by the analysis of the peptide-mediated intramolecular D−A ET as described in ref 39. In the considered bridging system formed by proline oligomers, the superexchange decay parameter amounts to $\beta \approx 1$ Å^{-1}. For such a β-value, a crossover from the dominance of the superexchange mechanism to that of the sequential mechanism occurs at $N = 3...4$. If β exceeds 1 Å^{-1}, as it is the case for a number of proteins studied in ref 43, the crossover region can even be shifted to $N = 2...3$. Although this statement is related to peptide bridges, it is supported by recent studies on DNA bridges where the superexchange mechanism with characteristic β-values of 0.6−1.5 Å works effectively for short-range transfer only (up to 10 Å).[44,45]

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Appendix A: Kinetic Equations and Rate Constants Following from a Coarse-Grained Description

1. Iteration Procedure. To derive a kinetic equation for $P_D(t)$ from eq 7, one has to substitute the off-diagonal elements $\rho_{1\alpha_1\, D\alpha_D}(t)$ and $\rho_{D\alpha_D\, 1\alpha_1}(t)$ on the right-hand side of eq 7 by expressions that exclusively contain diagonal density matrix elements. This substitution becomes possible if one notices eq 9, which may connect off-diagonal elements with the diagonal elements $\rho_{D\alpha_D\, D\alpha_D}(t)$ and $\rho_{1\alpha_1\, 1\alpha_1}(t)$, as well as with the additional off-diagonal elements $\rho_{2\alpha_2\, D\alpha_D}(t)$ and $\rho_{D\alpha_D\, 2\alpha_2}(t)$. The presence of additional off-diagonal elements indicates that the derivation of closed equations for the diagonal density matrix elements is embedded in an infinite iteration procedure. Within the first iteration step we obtain

$$\dot{P}_D(t) = -\frac{2}{\hbar}\sum_{\alpha_D}\sum_{\alpha_1}\left\{\left|V_{D\alpha_D\, 1\alpha_1}\right|^2 \frac{\Gamma_{1\alpha_1\, D\alpha_D}}{\Delta E^2_{1\alpha_1\, D\alpha_D} + \Gamma^2_{1\alpha_1\, D\alpha_D}} (\rho_{D\alpha_D\, D\alpha_D}(t) - \rho_{1\alpha_1\, 1\alpha_1}(t))\right\} + (\mathrm{OD})_1 \quad \text{(A1)}$$

where the contribution $(\mathrm{OD})_1$, which includes off-diagonal density matrix elements, reads

$$(\mathrm{OD})_1 = \frac{i}{\hbar}\sum_{\alpha_D}\sum_{\alpha_1}\sum_{\alpha_2}\left\{\frac{V_{D\alpha_D\, 1\alpha_1}V_{1\alpha_1\, 2\alpha_2}}{\Delta E_{1\alpha_1\, D\alpha_D} - i\Gamma_{1\alpha_1\, D\alpha_D}}\rho_{2\alpha_2\, D\alpha_D}(t) - \frac{V_{2\alpha_2\, 1\alpha_1}V_{1\alpha_1\, D\alpha_D}}{\Delta E_{1\alpha_1\, D\alpha_D} + i\Gamma_{1\alpha_1\, D\alpha_D}}\rho_{\mathrm{D}\alpha_D\, 2\alpha_2}(t)\right\} \quad \text{(A2)}$$

To derive the part on the right-hand side of eq A1, we used eq 4 but did not further specify the diagonal density matrix elements.

One easily realizes via an inspection of eq A1 that the first iteration step results in the formation of a rate that describes sequential ET. Using relation (4), the first term on the right-hand side of eq A1 reduces to the conventional kinetic form $-\kappa^{(\mathrm{seq})}_{D\to 1}P_D(t) + \kappa^{(\mathrm{seq})}_{1\to D}P_1(t)$. The rate constants characterize the transfer between sites $m = D$ and $n = 1$ (and $m = 1$ and $n = D$) and are given by

$$\kappa^{(\mathrm{seq})}_{m\to n} = \frac{2\pi}{\hbar}|V_{mn}|^2 \sum_{\alpha}\sum_{\beta}\langle\chi_{m\alpha}|\chi_{n\beta}\rangle^2 W(E_{m\alpha})L(E_{m\alpha} - E_{n\beta}) \quad \text{(A3)}$$

Note the use of eq 2 to specify the intersite coupling as well as eq 6 to introduce the thermal distribution function $W(E_{m\alpha})$. The quantity

$$L(E_{m\alpha} - E_{n\beta}) = \frac{1}{\pi}\frac{\Gamma_{m\alpha\, n\beta}}{(E_{m\alpha} - E_{n\beta})^2 + \Gamma^2_{m\alpha\, n\beta}} \quad \text{(A4)}$$

gives the Lorentzian-like broadening of the energy-conserving δ-function of the rate expressions.

Next we perform the second iteration step with respect to eq 9. In this manner the part $(\mathrm{OD})_1$ of eq A1, which is formed by off-diagonal density matrix elements, can be replaced by an expression that contains again diagonal and off-diagonal elements. This second iteration step starts from the set of equations

$$\rho_{D\alpha_D\,2\alpha_2}(t) = \rho^*{}_{2\alpha_2\,D\alpha_D}(t) = -\frac{1}{E_{2\alpha_2\,D\alpha_D} + i\Gamma_{2\alpha_2\,D\alpha_D}} \times \Big[\sum_{\alpha_1'} (V_{1\alpha'_1\,2\alpha_2}\rho_{D\alpha_D\,1\alpha'_1}(t) - V_{D\alpha_D\,1\alpha'_1}\rho_{1'\alpha'_1\,2\alpha_2}(t)) + \sum_{\alpha_3} V_{3\alpha_3\,2\alpha_2}\rho_{D\alpha_D\,3\alpha_3}(t)\Big] \quad (A5)$$

$$\rho_{D\alpha_D\,1\alpha'_1}(t) = \rho^*{}_{1\alpha'_1\,D\alpha_D}(t) = -\frac{1}{E_{1\alpha'_1\,D\alpha_D} + i\Gamma_{1\alpha'_1\,D\alpha_D}} \times \Big[V_{D\alpha_D\,1\alpha'_1}(\rho_{D\alpha_D\,D\alpha_D}(t) - \rho_{1\alpha'_1\,1\alpha'_1}(t)) + \sum_{\alpha_2'} V_{2\alpha'_2\,1\alpha'_1}\rho_{D\alpha_D\,2\alpha'_2}(t)\Big] \quad (A6)$$

and

$$\rho_{1\alpha'_1\,2\alpha_2}(t) = \rho^*{}_{2\alpha_2 D\,1\alpha'_1}(t) = -\frac{1}{E_{1\alpha'_1\,2\alpha_2} - i\Gamma_{1\alpha'_1\,2\alpha_2}} \times \Big[V_{1\alpha'_1\,2\alpha_2}(\rho_{1\alpha'_1\,1\alpha'_1}(t) - \rho_{2\alpha_2\,2\alpha_2}(t)) + \sum_{\alpha_3} V_{3\alpha_3\,2\alpha_2}\rho_{1\alpha'_1\,3\alpha_3}(t) - \sum_{\alpha_D'} V_{1\alpha'_1\,D\alpha'_D}\rho_{D\alpha'_D\,2\alpha_2}(t)\Big] \quad (A7)$$

which all follow from eq 9. These equations connect the off-diagonal density matrix elements $\rho_{2\alpha_2\,D\alpha_D}(t)$ and $\rho_{D\alpha_D\,2\alpha_2}(t)$ with diagonal elements $\rho_{D\alpha_D\,D\alpha_D}(t)$, $\rho_{1\alpha_1\,1\alpha_1}(t)$, and $\rho_{2\alpha_2\,2\alpha_2}(t)$, as well as with off-diagonal elements $\rho_{3\alpha_3\,D\alpha_D}(t)$ and $\rho_{D\alpha_D\,3\alpha_3}(t)$. With the help of the relations (A5)−(A7), the off-diagonal term (A2) can be reduced to a rather complicated expressions with additional diagonal and off-diagonal elements. However, due to the inequality (10), we can omit corrections to the terms that are proportional to $\rho_{1\alpha_1\,1\alpha_1}(t)$. These corrections are of the fourth order with respect to the intersite couplings and are small in comparison to the more important contribution given by the diagonal part on right-hand side of eq A1. Keeping only those terms that are different from the corrections to standard nonadiabatic ET rates, one obtains

$$(\mathrm{OD})_1 \approx \Bigg\{\frac{i}{\hbar}\sum_{\alpha_D,\alpha_2}\sum_{\alpha_1,\alpha_1'} \Bigg[\frac{V_{D\alpha_D\,1\alpha_1}V_{1\alpha_1\,2\alpha_2}V_{2\alpha_2\,1\alpha'_1}V_{1\alpha'_1\,D\alpha_D}\rho_{D\alpha_D\,D\alpha_D}(t)}{(\Delta E_{1\alpha_1\,D\alpha_D} - i\Gamma_{1\alpha_1\,D\alpha_D})(\Delta E_{1\alpha'_1\,D\alpha_D} - i\Gamma_{1\alpha'_1\,D\alpha_D})(\Delta E_{2\alpha_2\,D\alpha_D} - i\Gamma_{2\alpha_2\,D\alpha_D})} - \frac{V_{D\alpha_D\,1\alpha_1}V_{1\alpha_1\,2\alpha_2}V_{2\alpha_2\,1\alpha'_1}V_{1\alpha'_1\,D\alpha_D}\rho_{2\alpha_2\,2\alpha_2}(t)}{(\Delta E_{1\alpha_1\,D\alpha_D} - i\Gamma_{1\alpha_1\,D\alpha_D})(\Delta E_{1\alpha'_1\,2\alpha_2} + i\Gamma_{1\alpha'_1\,2\alpha_2})(\Delta E_{2\alpha_2\,D\alpha_D} - i\Gamma_{2\alpha_2\,D\alpha_D})}\Bigg] + c.c.\Bigg\} + (\mathrm{OD})_2 \quad (A8)$$

The part $(\mathrm{OD})_2$ contains the terms that are proportional to off-diagonal elements $\rho_{D\alpha_D\,3\alpha_3}(t)$, $\rho_{D\alpha_D\,2\alpha'_2}(t)$, $\rho_{3\alpha_3\,1\alpha'_1}(t)$ (and corresponding complex conjugated elements). With the utilization of relation (9), all these elements can be expressed via other diagonal and off-diagonal elements (the third iteration step). A detailed inspection shows that only terms that contain the off-diagonal elements $\rho_{D\alpha_D\,3\alpha_3}(t)$ and $\rho_{3\alpha_3\,D\alpha_D}(t)$ lead to terms that do not give higher-order corrections to the nonadiabatic rate expressions. So, the part of $(\mathrm{OD})_2$, eq A8, which is of main interest for us, reads

$$(\mathrm{OD})_2 \approx -\frac{i}{\hbar}\sum_{\alpha_D,\alpha_3}\sum_{\alpha_1,\alpha_2} \Bigg\{\frac{V_{D\alpha_D\,1\alpha_1}V_{1\alpha_1\,2\alpha_2}V_{2\alpha_2\,3\alpha_3}}{(\Delta E_{1\alpha_1\,D\alpha_D} - i\Gamma_{1\alpha_1\,D\alpha_D})(\Delta E_{2\alpha_2\,D\alpha_D} - i\Gamma_{2\alpha_2\,D\alpha_D})}\rho_{3\alpha_3\,D\alpha_D}(t) - \frac{V_{3\alpha_3\,2\alpha_2}V_{2\alpha_2\,1\alpha_1}V_{1\alpha_1\,D\alpha_\mathrm{D}}}{(\Delta E_{1\alpha_1\,D\alpha_D} + i\Gamma_{1\alpha_1\,D\alpha_D})(\Delta E_{2\alpha_2\,D\alpha_D} + i\Gamma_{2\alpha_2\,D\alpha_D})}\rho_{3\alpha_3\,D\alpha_D}(t)\Bigg\} \quad (A9)$$

Just this expression is the result of the third iteration step. It connects the diagonal elements $\rho_{D\alpha_D\,D\alpha_D}(t)$ with the diagonal elements $\rho_{3\alpha_3\,3\alpha_3}(t)$ and the off-diagonal elements $\rho_{D\alpha_D\,4\alpha_4}(t)$ and $\rho_{3\alpha_3\,D\alpha_D}(t)$. After the Nth iteration step, a connection is established between $\rho_{D\alpha_D\,D\alpha_D}(t)$ and $\rho_{A\alpha_A\,A\alpha_A}(t)$. The $(N+1)$th iteration step completes the iteration procedure, resulting in the formation of a kinetic equation for the site population $P_D(t)$. This equation contains only diagonal elements $\rho_{D\alpha_D\,D\alpha_D}(t)$ and $\rho_{n\alpha_n\,n\alpha_n}(t)$, ($n$ = 1, 2,...N, A). After N, iteration terms that connect D and A via the superexchange mechanism could be generated. Any further iteration steps result in less important corrections, which will be omitted.

According to the basic coarse-grained relation (4) and the required iteration, we may write down the kinetic equations in the form

$$\dot P_D(t) = -[\kappa^{(\mathrm{seq})}_{D\to1} + \sum_{n=2}^{N}\kappa^{(\mathrm{sup})}_{D\to n} + \kappa^{(\mathrm{sup})}_{D\to A}]P_D(t) + \kappa^{(\mathrm{seq})}_{1\to D}P_D(t) + \sum_{n=2}^{N}\kappa^{(\mathrm{sup})}_{D\leftarrow n}P_n(t) + \kappa^{(\mathrm{sup})}_{D\leftarrow A}P_\mathrm{A}(t) \quad (A10)$$

which contains sequential and superexchange types of rate constants.

The iteration procedure introduced so far can also be carried out for the A-site and any bridge unit n = 1, 2...N. One obtains

$$\dot P_A(t) = -[\kappa^{(\mathrm{seq})}_{A\to N} + \sum_{n=1}^{N-1}\kappa^{(\mathrm{sup})}_{A\to n} + \kappa^{(\mathrm{sup})}_{A\to D}]P_A(t) + \kappa^{(\mathrm{seq})}_{N\to A}P_N(t) + \sum_{n=2}^{N}\kappa^{(\mathrm{sup})}_{A\leftarrow n}P_n(t) + \kappa^{(\mathrm{sup})}_{A\leftarrow D}P_\mathrm{D}(t) \quad (A11)$$

and

$$\dot P_n(t) = -[\kappa^{(\mathrm{seq})}_{n\to n+1} + \kappa^{(\mathrm{seq})}_{n\to n-1} + \sum_{j\neq n}\kappa^{(\mathrm{sup})}_{n\to j}]P_n(t) + \kappa^{(\mathrm{seq})}_{n+1\to n}P_{n+1}(t) + \kappa^{(\mathrm{seq})}_{n-1\to n}P_{n-1}(t) + \sum_{j\neq n}\kappa^{(\mathrm{sup})}_{n\leftarrow j}P_j(t) \quad (A12)$$

Note that the summation with respect to j covers all possible DBA sites, i.e., $j = D$, 1, 2,...N, A.

2. Rate Constants. In the set of kinetic eqs A10−A11, all sequential rate constants are given by eq A3. The superexchange rate constants read (n, j = 0, 1, 2,...N, N + 1, 0 ≡ D, N + 1 ≡ A)

$$\kappa_{n\to j}^{(\mathrm{sup})} = -\frac{i}{\hbar}\sum_{\alpha_n,\alpha_j}\sum_{\alpha_{n+1},\alpha'_{n+1}}\cdots\sum_{\alpha_{j-1},\alpha'_{j-1}} \times \left\{ \frac{\prod_{k=n+1}^{j} V_{k\alpha_k\,k-1\alpha_{k-1}} V_{k-1\alpha'_{k-1}\,k\alpha'_k}}{\prod_{k=n+1}^{j-1} (\Delta E_{q\alpha_q\,n\alpha_n} - i\Gamma_{q\alpha_q\,n\alpha_n})(\Delta E_{q\alpha'_q\,n\alpha_n} - i\Gamma_{q\alpha'_q\,n\alpha_n})(\Delta E_{n\alpha_n\,j\alpha_j} + i\Gamma_{n\alpha_n\,j\alpha_j})} - \frac{\prod_{k=n+1}^{j} V_{k\alpha'_k\,k-1\alpha'_{k-1}} V_{k-1\alpha_{k-1}\,k\alpha k}}{\prod_{k=n+1}^{j-1} (\Delta E_{q\alpha_q\,n\alpha_n} + i\Gamma_{q\alpha_q\,n\alpha_n})(\Delta E_{q\alpha'_q\,n\alpha_n} + i\Gamma_{q\alpha'_q\,n\alpha_n})(\Delta E_{n\alpha_n\,j\alpha_j} - i\Gamma_{n\alpha_n\,j\alpha_j})} \right\} W(E_{n\alpha_n}) \tag{A13}$$

and

$$\kappa_{n\leftarrow j}^{(\mathrm{sup})} = -\frac{i}{\hbar}\sum_{\alpha_n,\alpha_j}\sum_{\alpha_{n+1},\alpha'_{n+1}}\cdots\sum_{\alpha_{j-1},\alpha'_{j-1}} \times \left\{ \frac{\prod_{k=n+1}^{j} V_{k\alpha_k\,k-1\alpha_{k-1}} V_{k-1\alpha'_{k-1}\,k\alpha'_k}}{\prod_{k=n+1}^{j-1} (\Delta E_{q\alpha_q\,n\alpha_n} - i\Gamma_{q\alpha_q\,n\alpha_n})(\Delta E_{q\alpha'_q\,j\alpha_j} + i\Gamma_{q\alpha'_q\,j\alpha_j})(\Delta E_{n\alpha_n\,j\alpha_j} + i\Gamma_{n\alpha_n\,j\alpha_j})} - \frac{\prod_{k=n+1}^{j} V_{k\alpha'_k\,k-1\alpha'_{k-1}} V_{k-1\alpha_{k-1}\,k\alpha_k}}{\prod_{k=n+1}^{j-1} (\Delta E_{q\alpha_q\,n\alpha_n} - i\Gamma_{q\alpha_q\,n\alpha_n})(\Delta E_{q\alpha'_q\,n\alpha_n} + i\Gamma_{q\alpha'_q\,n\alpha_n})(\Delta E_{n\alpha_n\,j\alpha_j} - i\Gamma_{n\alpha_n\,j\alpha_j})} \right\} W(E_{j\alpha_j}) \tag{A14}$$

Note that eqs A13 and A14 are written for the case where $n > j$. The case $n < j$ is described by similar expressions.

The expressions (A13) and (A14) for the transfer rates show that $\kappa_{n\leftarrow j}^{(\mathrm{sup})} \neq \kappa_{j\to n}^{(\mathrm{sup})}$. This is due to the fact that the iteration procedure has been carried out in using a representation of the density matrix in a local basis, which results in different denominators in the above given expressions. In particular, the denominator of $\kappa_{n\to j}^{(\mathrm{sup})}$ contains only energy differences $\Delta E_{q\alpha_q\,n\alpha_n}$ whereas the denominator of $\kappa_{n\leftarrow j}^{(\mathrm{sup})}$ contains (in a symmetric form) both types of energy differences, $\Delta E_{q\alpha_q\,n\alpha_n}$ and $\Delta E_{q\alpha_q\,j\alpha_j}$. Note, however, that our description of site-to-site transitions is based on the assumption of small intersite couplings $V_{m\alpha_m\,n\alpha_n}$. Therefore, the use of local basis states $|m\alpha_m\rangle$ may lead to correct results (i.e., the steady density matrix, $\rho(\infty)$, coincides with the correct equilibrium expression). Such a correct description provides that the ET process is mainly accompanied by isoenergetic intersite transitions, $E_{m\alpha_m} \approx E_{n\alpha_n}$ (see the discussions in, e.g., refs 15, 33). Therefore, according to relation $E_{j\alpha_j} \approx E_{n\alpha_n}$ we may conclude that $\kappa_{n\to j}^{(\mathrm{sup})} \approx \kappa_{j\leftarrow n}^{(\mathrm{sup})}$. Because this relation is fulfilled with high accuracy, we will take a symmetric form (with respect to energy differences $\Delta E_{q\alpha_q\,n\alpha_n}$ and $\Delta E_{q\alpha_q\,j\alpha_j}$) of the transfer rates, eq A14.

The superexchange mechanism of ET between the sites n and j is important when the lowest energy levels E_{q0} of an internal bridge site q differs considerably from the lowest energy levels E_{n0} and E_{j0} of sites n and j. As far as the superexchange transition takes place for $E_{j\alpha_j} \approx E_{n\alpha_n}$, we may omit the broadenings $\Gamma_{q\alpha_q\,n\alpha_n}$ and $\Gamma_{q\alpha_q\,j\alpha_j}$ in comparison with the corresponding energy differences $\Delta E_{q\alpha_q\,n\alpha_n}$ and $\Delta E_{q\alpha_q\,j\alpha_j}$, respectively. But the broadening $\Gamma_{n\alpha_n\,j\alpha_j}$ cannot be omitted. Below, the superexchange transfer rates are given for the case where the vibrational energies are small compared to the energy gaps $\Delta E_{qn} = E_{q0} - E_{n0}$ and $\Delta E_{qj} = E_{q0} - E_{j0}$. Accordingly, one can set $\Delta E_{q\alpha_q\,n\alpha_n} \approx \Delta E_{qn}$ and $\Delta E_{q\alpha_q\,j\alpha_j} \approx \Delta E_{qj}$. The following use of expression (2) and the summation with respect to all interior vibrational states reduces eq A14 to ($n > j$)

$$\kappa_{j\leftarrow n}^{(\mathrm{sup})} \approx \kappa_{n\to j}^{(\mathrm{sup})} \approx \frac{2\pi}{\hbar}|T_{nj}|^2 \sum_{\alpha}\sum_{\beta} \langle \chi_{j\alpha_j}|\chi_{n\alpha_n}\rangle^2 W(E_{n\alpha_n}) L(E_{n\alpha_n} - E_{j\alpha_j}) \tag{A15}$$

The pure electronic superexchange matrix element, T_{nj}, is given in a symmetric form (with respect to energy gaps ΔE_{qn} and ΔE_{qj}),

$$T_{nj} = \frac{V_{jj-1}V_{j-1\,j-2}\cdots V_{n+2\,n+1}V_{n+1n}}{\sqrt{|\Delta E_{n+1n}\Delta E_{n+1j}\Delta E_{n+2n}\Delta E_{n+2j}\cdots\Delta E_{j-1n}\Delta E_{j-1j}|}} \tag{A16}$$

This symmetric form, $T_{nj} \equiv T_{nj}^{(\mathrm{sim})}$, follows from eq A14. If one notices eq A13, the coupling $T_{nj} = T_{nj}^{(\mathrm{nonsim})}$ will contain only energy gaps ΔE_{qn}. However, both forms differ insignificantly, $T_{nj}^{(\mathrm{nonsim})} \approx T_{nj}^{(\mathrm{sim})}[1 + (1/2)\sum_{q=n+1}^{j-1}(\Delta E/\Delta E_{qj})]$, if the driving force of the $n \to j$ ET reaction, ΔE, is much smaller than the gaps ΔE_{qj} (i.e., if $|\Delta E/\Delta E_{qj}| \ll 1$) and if the amount of bridging sites, $n - j$, is not too large. Just such a situation is valid for superexchange ET.

The sequential and superexchange transfer rates, eqs A3 and A15, completely specify the ET processes in the DBA system. The rates are defined via pure electronic couplings $V_{nn\pm1}$ or T_{nj}, overlap integrals $\langle \chi_{j\alpha_j}|\chi_{n\alpha_n}\rangle$, distributions $W(E_{m\alpha})$, and Lorentzians $L(E_{m\alpha} - E_{n\beta})$. If the energy spectrum $E_{m\alpha}$ within each site is dense and forms a quasi-continuum, the broadening of the energy levels can be ignored and the Lorentzian $L(E_{m\alpha} - E_{n\beta})$ changes to a delta-function $\delta(E_{m\alpha} - E_{n\beta})$. Such a substitution reduces the above given transfer rates to the conventional form

$$\kappa_{m\to n}^{(\mathrm{seq})} = \frac{2\pi}{\hbar}|V_{nm}|^2(\mathrm{FC})_{mn} \tag{A17}$$

and

$$\kappa_{n\to j}^{(\mathrm{sup})} = \frac{2\pi}{\hbar}|T_{nj}|^2(\mathrm{FC})_{nj} \tag{A18}$$

The expression

$$(\mathrm{FC})_{kl} = \sum_{\alpha_k}\sum_{\alpha_l} |\langle \chi_{\alpha_l}|\chi_{\alpha_k}\rangle|^2 W(E_{k\alpha_k})\delta(E_{k\alpha_k} - E_{l\alpha_l}) \tag{A19}$$

gives the Franck Condon factor[3−5] for the $k \to l$ ET. If the vibrational frequencies are equal for all ET sites, this factor can be rewritten as[46]

$$(\mathrm{FC})_{kl} = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t\; \mathrm{e}^{-i\Delta E_{kl}t/\hbar}\; \mathrm{e}^{-Q_{kl}(t)} \tag{A20}$$

This expression is well known from the spin-boson model.[10,32,47,48] The quantity

$$Q_{kl}(t) = 2\int_{-\infty}^{+\infty} \mathrm{d}\omega\, \frac{J_{kl}(\omega)}{\omega^2}[\coth(\hbar\omega/2k_{\mathrm{B}}T)(1 - \cos\omega t) - i\sin\omega t] \tag{A21}$$

can be expressed via the vibrational spectral functions $J_{kl}(\omega)$, which are specified by the coupling to the vibrational modes and the respective frequency spectrum.[10,32,47,48] Since the rather popular model of a single reaction coordinate of frequency ω_0 coupled to a nonpolar solution will be used, the spectral function as shown by Song and Marcus[35,36] has to be chosen in the form $J_{kl}(\omega) = (1/2\hbar)\lambda_{kl}\omega\delta(\omega - \omega_0)$, where λ_{kl} is the reorganization energy of the $k \rightarrow l$ ET. It results the well-known Jortner expression[7,49]

$$(\mathrm{FC})_{kl} = \frac{1}{\hbar\omega_0}\,\mathrm{e}^{-S_{kl}\coth\hbar\omega_0/2k_{\mathrm{B}}T}\left(\frac{1+n(\omega_0)}{n(\omega_0)}\right)^{\nu_{kl}/2} \times I_{|\nu_{kl}|}\left(2S_{kl}\sqrt{n(\omega_0)(1+n(\omega_0))}\right) \quad \text{(A22)}$$

Here, $\nu_{kl} \equiv \Delta E_{kl}/\hbar\omega_0$, $\Delta E_{kl} = E_{k0} - E_{l0}$ denotes the driving force of the $k \rightarrow l$ ET, $S_{kl} \equiv \lambda_{kl}/\hbar\omega_0$, $n(\omega_0) = [\exp(\hbar\omega_0/k_BT) - 1]^{-1}$ is the Bose distribution, and $I_\nu(z)$ represents the modified Bessel function.

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